

ORGANIC ELECTROCHEMISTRY IN APROTIC
SOLVENTS, PARTICULARLY LIQUID AMMONIA

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1978



To

CAROLYN

ACKNOWLEDGEMENTS

I should first like to express my thanks to Dr. A. J. Bellamy for his help and understanding throughout the duration of these studies.

Also my thanks and appreciation go to the staff, technical staff and fellow students of the Chemistry Department, particularly to Mrs. Ranken for typing the manuscript with such speed and Mr. C. Baxter for his role as photographer.

Many thanks go to Graham for his help at home and the staff of the University Day Nursery for their excellent service.

Finally I wish to express my gratitude to the Science Research Council for financial support.

ABSTRACT

The Introduction is concerned with some general aspects of organic electrochemistry.

The Discussion is divided into two sections: electrochemistry in acetonitrile (Section A) and liquid ammonia (Section B). Practical aspects e.g. solvent purification, cell design and electrode construction are considered. Several supporting electrolytes and electrode materials are also assayed.

In Section A, the reduction of acetophenone has been studied. The formation of nitrile containing products has been rationalised in terms of the production of the cyanomethyl anion. Addition of the latter to acetophenone, and subsequent dehydration to 3-methylcinnamionitrile are believed to occur. The reduction of the latter compound was therefore also carried out. In addition electrolysis of acetone was conducted in the presence of azobenzene. Finally the influence of supporting electrolyte cations on the rate of charge transfer to benzoylcyclopropane was examined.

Two aspects of electrochemistry in liquid ammonia are considered in Section B. Firstly electrochemically generated solvated electrons have been used to reductively open the ring in acetylcyclopropanes. A comparison of the product ratios obtained from the reduction of 1-acetyl-2, 2-dimethylcyclopropane with those obtained by other workers using alkali metal/ammonia solutions suggests a similar reduction mechanism in each case. When the reduction was conducted in the presence of tetraethylammonium cations, however reductive ethylation to form tertiary-alcohols was the major reaction. Attempts are made to rationalise this result in terms of the higher stability of the tetraethylammonium cation, compared to that of other quaternary ammonium salts, in the presence of solvated electrons. Oct-4-yne was similarly reduced in an attempt to promote alkylation, but this did not occur.

Secondly the electrode reductions (analytical and preparative) of benzophenone, acetophenone, benzoylcyclopropane, azobenzene, cis- and trans-stilbene, and diphenylacetylene have been investigated in liquid ammonia.

A comparison with results obtained by other workers has been made wherever possible and the influence of proton donors and supporting electrolyte cations on the reduction has been studied.

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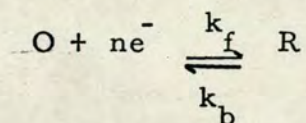
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INTRODUCTION

The electrochemical transformation of an organic compound may be carried out by applying an appropriate voltage to two electrodes immersed in an electrically conducting solution of the compound. The events resulting in this transformation can simply be described as (a) transfer of the substrate to and from the electrode, (b) electron transfer to or from the electrode and (c) coupled chemical reactions. For a complete understanding of these events some knowledge of heterogeneous catalysis (surface effects), reactive intermediates, kinetics, theoretical chemistry, salt effects, reaction mechanisms and electronics, to mention but a few, would be helpful. Obviously a survey of such a wide variety of disciplines is outside the scope of this introduction, therefore only some aspects of some of these topics, as far as they are relevant to the studies to be described, will be discussed.

Consider first (a) the mass transfer to the electrode of an electroactive organic species by a combination of the processes of migration, diffusion and convection. In order to provide electrical conductivity in the solution and also to minimise migration - the movement of a species in an electric field - thereby simplifying the study of transfer phenomena, a salt known as the supporting electrolyte is dissolved in the medium. Such salts, frequently quaternary ammonium salts, must be inert, have a high solubility and be highly dissociated in the medium used. Mass transfer by diffusion results from the disappearance of an electroactive species at an electrode due to electron transfer, thereby setting up a concentration gradient for that substance between the electrode and the bulk of the solution. The type of diffusion - linear, cylindrical or spherical - depends upon the geometry of the electrode. This is the only method of mass transfer during analytical procedures such as polarography and cyclic voltammetry, the solutions being unstirred. Convection contributes to mass transfer in preparative electrochemical experiments such as controlled potential electrolyses, since in these cases the solution is mechanically stirred.

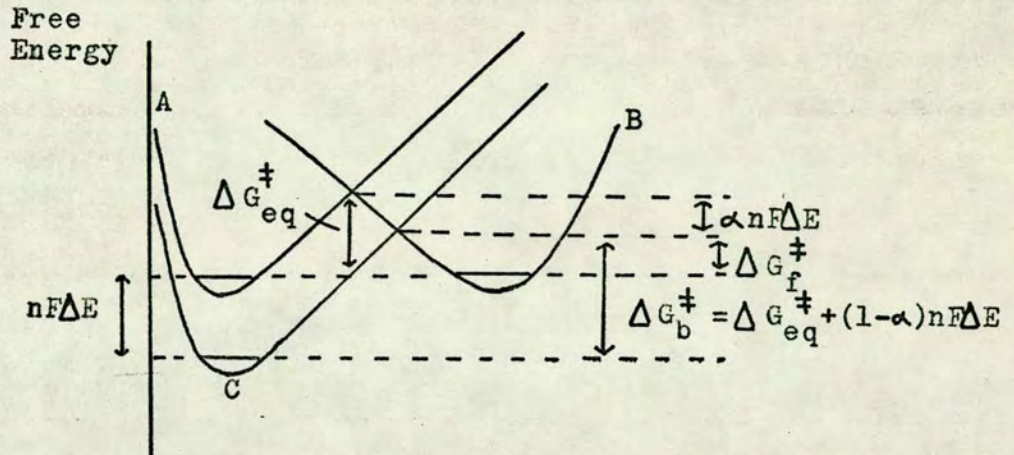
Once the electroactive species has been transported to the electrode, step (b) follows. The net rate of electron transfer at an electrode is related to the electrode potential just as the rate of a chemical reaction is related to temperature. In a simple redox couple, where k_f and k_b are the heterogeneous rate constants for the forward and backward half-reactions, and n is the number of electrons transferred, we may write for oxidised and reduced species O and R respectively:



and from thermodynamic considerations the Nernst equation may be applied:

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{C_{\text{ox}}^{\circ}}{C_{\text{red}}^{\circ}}$$

where E° , the standard potential for the redox couple, is the potential at which the concentrations of R and O are equal, and C_{ox}° and C_{red}° are the concentrations of O and R at the electrode respectively. From kinetic considerations, assuming that the electron transfer is the rate determining step (that is slower than mass transfer), equations can be derived to show the relationship between current and potential. In the reaction co-ordinate diagram curves A and B represent the potential energy profiles of the reduced and oxidised forms respectively of the above redox couple at the equilibrium potential of the system (i. e. $k_f = k_b$). To effect electrochemical reduction or oxidation, an activation barrier, $\Delta G_{\text{eq}}^{\ddagger}$, must be overcome.



(After Kolthoff and Elving, 1963, 'Treatise on Analytical Chemistry', Interscience, New York.)

If the electrode potential is displaced from its equilibrium value by an amount ΔE in such a direction as to favour reduction (as represented in Curve C), the decrease in free energy for the reduced species is $\Delta G_f^\ddagger = nF\Delta E$. The new activation energy for reduction, ΔG_f^\ddagger , will however be lower than ΔG_{eq}^\ddagger by only a fraction α (where α = transfer coefficient), of the total free energy decrease imposed on the system. The remainder acts to raise the activation energy for oxidation. Using the relationships expressed in the free energy diagram:

$$\begin{aligned}\Delta G_f^\ddagger &= \Delta G_{eq}^\ddagger - \alpha nF\Delta E \\ \Delta G_b^\ddagger &= \Delta G_{eq}^\ddagger + nF\Delta E - \alpha nF\Delta E \\ &= \Delta G_{eq}^\ddagger + (1-\alpha)nF\Delta E\end{aligned}$$

where $0 < \alpha < 1$

Using absolute reaction-rate theory¹ it has been shown that:

$$k_f = k_f^{\text{ref}} \exp \left[\frac{-\alpha nF(E - E_{\text{ref}})}{RT} \right]$$

$$\text{and } k_b = k_b^{\text{ref}} \exp \left[\frac{(1-\alpha)nF(E - E_{\text{ref}})}{RT} \right]$$

where k_f and k_b are the heterogeneous rate constants for the cathodic and anodic currents. This exponential dependence of the electron transfer rate on potential shows that electrochemical reaction rates may be changed readily over many orders of magnitude by adjustment of the electrode potential. For a one electron transfer and the usual range of α (0.5), activation barriers may be modified by up to 3eV (ca. 70Kcal mol⁻¹), the equivalent of a formidable rise in temperature, thereby making possible very difficult electron transfers. The usefulness of aprotic solvents such as acetonitrile, which are inert over a range of 5-6V may now be appreciated.

Relating electrolysis current to potential, we may write:

$$i_c = nFA C_{ox}^o k_f^{ref} \exp \left[\frac{-\alpha nF(E-E_{ref})}{RT} \right]$$

$$i_a = -nFA C_{red}^o k_b^{ref} \exp \left[\frac{[(1-\alpha)nF(E-E_{ref})]}{RT} \right]$$

A commonly used reference potential is the normal hydrogen electrode (N. H. E.) which is zero volts by definition, allowing the above equations to be written:

$$i_c = nFA C_{ox}^o k_f^o \exp - \frac{\alpha nFE}{RT}$$

$$i_a = -nFA C_{red}^o k_b^o \exp \frac{(1-\alpha)nFE}{RT}$$

where k_f^o and k_b^o are the rate constants for electron transfer at the potential of the N. H. E.

At the standard potential, E^o , while the net current is zero, there is a state of dynamic electrochemical equilibrium, consisting of equal and opposite currents due to the equal rate of oxidation and reduction.

Equating the above expressions, we have:

$$nFA C_{ox}^o k_f^o \exp \left[\frac{-\alpha nFE^o}{RT} \right] = nFA C_{red}^o k_b^o \exp \left[\frac{[(1-\alpha)nFE^o]}{RT} \right]$$

Rearrangement affords:

$$\frac{C_{ox}^o k_f^o}{C_{red}^o k_b^o} = \exp \frac{nFE^o}{RT}$$

Taking logarithms of both sides and solving for E^o ,

$$E^{\circ} = \frac{RT}{nF} \ln \frac{k_f^{\circ}}{k_b^{\circ}} \quad (\text{Since at } E^{\circ}, C_{\text{ox}}^{\circ} = C_{\text{red}}^{\circ})$$

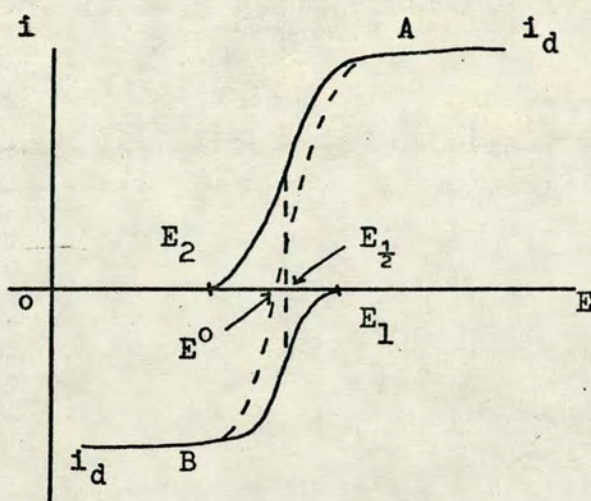
Substituting for E° in the Nernst equation, we have

$$E = \frac{RT}{nF} \ln \frac{k_f^{\circ}}{k_b^{\circ}} - \frac{RT}{nF} \ln \frac{C_{\text{red}}^{\circ}}{C_{\text{ox}}^{\circ}}$$

This kinetic form of the Nernst equation may be used to explain the phenomenon of rapid (reversible) and slow (irreversible) electron transfer. Suppose that the potential of an electrode in a solution containing the redox couple is suddenly changed to a new value and that after a short given time interval the concentrations C_{ox}° and C_{red}° are measured. If C_{ox}° and C_{red}° cannot attain their new equilibrium values in this time interval the system will appear to deviate from the Nernst equation and is said to be irreversible. Conversely a system in which C_{ox}° and C_{red}° can reach their equilibrium values at any potential during the time scale of the experiment is said to be reversible or Nernstian. The type of behaviour observed will depend on the magnitudes of the electron transfer rate constants k_f° and k_b° in the above equation and of course on the time scale of measurement. The borderline between reversible and irreversible processes is placed at about $10^{-2} \text{ cm s}^{-1}$.

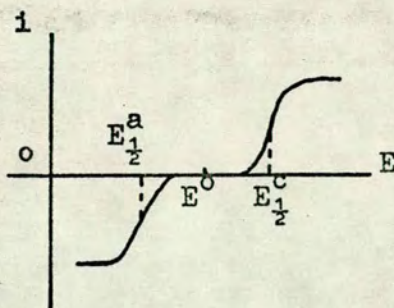
In the present work the electron transfer process of several systems was studied by both polarography and cyclic voltammetry, both techniques being specified examples of the general voltammetric technique which is the study of the current-potential relationship at a microelectrode. Both techniques involve a linear variation of potential with time and by the analysis of the wave-shape, information regarding the degree of reversibility of the electron transfer step may be obtained. Consider first the voltammetric curves obtained by a very slow variation of potential at a stationary solid electrode. For the oxidised and reduced forms of a reversible redox couple, reduction of O (curve A) gives a cathodic curve and oxidation of R (curve B) an anodic current. The maximum current,

i_d , attainable in each case is limited by the rates of diffusion of O and R to the electrode surface.



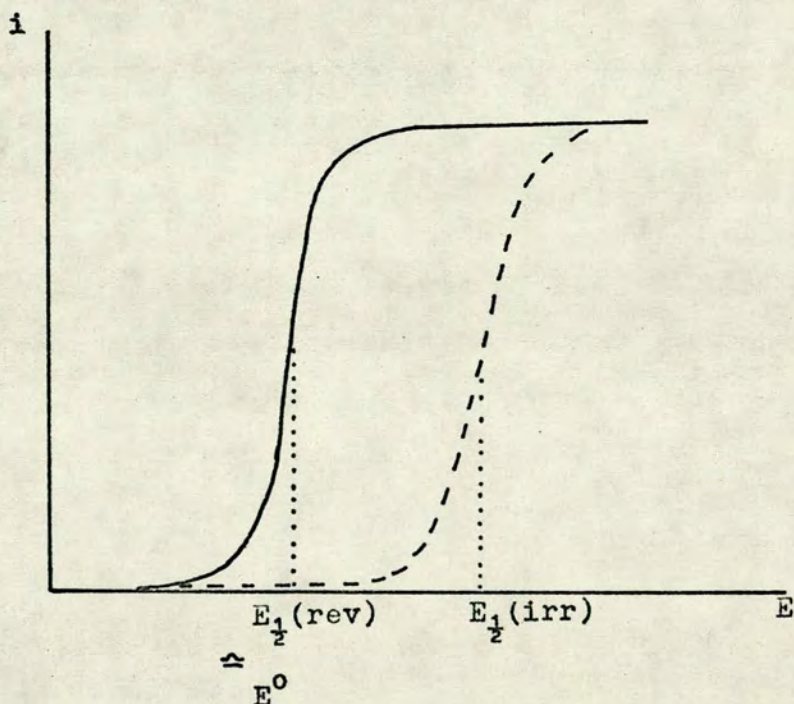
(After 'Organic Electrochemistry', ed. M. M. Baizer, Marcel Dekker, Inc. New York, 1973, p23.)

Oxidation or reduction at a finite rate can be achieved by bringing the electrode potential slightly above or below the equilibrium potential E^0 . At potentials cathodic of E_1 only reduction of O will occur; conversely at potentials anodic of E_2 only oxidation of R will take place. The net current flowing is represented by the dashed line, this current being zero at E^0 , since oxidation and reduction are taking place at exactly the same rate. The absolute value of the individual currents at the E^0 is known as the exchange current. The half-wave potential, $E_{1/2}$, is defined as the potential at which the current is $\frac{1}{2} i_d$. In the irreversible case, the cathodic and anodic electron transfers take place in such widely separated potential ranges that it is impossible to realise either an oxidation or a reduction at a finite rate in the vicinity of E^0 , as shown below.



(After 'Organic Electrochemistry', ed. M.M. Baizer, Marcel Dekker, Inc. New York, 1973, p24.)

A similar situation is observed in a polarographic experiment in which only R is present. The solid line represents a reversible couple and the dashed line an irreversible couple. It can be shown that in the former case the $E_{\frac{1}{2}}$ is very close to the standard potential, E° .



(After 'Synthetic Organic Electrochemistry', A.J. Fry, Harper and Row, 1972, p.43.)

The polarographic diffusion current, i_d , is given by the Ilkovic equation for a diffusion controlled process.

$$i_d = 708 n D^{1/2} t^{1/6} m^{2/3} c$$

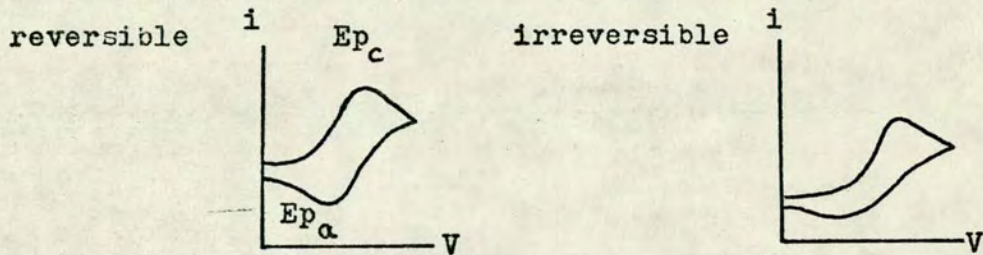
where i_d is in μA , c is the concentration of the electroactive material (m. moles l^{-1}), m is the rate of mercury flow (mg s^{-1}), D is the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) and t is the drop time (s). Verification of a diffusion controlled process may be achieved by a plot of $i_{\text{lim}} \text{ vs } h_{\text{corr}}^{1/2}$ where h is the height of the mercury column (corrected for back pressure), and i_{lim} is the current at the top of the wave. The half-wave potential, $E_{1/2}$, is significant for a number of reasons. It is independent of the bulk concentration of the electroactive species and can also be used as a guide to the reversibility of electron transfer by means of the relationship

$$E = E_{1/2} - \frac{0.0592}{n} \log \frac{i}{i_d - i}$$

A plot of $\log \frac{i}{i_d - i} \text{ vs. } E$ should have a slope of $\frac{59.2}{n} \text{ mV}$. Another test of reversibility, indicated below, is known as Tomes' Criterion

$$E_{3/4} - E_{1/4} = \frac{0.0564}{n} V$$

The major features which distinguish cyclic voltammetry (CV) technique from polarography are the use of a stationary electrode, faster potential scan rates, and the use of a cyclic triangular wave-form; after the voltammogram has been recorded to a potential beyond the peak potential, E_p , the direction of voltage scan is reversed. Typical cyclic voltammograms are shown below for reversible and irreversible systems. The peaked current is a consequence of the use of a stationary electrode: as the potential moves into the region where the substrate is reduced, the region adjacent to the electrode becomes depleted of material and the current decreases, the rate of variation of potential being too rapid for diffusional processes to maintain equilibrium with the bulk of the solution.



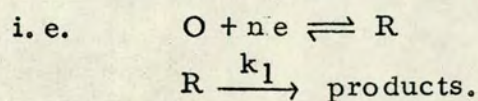
(After 'Synthetic Organic Electrochemistry', A.J.Fry, Harper and Row, 1972, p82.)

It can be shown that for a reversible process $E_{P_a} - E_{P_c}$ and $E_{P_c/2} - E_{P_a/2}$ will each be equal to $\frac{0.059}{n}$ V;

$$E_{P_c/2} = E_{P_a} = E^{\circ} + \frac{0.028}{n} \text{ V ;}$$

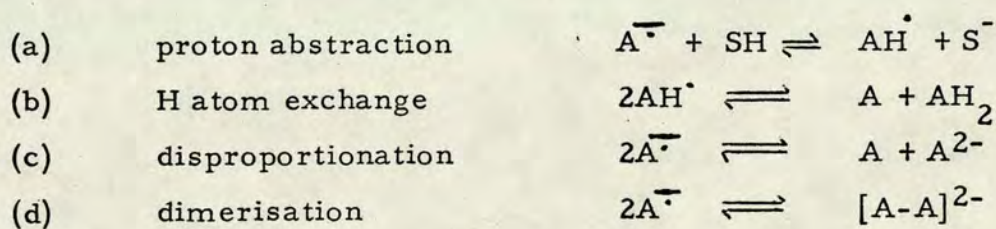
$$E_{P_a/2} = E_{P_c} = E^{\circ} - \frac{0.028}{n} \text{ V ; } i_{P_a/i_{P_c}} \text{ (the ratio of anodic to cathodic peak currents) = 1.}$$

So far only redox systems in which both the oxidised and reduced forms are chemically stable have been considered. Let us now consider situations where homogeneous chemical reactions are coupled to the electron transfer step; these may precede or follow a reversible or irreversible electron transfer, and the chemical reactions may themselves be reversible or irreversible.* A frequently encountered situation is the ec mechanism, whereby a reversible electron transfer is followed by chemical reaction



* Since the work to be discussed concerns electro-reduction, the electron transfer process will hereafter be considered from this point of view.

Such a mechanism is readily characterised by CV experiments since a fraction of R reacts chemically and is not available for re-oxidation upon scan reversal, resulting in a diminished anodic peak. This situation may be distinguished from the irreversible charge transfer case by the marked effects of scan rate upon the shape of the voltammogram. In the ec case an increase in scan rate will result in less time available for the follow-up chemical reaction, thereby making the cyclic voltammogram appear more reversible whereas the effect of an increase in scan rate on a slow charge transfer would if anything make the cyclic voltammogram appear less reversible for reasons already put forward. The nature of follow-up chemical reactions has been classified by Savéant² as (a) acid-base (or nucleophile-electrophile) reactions in which the solvent in particular may play an important role, (b) atom exchange, in particular H atom exchange, (c) electron exchange in solution, for example disproportionation, (d) condensation reactions, for example dimerisation, and (e) reactions on the electrode surface, for example specific adsorption. For a radical anion $A^{\cdot-}$, reactions (a)-(d) may be illustrated as follows:



The reactivity of the species $A^{\cdot-}$ would of course be highly dependent upon its structure and the nature of the medium, stability generally being greater for highly delocalised species in aprotic conditions. Thus subsequent electron transfers may occur to not only the radical anion itself, but also to any of the species resulting from its transformation by one of the routes mentioned above. The transfer of a second electron to a radical anion is generally considered² as more difficult than transfer of the first, due to coulombic repulsion, although this may be modified by processes such as delocalisation, solvation and ion-pairing. However direct simultaneous transfer of two electrons to a substrate is very unusual. The resulting

di-anionic species may undergo any of the follow-up reactions mentioned above.

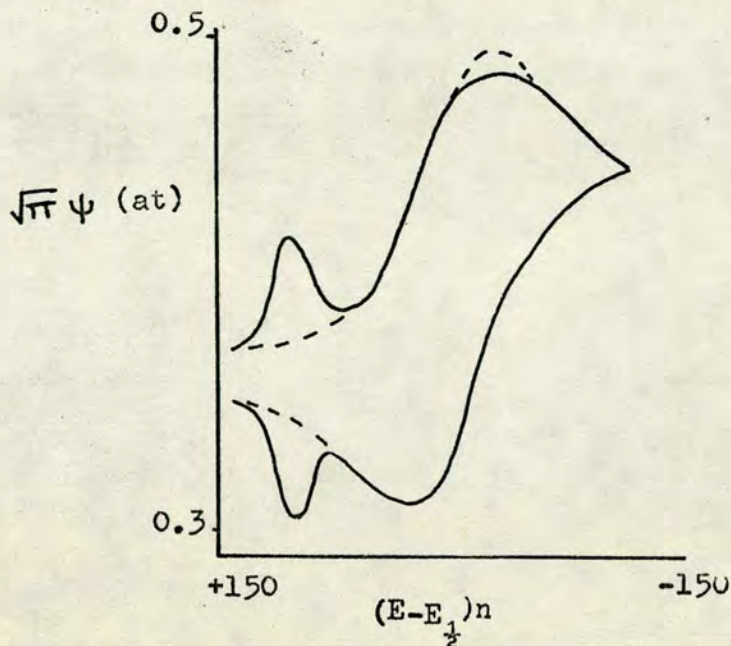
Quantitative analyses of the shapes of cyclic voltammograms have been carried out by Nicholson and Shain and others³⁻⁸ who used computer assisted numerical methods to solve complex differential equations relating the current to rates of diffusion, coupled chemical reactions and potential, thereby allowing determination of heterogeneous and chemical rate constants. An alternative approach has been used by Saveant⁹⁻¹² whose diagnostic criteria involve determination of the variation in peak current and peak potential with sweep rate and concentration, allowing characterization of the mechanism of the electrode reaction. However, such analyses were outside the scope of these studies and simpler techniques such as wave-clipping, which involves sweep reversal at selected potentials, and the effect of added proton donors on the cyclic voltammogram have been used, coupled with preparative electrolyses at controlled potential. Such methods can only be indicative and cannot give any conclusive evidence or quantitative information on the mechanism of reduction.

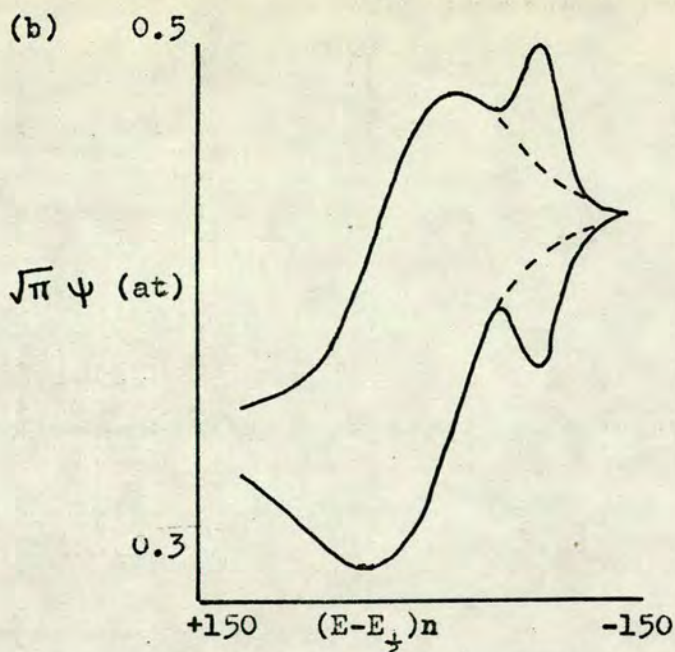
Wave-shape analyses may be complicated by two processes, namely maxima and adsorption. Polarographic maxima are caused by a convection or streaming of the solution surrounding the mercury drop. The process is caused by the electrode reaction itself and results in considerably higher currents than those controlled by diffusion. Maxima of the first kind are usually acute and appear at the beginning of the wave, whereas those of the second kind are usually rounded and return to the value of the limiting current at more negative potentials. The latter are generally observed with more concentrated solutions (>0.1M supporting electrolyte) and at high flow rates of mercury. Both types of maxima can frequently be suppressed by traces of surface active materials such as gelatin or methyl cellulose.

Adsorption on the other hand results from changes in the composition of the interfacial region which occur on application of an external potential. The specific structure adopted by a solution in contact with an electrode constitutes the double layer, the complex nature of which allows only model representation, although detailed descriptions are available.^{13, 14} The

model of Grahame¹⁵ suggests that the distance of closest approach of solvated cations is limited both by a layer of dipole oriented solvent molecules and by the solution sheath of the ions themselves. The plane passing through the centres of the solvated ions is known as the Outer Helmholtz Plane (OHP). On the solution side of this plane there is an inhomogeneous distribution of anions and cations - the diffuse layer - with cations predominating. The region in which there is an effective perturbation of the structure of the solution is very thin (10^{-6} cm) when compared to the diffusion layer thickness (10^{-3} cm). In some cases molecules other than those of the solvent may penetrate the OHP leading to the phenomenon of specific adsorption, believed to involve short range chemical forces. The plane through the centres of the specifically adsorbed ions and molecules is known as the Inner Helmholtz Plane. There are many examples of the effects of specific adsorption on organic electrode processes, some of which will be discussed in the text, but a general account has been given by Ebersson and Nyberg.¹⁶ The occurrence of specific adsorption may be suggested by preparative studies - variations in the product distribution with conditions being attributed to changes in the double layer structure - and also by voltammetric studies. Theoretical CV curves for strong adsorption of product (a), and strong adsorption of reactant (b) are shown below. Dotted lines show the normal reversible curves.

(a) After 'Techniques of Chemistry' Vol.1, ed. A.Weissberger, 'Physical Methods of Chemistry', Part 11A, Wiley-Interscience, 1971, p504,506.





The previous discussion has mainly been concerned with electron transfer at micro-electrodes and at analytical concentrations. Additional factors may be considered during electrolysis at electrodes of relatively large surface area and higher concentrations, giving rise to cell currents in the mA-A range. The usefulness of such experiments may be two-fold to corroborate postulated reaction mechanisms deduced from analytical studies, and as a tool for organic synthesis. The method most commonly used involves reduction at a controlled potential, selected by consideration of electro-analytical data, during which the total voltage V impressed across the cell is distributed in the following manner.

$$V = E_a - E_c + iR$$

where E_a and E_c are the potentials of the anode and cathode, i is the current (A), and R is the cell resistance (ohms). The working electrode potential, E_c in the case of a reduction, is controlled by varying V so that the potential between the cathode and the reference electrode is maintained at a pre-selected value, the most essential quality of the reference electrode being that it should exhibit a well-defined potential which is stable for long periods. A large voltage (iR) drop may be experienced between the cathode and reference electrode, particularly in aprotic solvents of high resistance when R may be in the region of 10-20 K ohms. This may frequently result in a cathode potential located on the rising portion of the $i-V$ curve rather than on the plateau, particularly at the beginning of an electrolysis when the current and hence the iR drop are high. An interesting study of the effects of potential

distribution and cell design on controlled potential electrolyses has been carried out by Harrar and Shain¹⁷. Other factors which may effect differences between micro- and macro-results are the time scale of the experiment, the surface area of the electrode, the concentration of substrate and pH changes in the vicinity of the electrode. The latter factor has particular relevance to the present studies carried out using acetonitrile as solvent.

Finally the solvent itself can have an important influence on the pathway of an electrochemical reaction. The influence may be the result of (a) the solvation of dissolved species, (b) donor or acceptor properties towards dissolved species, (c) modification of the nature or properties of species that participate in or that are produced by the charge transfer, and (d) variation in the charge transfer itself via the electrode reaction kinetics, double layer structure and adsorption phenomena. The solvating properties of a solvent can be estimated from the di-electric constant. In a dissociating solvent ($\epsilon > 30$) e. g. water, ethanol, and acetonitrile, ion-pairs are believed to be completely dissociated and solvation of dissolved species would be expected. The extent of solvation can affect the $E_{\frac{1}{2}}$ of a reversible system in different solvents. The availability of protons is also an important factor when considering solvent effects and leads to the convenient division of solvents into protic and aprotic. Protic solvents are those which can function as acids towards strongly basic species and include alcohols, acids and primary and secondary amines; liquid ammonia also belongs to this class. Aprotic solvents e. g. acetonitrile and N,N'-dimethylformamide, by contrast cannot normally function as acids and their use frequently results in a simpler electrode mechanism since the product of the first electron transfer is generally more stable than in a protic medium. The controlled addition of proton donors can also provide mechanistic information. However it must be remembered that residual water is frequently the major impurity in aprotic solvents. Drying procedures (e. g. the action of dehydrating agents and distillation) may produce a solvent which typically contains 10^{-3} mole l^{-1} (20 ppm) of water and addition of an electrolyte and manipulation of the medium may increase this concentration to 5×10^{-3} to

$10^{-2} \text{ mol l}^{-1}$. Thus analytical 'non-aqueous' electrochemistry usually takes place in a medium containing between 10 and 100 times more water than the compound under study.

DISCUSSION

FIGURE 1
 Et_4NBF_4 (10^{-1}M) in CH_3CN vs. $\text{Ag}/10^{-1}\text{M Ag}^+$; DME.

- (a) Before pre-treatment
(b) After pre-treatment at -3.0V

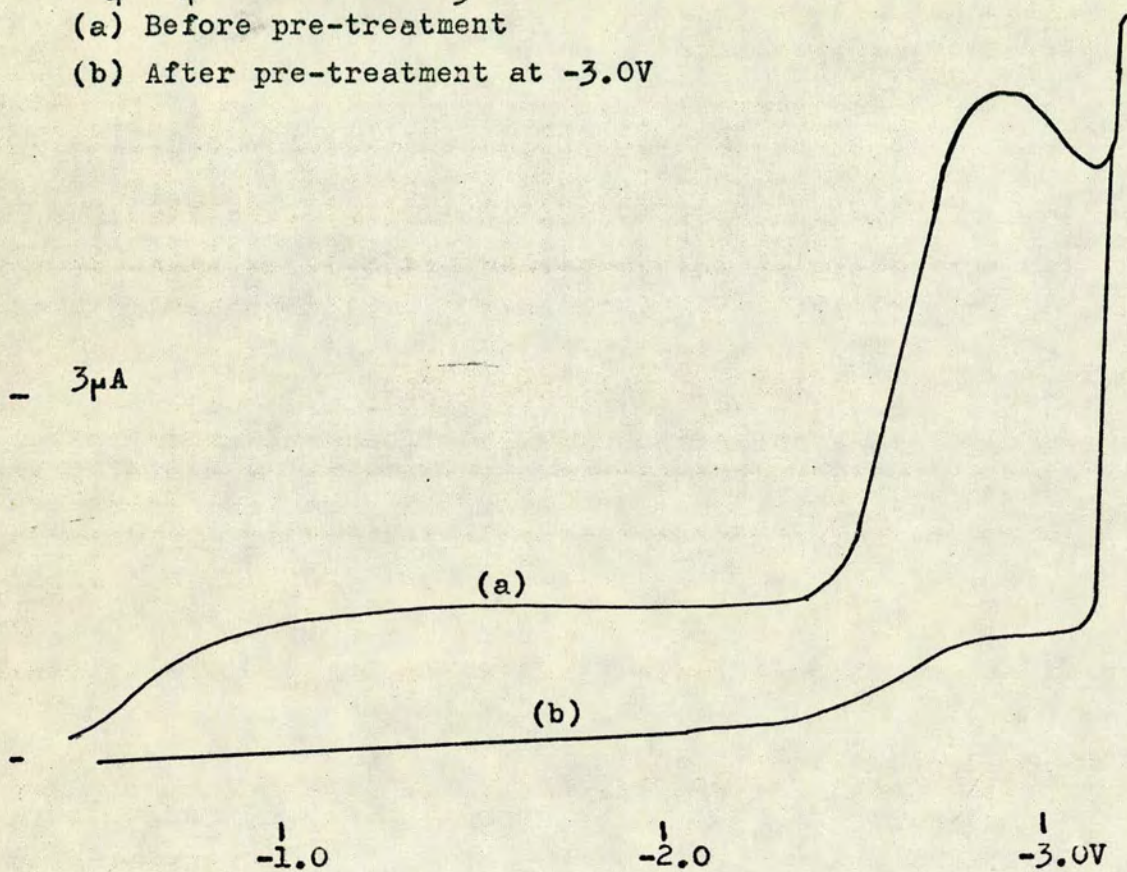


FIGURE 2
 Et_4NBF_4 (10^{-1}M) in CH_3CN vs. $\text{Ag}/10^{-1}\text{M Ag}^+$; Pt wire.

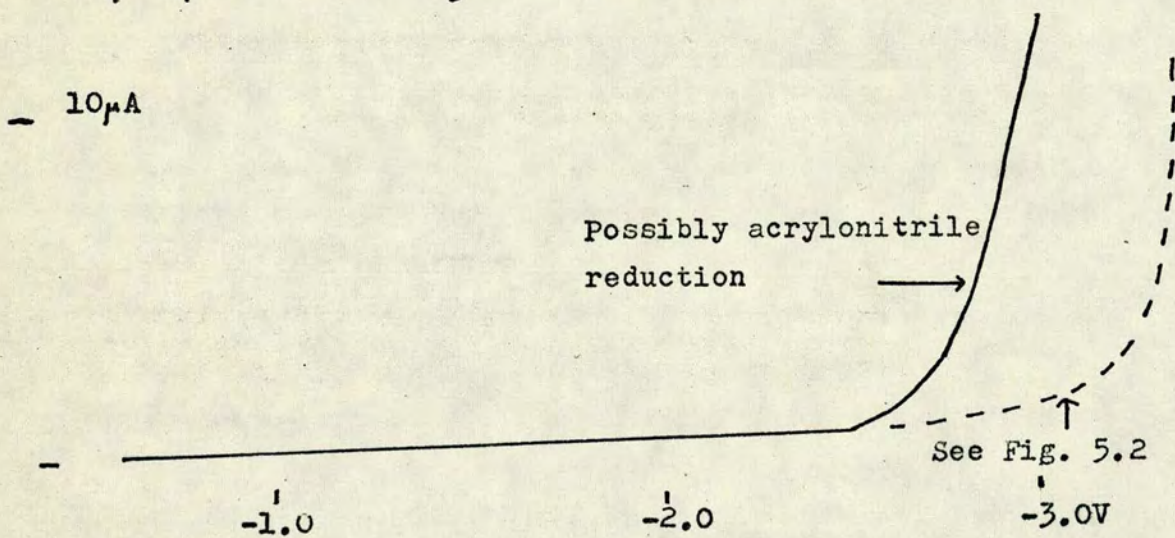
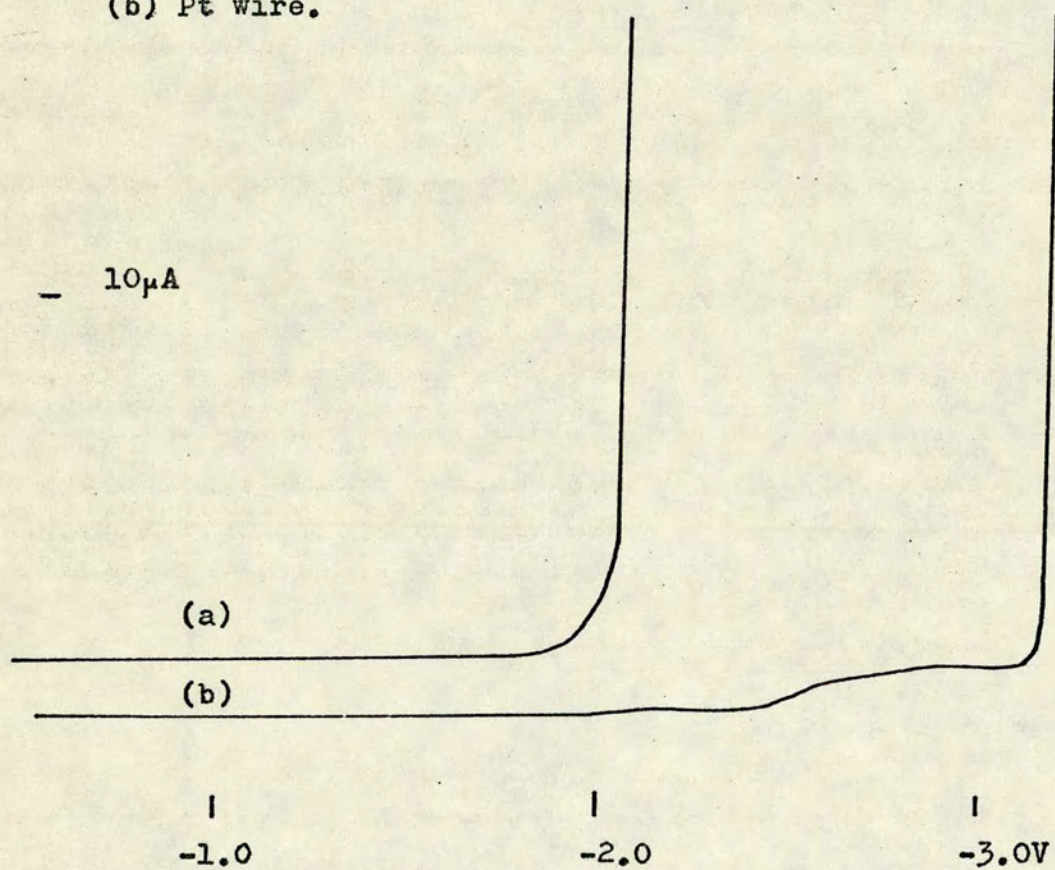


FIGURE 3

LiClO_4 (10^{-1}M) in CH_3CN vs. Ag/Ag^+ (10^{-1}M).

(a) DME.

(b) Pt wire.



A. Electrochemistry in Acetonitrile

1. Introduction

Acetonitrile (b. p. 82°C ; $\epsilon = 37$; pK_a 25) is a frequently used aprotic solvent for electrochemical studies owing to its excellent solvent properties for organic and inorganic compounds and its wide, usable potential range.

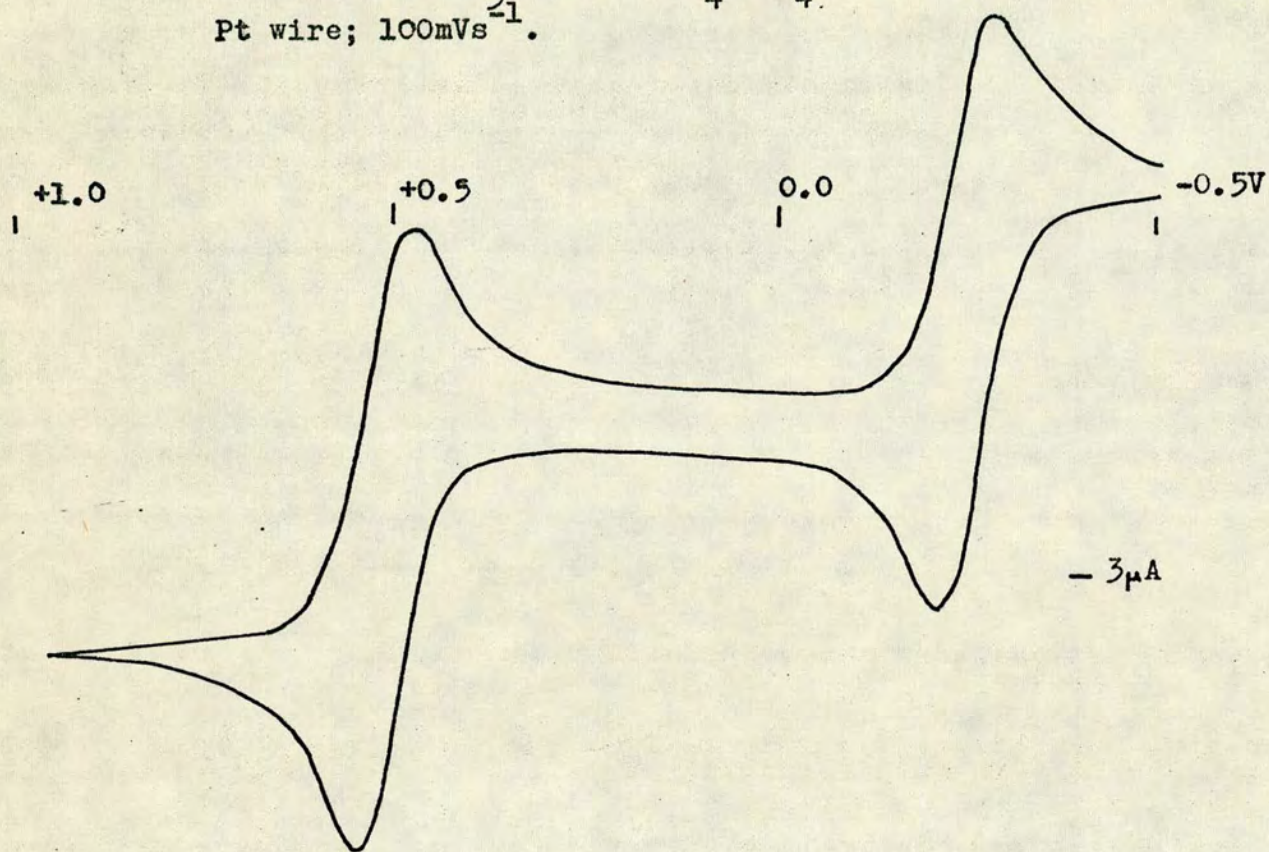
Commercial acetonitrile contains impurities which include acrylonitrile (~~from which it is manufactured~~), hydrolysis products of acetonitrile (e. g. ammonia, acetic acid and acetamide) and water. The acrylonitrile, water and acetic acid lower the cathodic limit. The methods^{18, 19} employed to purify 'Reagent Grade' acetonitrile serve primarily to remove the water e. g. 1000 p. p. m. H_2O was reduced to 120 p. p. m (Karl Fischer titration) after treatment with phosphorus pentoxide and calcium hydride. A background scan of the solvent/supporting electrolyte systems (e. g. Fig. 1a) showed an impurity peak at $E_{\frac{1}{2}} -2.6\text{V}$ which was attributed to acrylonitrile. This impurity could be removed by pre-treating the solution (Fig. 1b) at a mercury pool electrode held at a constant potential of -3.0V until the background current had decreased to an acceptable level ($<5\text{mA}$). An alternative procedure²⁰ for the removal of acrylonitrile from the solvent involves distillation from sodium hydride during the purification process.

Cathodic Limits in Acetonitrile

Throughout these studies a silver-silver nitrate (0.1M) reference electrode was employed, its use in acetonitrile being well documented.²¹ Cathodic limits were recorded in the presence of tetraethylammonium (Figs 1 and 2) and lithium (Fig. 3) cations, at a dropping mercury electrode (DME) and platinum wire/glass tip electrode. Tetramethyl- and tetrabutylammonium salts did not show any advantage over the tetraethylammonium salt. The range at platinum in the presence of the latter salt (Fig. 2) was somewhat lower than expected, although in the presence of a reducible substrate e. g. acetophenone (Fig. 5. 2) the range clearly extended beyond -3.0V . The reduced range in Fig. 2 can probably be attributed to acrylonitrile reduction, the surface area of the platinum electrode being considerably greater than that of the DME. In general, the commonly

FIGURE 4.1

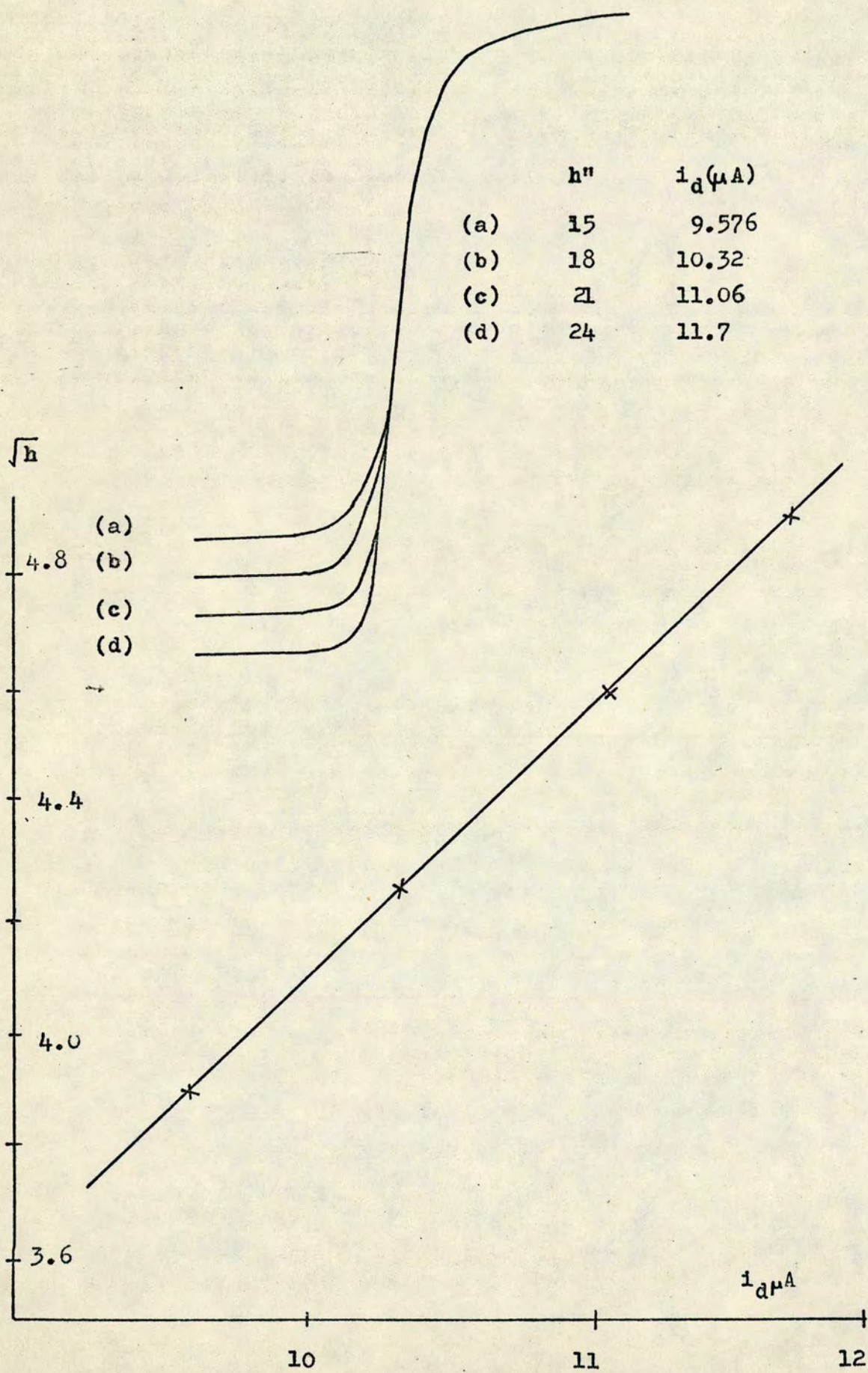
DMPZ(2mM) in $\text{CH}_2\text{CN}(10^{-1}\text{M Et}_4\text{NClO}_4)$ vs. $\text{Ag}/10^{-1}\text{M Ag}^+$;
 Pt wire; 100mVs^{-1} .



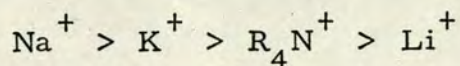
wave	E_{p_a} (V)	$E_{p_a} - E_{p_c}$ (mV)	i_p (μA)	$\frac{i_{p_c}}{i_{p_a}}$
I	-0.2	80	3.5	1.0
II	+0.56	80	3.5	1.0

FIGURE 4.4

Variation of i_d with mercury column height.



used cations increase in reducibility in the order



and cathodic limits at mercury are displaced slightly to more negative potentials compared to platinum. The cathodic limit at a DME is believed to be due to amalgam formation, which occurs very readily in the case of lithium (Fig. 3a). At platinum, formation of metallic lithium is the cathodic reaction as shown by deposition on the electrode, whereas cleavage is probably the limiting reaction in the case of the quaternary ammonium ions.

The ranges are summarised (Table I) and some literature values²² for these and other supporting electrolytes are also given for comparison.

Estimation of Electrode Reversibility

5,10-Dihydro-5,10-dimethylphenazine (DMPZ) has been shown²³ to exhibit two, completely reversible, 1e transfers in acetonitrile. This compound was chosen to estimate the electrode reversibility. Slow sweep cyclic voltammetry (100 mV s^{-1}) showed two 1e oxidation waves which exhibited well defined cathodic counterparts on sweep reversal (Fig. 4.1). The ratio of cathodic to anodic peak heights ($\frac{i_{pc}}{i_{pa}}$) was unity in each case suggesting a stable radical cation and di-cation, although the peak separation ($E_{p_a} - E_{p_c}$) was considerably larger (80mV) than the theoretical value (59mV) for a reversible system. This may be attributed to iR drop across the cell and possibly recorder lag. A polarogram of the first wave (Fig. 4.2) showed behaviour typical of a reversible system ($E_{1/4} - E_{3/4} = 60\text{mV}$) and a graph of $\log \frac{i}{i_d - i}$ vs. $-(\text{potential})$ (Fig. 4.3) gave a straight line of slope $64.8 \pm 2.3 \text{ mV}$, close to the required value of 56mV for a reversible system. A study of the peak height versus the square root of the mercury column height (\sqrt{h}) (Fig. 4.4) gave a straight line plot, thereby confirming that a diffusion controlled process was occurring.

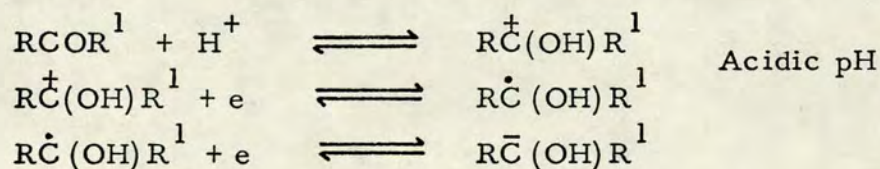
2. The Reduction of Acetophenone in Acetonitrile.

Introduction

The carbonyl group is capable of three types of reduction depending upon the conditions used. These result in formation of a hydrodimer or pinacol ($1F \text{ mol}^{-1}$), a dihydro-product or alcohol ($2F \text{ mol}^{-1}$) and a methylene compound ($4F \text{ mol}^{-1}$). Formation of the latter type of product shall not be considered here.

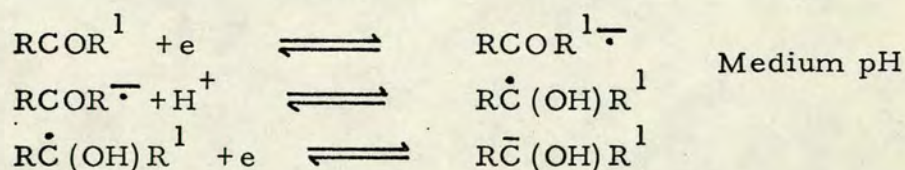
(a) Reduction in Aqueous Media

Many of the earlier studies on the reduction of carbonyl compounds were carried out in aqueous solution at various pH values using polarographic techniques. The results of such an investigation on the reduction of aryl alkyl ketones were reported by Zuman²⁴ together with a comprehensive list of references to the preceding literature. In strongly acid solutions two 1e waves were obtained, corresponding to formation of the pinacol and alcohol respectively. Under these conditions protonation was believed to precede the first electron transfer, which thus afforded the neutral ketyl radical. For the ketone RCOR^1 we may write:



Scheme (1)

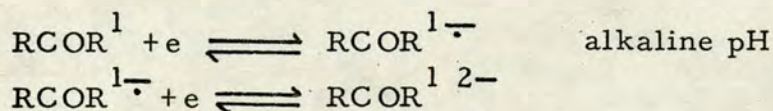
As the pH was increased the two successive 1e waves were replaced by a single 2e wave associated with alcohol formation. Under these conditions it is believed that protonation follows the first electron transfer rather than precedes it, resulting in an ece mechanism, shown below:



Scheme (2)

By analogy with studies on aromatic hydrocarbons,²⁵ the electron affinity of the ketyl radical $\text{RC}^\bullet(\text{OH})\text{R}^1$ was thought to be always greater than that of the parent carbonyl compound, thereby causing coalescence of the first and second electron transfers.

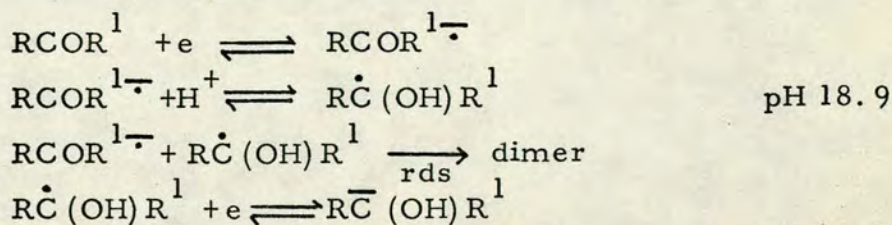
Further increases in pH resulted in a decrease of the 2e wave to half its initial height and the appearance of a second 1e wave at more negative potentials. This was attributed to a slowing down of the protonation step in the above ece scheme, electron transfer to the radical anion affording a di-anion as indicated below.



Scheme (3)

Under these conditions Zuman found the height of the first wave and the $E_{1/2}$ of the second wave to be highly dependent upon the nature and concentration of the cation of the supporting electrolyte, the effects being attributed to double layer and ion pairing phenomena.

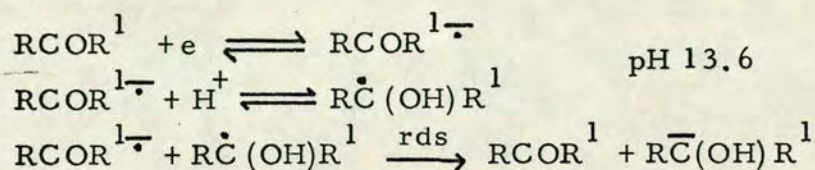
A further comprehensive study on the reduction of aromatic carbonyl compounds in an alkaline, ethanolic buffer (pH range 13.6-18.9) has been carried out by Nadjo and Savéant.¹² Acetophenone was shown to exhibit two 1e waves in the most alkaline medium, hydrodimerisation occurring at the potential of the first wave. This was indicated by the irreversibility of the first wave and the small height of the second wave on cyclic voltammetry at low sweep rates. A kinetic analysis, using E_p vs. \log (sweep rate) behaviour,^{26, 27} suggested that dimerisation was due to a rate determining coupling of the neutral ketyl radical, $\text{RC}^\bullet(\text{OH})\text{R}^1$, with the ketyl radical anion RCOR^{1-} . The second wave, which was associated with alcohol formation, resulted from electron transfer to the ketyl radical.



Scheme (4)

The two 1e waves resulted from the dimerisation process which caused a shift of the first wave to more anodic and a shift of the second wave to more cathodic potential.

In less basic conditions, a single, 2e wave, associated with alcohol formation, was obtained. Rather than an ece mechanism, as suggested by Zuman, Savéant et al supported a second order disproportionation mechanism (Scheme 5).



Scheme (5)

(b) Reduction in Aprotic Media

Studies of carbonyl compounds in aprotic solvents are related to those in alkaline aqueous or alcoholic media, two waves being observed corresponding to the formation of the radical anion and di-anion respectively. A polarographic study of acetophenone in DMF by Wawzonek and Gunderson²⁸ showed that addition of water effected an anodic shift of both waves, but particularly of the second wave, and also an increase in the height of the second wave at the expense of the first. Preparative scale reductions of acetophenone by these and other workers²⁹⁻³² all afforded high yields of the pinacol (even when carried out at the potential of the second wave³²) and attempts²⁸ to trap the acetophenone radical anion by carbon dioxide were unsuccessful, suggesting that dimerisation was rapid.

The mechanism of dimerisation of acetophenone to the corresponding pinacol was the subject of a study by Savéant and Tessier³³ using convolution potential sweep voltammetry. The reductions were carried out in acetonitrile containing tetraethylammonium perchlorate as supporting electrolyte and the results indicated that pinacol formation resulted from a rate determining dimerisation of two radical anions. The rate constant for dimerisation increased with increasing water content of the solvent

FIGURE 5.1

PhCOCH₃ (2mM) in CH₃CN(10⁻¹M Et₄NBF₄) vs. Ag/10⁻¹M Ag⁺; DME.

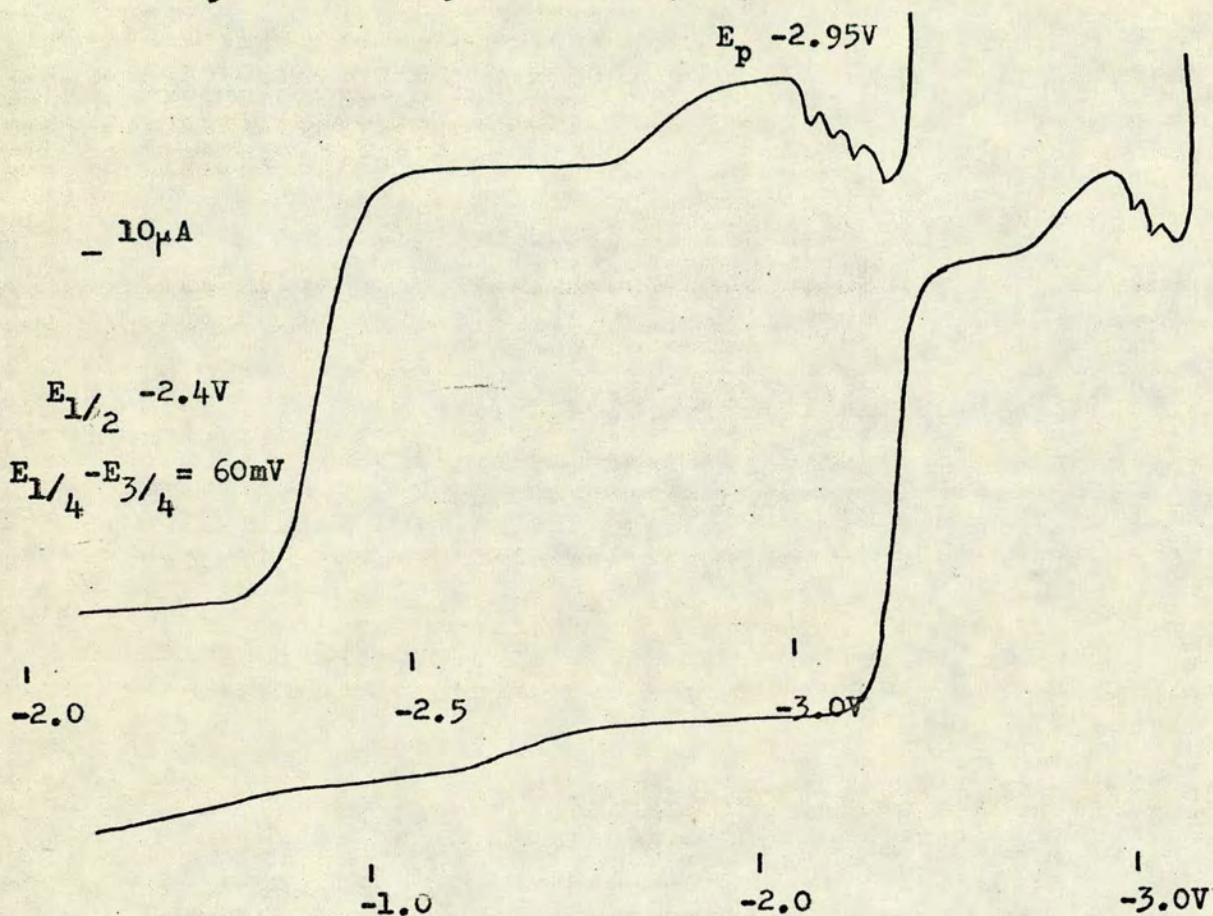
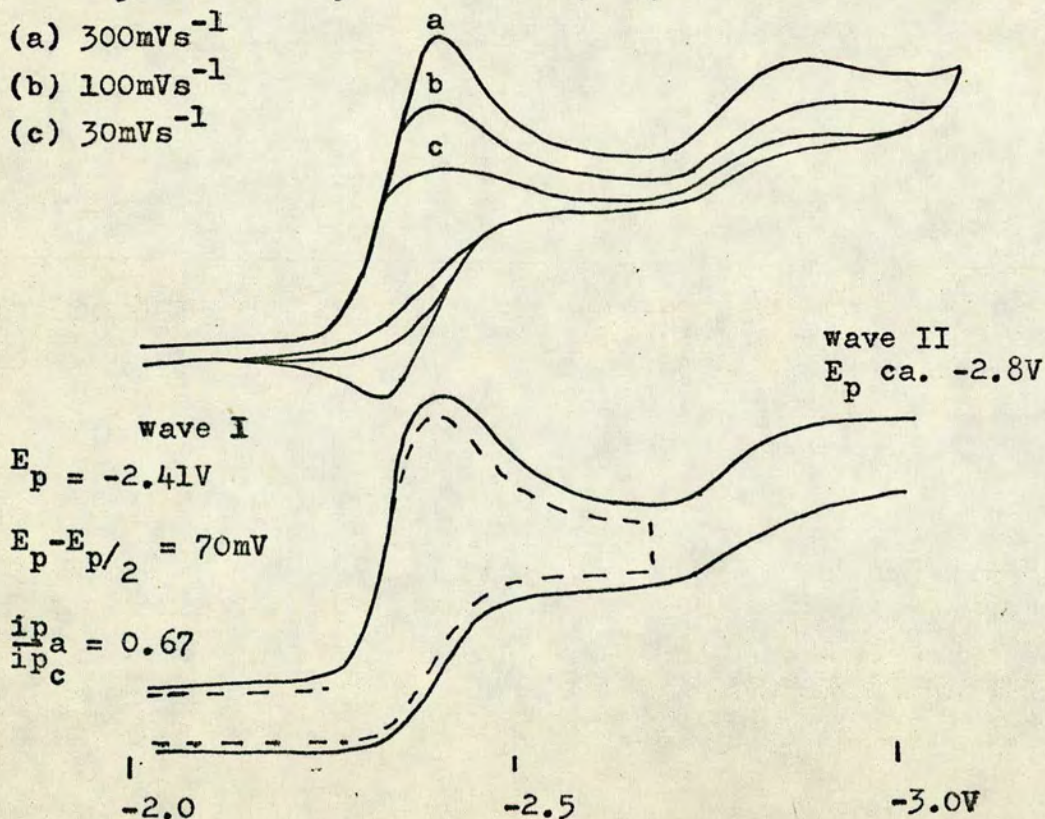


FIGURE 5.2

PhCOCH₃(2mM) in CH₃CN (10⁻¹M Et₄NBF₄) vs. Ag/10⁻¹M Ag⁺; Pt wire.

- (a) 300mVs⁻¹
- (b) 100mVs⁻¹
- (c) 30mVs⁻¹



($k_d = 3 \times 10^4$, 4×10^5 , and $1.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for water content 0.3, 1.0, and 5.0% respectively). Also the standard potential for the first wave was found to decrease by 59mV on increasing the water content from 0.3 to 1%. These observations were attributed to increased solvation of the radical anions resulting in a smaller coulombic repulsion between them, and hence an acceleration in the rate of dimerisation.

(c) The Stereochemistry of Pinacolisation

The mechanism of pinacolisation of acetophenone with respect to the ratio of isomers (d+l:meso) has been the subject of several studies. The effect of added water and supporting electrolyte cation has been particularly noted, and the results have been explained in terms of hydrogen bonding and ion-pairing of intermediates. 29-31

Discussion

(a) Polarography and Cyclic Voltammetry of Acetophenone in Acetonitrile

The polarography and cyclic voltammetry (CV) of acetophenone in purified acetonitrile was studied in the presence of several supporting electrolytes.

(i) Tetraethylammonium Perchlorate

In the presence of tetraethylammonium perchlorate, acetophenone exhibited two 1e transfers corresponding to formation of a radical anion and di-anion respectively. As indicated in the introduction, this is the behaviour expected in an aprotic solvent. The polarogram (Fig. 5.1) suggested a reversible first wave ($E_{1/4} - E_{3/4} = 60\text{mV}$) and this was supported by CV results at variable sweep rates (Fig. 5.2). At fast sweep rates the wave tended towards a reversible situation, indicating that a chemical reaction, presumably dimerisation of the radical anion, perturbs the system at slower sweep rates. This was supported by the height of the second wave being considerably smaller than that of the first. A similar small second wave (the erratic form of which was attributed to the rapid flow rate of the DME at these very negative potentials) was

FIGURE 5.3

PhCOCH_3 (2mM) in CH_3CN ($10^{-1}\text{M Et}_4\text{NClO}_4$) vs. $\text{Ag}/10^{-1}\text{M Ag}^+$; DME.

———— prior to addition of water $E_{1/2} -2.35\text{V}$

----- plus water (ca. 1.0M) $E_{1/2} -2.24\text{V}$

(a) Y-axis attenuation x1

(b) Y-axis attenuation x2

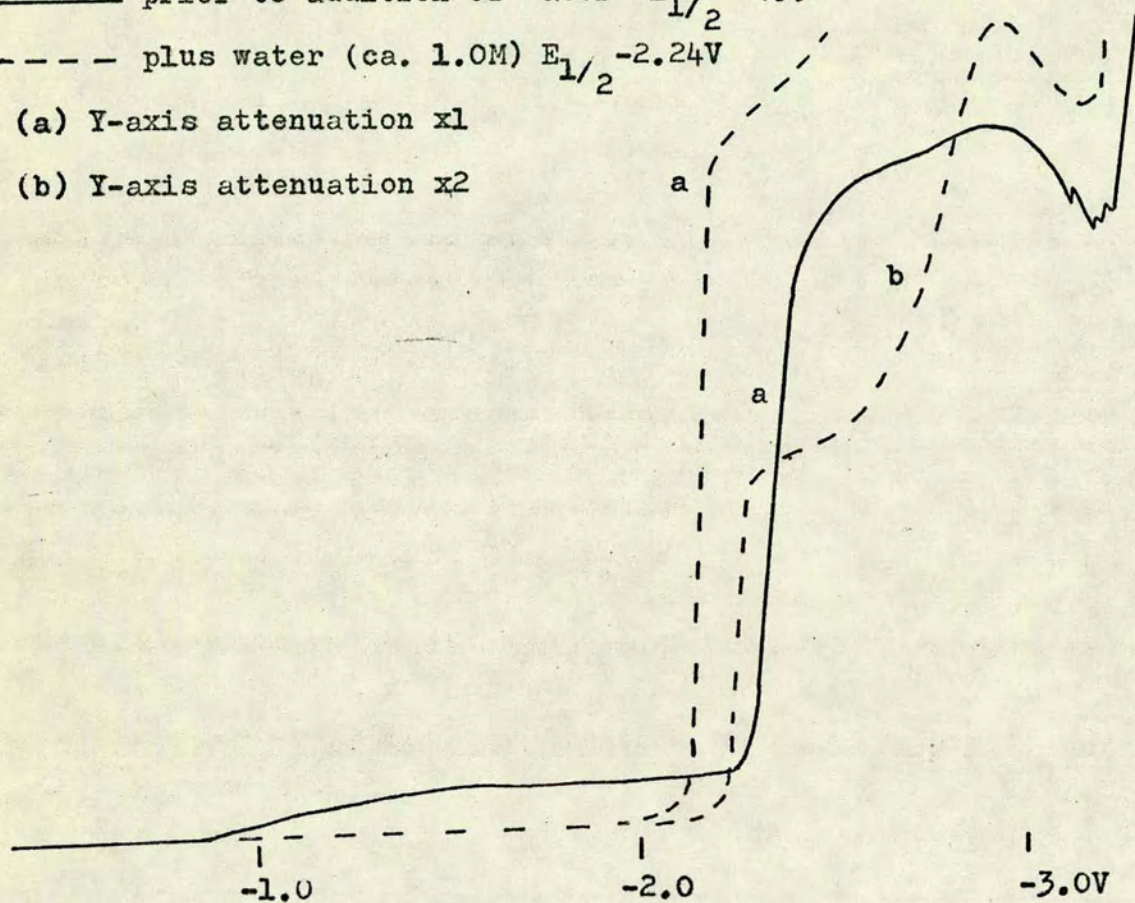
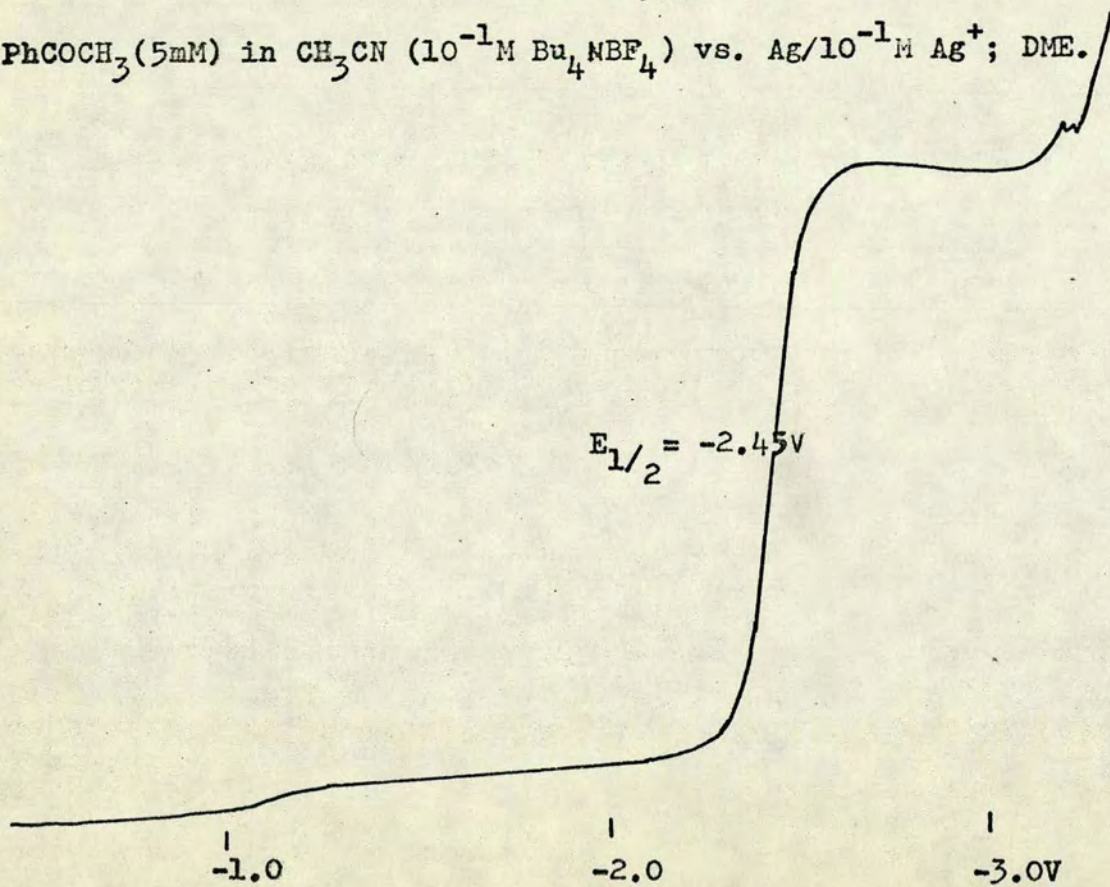


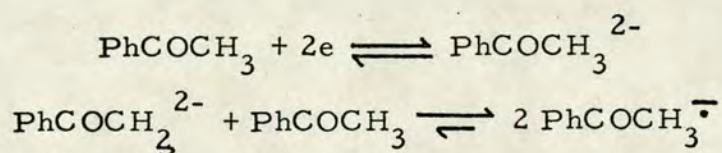
FIGURE 5.4

PhCOCH_3 (5mM) in CH_3CN ($10^{-1}\text{M Bu}_4\text{NBF}_4$) vs. $\text{Ag}/10^{-1}\text{M Ag}^+$; DME.

$E_{1/2} = -2.45\text{V}$



observed in the polarogram, but an alternative explanation must be sought here since this technique involves essentially constant potential and a continually renewed solution in the vicinity of the electrode. At the top of the second wave the concentration of the radical anion at the electrode surface can be considered zero and reduction must involve a $2e$ transfer to give the di-anion. Deactivation of the radical anion by dimerisation would therefore have no influence on the height of the second wave. A possible explanation³⁴ may be a solution electron transfer which would result in a decrease in the concentration of the acetophenone at the electrode. The process may be written:



Scheme (6)

At equilibrium, the solution electron transfer can be assumed to be largely in favour of the radical anion since for organic compounds it is generally found that the standard potential of the $A^{\cdot-}/A^{2-}$ couple is much more negative than that of the $A/A^{\cdot-}$ couple. This is substantiated by controlled potential reduction of acetophenone in aprotic solvents which results in very little alcohol and predominantly pinacol formation even at the potential of the second wave (see Introduction).

The effect of the addition of water (1.0M) to the solution was also studied (Fig. 5.3). An increase in the height of the second wave occurred until it became equal in height to the first wave. This may be explained in terms of protonation of the di-anion to form $\text{PhC}^-(\text{OH})\text{CH}_3$ [$\text{PhCH}(\text{OH})\text{CH}_3$ is unlikely since controlled potential reductions in aqueous acetonitrile are found to afford pinacol and not alcohol], thereby making the solution electron transfer described above less favourable.

(ii) Tetrabutylammonium Fluoroborate

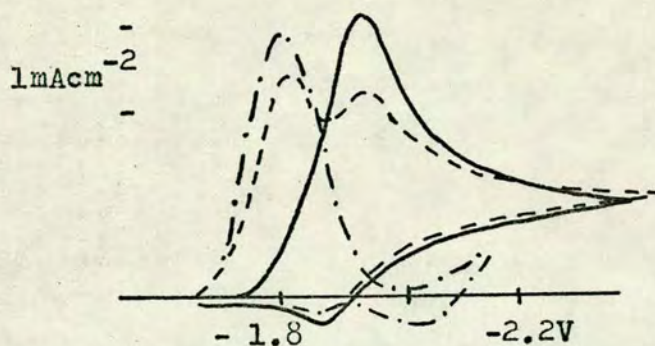
In the presence of the tetrabutylammonium cation the second polarographic wave for the reduction of acetophenone was only just visible prior to the cathodic limit (Fig. 5.4) and was considerably cathodic of the wave

observed in the presence of a tetraethylammonium salt (Fig. 5.3).

This cathodic shift may be analogous to that observed by Jensen and Parker³⁵ in their studies of the reduction of aromatic hydrocarbons in the presence of quaternary ammonium cations. The bulkier tetrabutylammonium cations are believed to slow down the rate of electron transfer to the radical anion thereby shifting the wave to more negative potentials.

(iii) Lithium Iodide

No waves for the reduction of acetophenone were observed in a solution of lithium iodide in acetonitrile. The addition of this supporting electrolyte also caused the disappearance of waves observed at a platinum electrode in the presence of tetraethylammonium cations, indicating that the former observation was not attributable to a non-conducting solution due to poor dissociation of the lithium salt in the medium. Lithium ions have frequently been observed to influence both analytical and preparative electrochemical results. Explanations for this often involve the ability of the small lithium cation to form ion-pairs or even co-valent bonds with anions. Ion-pairing may result in an anodic shift for the wave³⁶ and, by lowering the electron density of a radical anion, may result in favoured dimerisation and reduced nucleophilicity.³⁷ Also, as indicated previously, although disproportionation equilibria normally lie well on the side of the radical anions, ion-pairing may result in di-anion formation.³⁸ Further influence may arise from the strong solvation of the lithium cations leading to a layer at the electrode with a high water content.³⁹ More specific to the case of acetophenone are the observations of Bewick³⁰ and van Tilborg³² and co-workers. Bewick recorded cyclic voltammograms at a mercury electrode in DMF in the presence of tetrabutylammonium perchlorate with increasing concentrations of lithium ions, and obtained evidence for ion-pairing and adsorption when lithium was present viz. an anodic shift of 160mV in the cathodic peak potential and a sharp symmetric cathodic wave typical of adsorption, as indicated below.



30

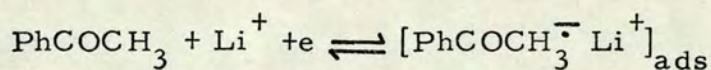
LSV 200 mV s^{-1} ; Dry DMF 10^{-2} M acetophenone

— 10^{-1} M $\text{Bu}_4^t \text{NClO}_4$

--- 10^{-1} M $\text{Bu}_4^t \text{NClO}_4$; 10^{-2} M LiClO_4

·-·-· 10^{-1} M $\text{Bu}_4^t \text{NClO}_4$; 10^{-1} M LiClO_4

It was suggested that the peak in the presence of lithium ions was due to the process:

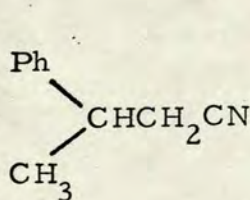


van Tilborg and Smit³² also failed to observe an AC polarographic wave for acetophenone in acetonitrile using lithium fluoride as supporting electrolyte, but addition of tetraethylammonium salt restored normal behaviour. The authors suggested that ion-association between the carbonyl oxygen and the quaternary ammonium cation is required in order for electron transfer to take place. Our studies indicate that the cathodic range in the presence of lithium ions at a mercury cathode is in the region of -2.0 V i. e. prior to the first wave for acetophenone ($E_{1/2} -2.36 \text{ V}$). The apparently wide range achieved by van Tilborg and Smit under similar conditions ($> -2.5 \text{ V}$) may perhaps be attributed to poor dissociation of the lithium fluoride in acetonitrile, in which case the absence of reduction waves for acetophenone and their appearance on addition of a tetraethylammonium salt is not surprising. On the other hand, assuming lithium fluoride is dissociated in acetonitrile, one may expect the lithium ions to ion-associate even more effectively with the carbonyl oxygen than the

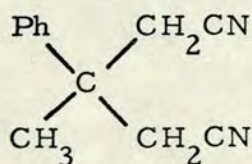
tetraethylammonium cations, thereby negating the authors' explanation. Our results using lithium iodide are difficult to explain but may result from contamination or filming of the platinum electrode in the presence of this salt, thereby inhibiting electron transfer. An insoluble deposit has been observed⁴⁰ to form on the mercury electrode during reduction of metal ions in acetonitrile, and is believed to be analogous to the insoluble hydroxides formed upon deprotonation of aquated metal ions in aqueous media. Lithium salts have also been shown to be too hygroscopic or unstable for precise measurements of equivalent conductances in acetonitrile.⁴¹

(b) Controlled Potential Reduction of Acetophenone in Acetonitrile

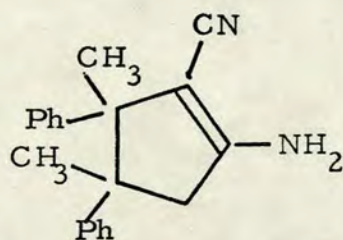
The controlled potential electrolysis of acetophenone was carried out in dry acetonitrile at the potential of the second wave at a mercury pool electrode. The conditions closely resembled those of Stocker³¹ and van Tilborg³² and co-workers. Our results⁴² however indicated only traces of pinacol and relatively high yields of nitrile containing products; namely 3-phenylbutyronitrile (I), 3-methyl-3-phenylglutaronitrile (II) and 1-amino-2-cyano-3,4-dimethyl-3,4-diphenylcyclopent-1-ene (III). Small amounts of 3-methylcinnamonnitrile (IV) were also detected.



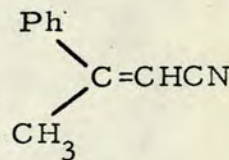
I



II



III



IV

A summary of the product yields obtained under varying electrolysis conditions is given in Table II.

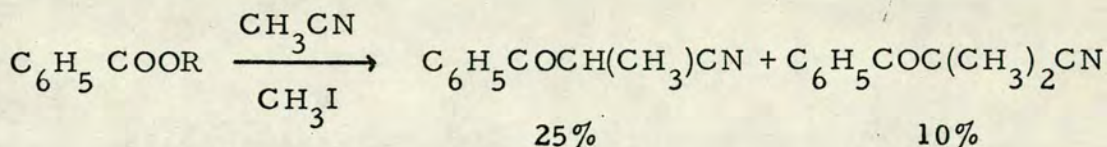
The compounds I-IV were separated by wet column chromatography and in some cases (compounds I and IV) by preparative g.l.c. Their structures were confirmed by synthesis of authentic samples. A similar product mixture was obtained at the potential of the first wave and at a platinum electrode, as indicated by nmr and ir spectroscopic analysis of the crude

reaction mixture. Nitrile products were also formed when the electrolysis solution contained 1% water, but in the presence of 10% water only the pinacol of acetophenone was isolated. The latter conditions were found to be more efficient for preparation of the pinacol (82% yield), than reduction in 80% aqueous ethanol (16% yield).

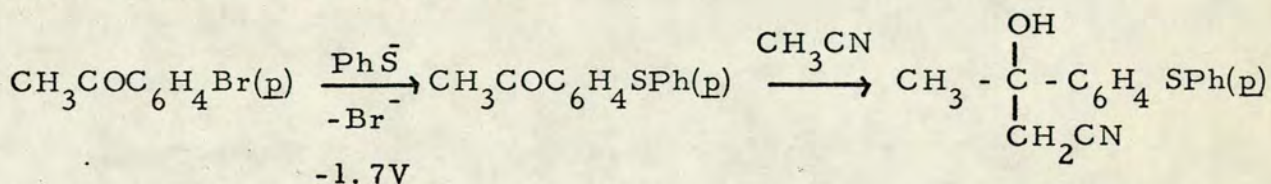
It is clear that the presence of water in the medium inhibits the formation of products I-IV, thereby suggesting that the supporting electrolyte/solvent systems described in the literature^{31, 32} contained more water than reported. A further factor in the discrepancy of our results and those of other workers may be the duration of electrolysis. There is evidence⁴³ that in DMF, the reduction of pinacols $R^1RC(OH).C(OH)RR^1$ ($R=R^1=Ph$, $p\text{-Me } C_6H_4$ and $R=Ph$, $R^1 = \text{cyclopropyl, Me}$) at a mercury cathode involves a first step corresponding to reduction of the ketone $RCOR^1$, formed by pinacol decomposition. Also the cleavage of pinacols in aprotic media is believed⁴⁴ to be initiated by strong bases that are generated at the cathode, a condition adequately fulfilled in the reduction of acetophenone (as will be discussed later). It is therefore possible that the pinacol, initially formed from the reduction of acetophenone in acetonitrile may be unstable under the electrolysis conditions and that continued electrolysis may result in reversion to ketone and increased formation of nitrile containing products.

The formation of compounds I-IV may be explained in terms of nucleophilic attack of the cyanomethyl anion, $^-CH_2CN$, on acetophenone to afford 3-hydroxy-3-phenylbutyronitrile (V). Dehydration of V would yield 3-methylcinnamionitrile IV, which could then undergo reduction to I or III, or participate in a Michael addition to give compound II. Further evidence for the intermediacy of 3-methylcinnamionitrile is that reduction of the latter similarly affords products I, II and III. The proposed mechanism, which will be discussed in greater detail later, may be written (Scheme 7):

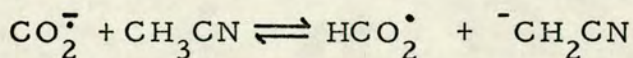
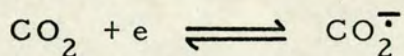
products containing a nitrile group, according to the reaction:



Recent studies by van Tilborg⁴⁷ have also described an analogous reaction involving *p*-substituted acetophenones. Nucleophilic substitution by mercaptide ion was followed by further reaction with the solvent to afford the corresponding hydroxy nitrile:



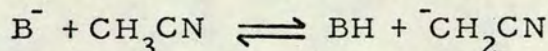
It is also reported⁴⁸ that electrolysis beyond the cathodic limit of acetonitrile at platinum in the presence of quaternary ammonium halides and organoboranes, and in an undivided cell, results in the formation of aliphatic nitriles. Similarly the addition of acetophenone to a pre-electrolysed solution of acetonitrile at -2.7V has been reported⁴⁹ to yield 2-methylcinnamonnitrile in 20% current yield. The electrolytic carboxylation of acetonitrile (and α -substituted acetonitrile) has also been conducted at a mercury pool cathode in the presence of a stream of dry carbon dioxide.⁵⁰ A constant current of 0.7A was maintained, the observed cathode potential being -2.0V (vs. SCE). The product was cyanoacetic acid. A mechanism for the reaction was not presented but presumably involves formation of the cyanomethyl anion which nucleophilically attacks carbon dioxide. The origin of the anion could either be from reduction of the solvent (although the observed potential would not normally be negative enough to achieve this) or by reduction of carbon dioxide to a radical anion, followed by proton abstraction from the solvent.



(i) The Mechanism of Reduction.Electrochemical Generation of the Cyanomethyl Anion

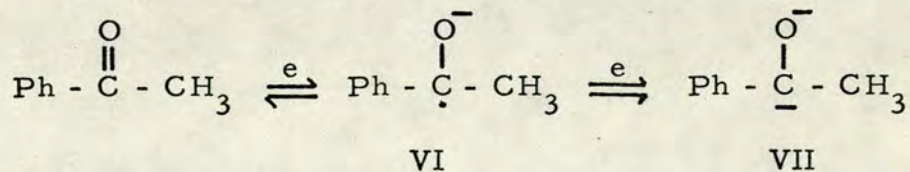
It seems unlikely that the cyanomethyl anion is formed from direct reduction of the solvent during electrolysis of acetophenone. The measured applied voltage of -3.0V (vs. Ag/Ag^+) would produce an actual voltage anodic of that figure due to iR drop across the cell, bringing it to well below the cathodic limit of -3.2V . Also nitrile products were produced at the potential of the first wave for acetophenone (-2.5V) (Table II, expt. 5).

A more likely origin of the anion is by proton abstraction from the solvent in the vicinity of the electrode by the products of electron transfer to the substrate, acetophenone. During the course of the electrolysis the catholyte solution became alkaline presumably due to the production of bases (anions) at the electrode. This was accompanied by a brown coloration at the electrode until the final catholyte solution acquired a dark brown colour. The process may be formulated as



and has been observed by other workers.^{47, 51, 52, 53} The electrogeneration of the cyanomethyl anion has also been effected by the reduction of azobenzene in acetonitrile, which is reported⁵⁴ as exhibiting an irreversible second wave owing to the abstraction of a proton from the solvent by the di-anion. This reaction will be discussed in further detail later.

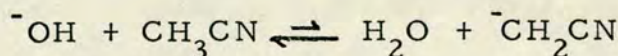
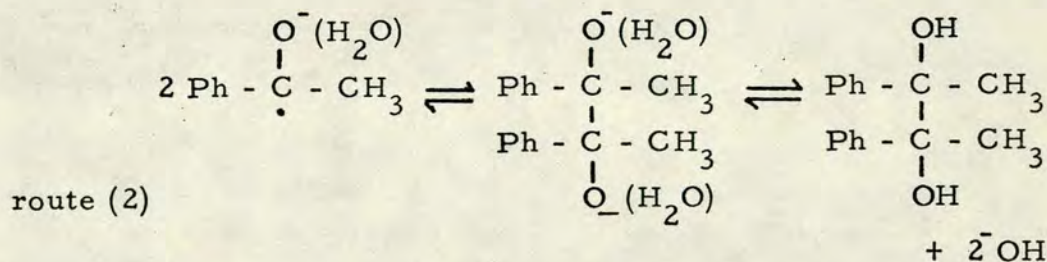
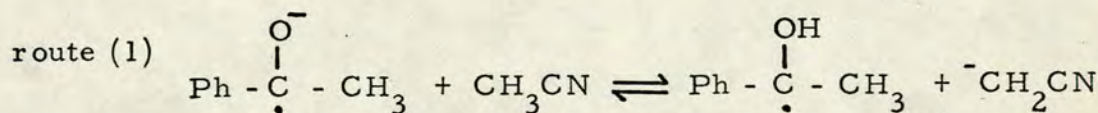
As already indicated, electron transfer to acetophenone in acetonitrile affords the radical anion VI and the di-anion VII (Scheme 8).

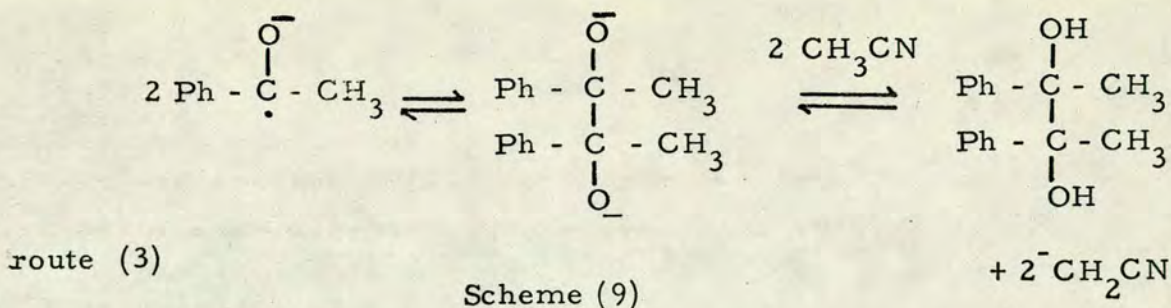


Scheme (8)

Disproportionation of the di-anion to the radical anion may be inferred from the absence of 1-phenylethanol from the electrolysis of acetophenone

at the second wave in aprotic media, and suggests that abstraction of a proton from the solvent by VII is unlikely. The results of Savéant et al,¹² carried out in acetonitrile containing $\approx 0.3\%$ water, suggest that rapid dimerisation ($k_d = 3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$) of the radical anion to the pinacol di-anion takes place. An extrapolation of this, and the values at higher water content, indicates that in the drier conditions (0.01% water) used here the rate of dimerisation would be slower due to poorer solvation (an estimated value has since been put⁵⁵ at $2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$), in which case abstraction of a proton from the solvent by VI may occur (Scheme 9, route 1). The extent of solvation of the pinacol di-anion and/or its protonation by residual water is difficult to estimate. Certainly the results of Savéant et al. suggest that considerable solvation of the radical anion of acetophenone occurs in a $\approx 0.3\%$ aqueous solution despite the use of a quaternary ammonium salt as supporting electrolyte (the latter is generally believed to maintain a relatively anhydrous medium in the vicinity of the electrode). The higher acidity of water (pK_a 14) compared to acetonitrile (pK_a 25) suggest that, if available, it would preferentially protonate the pinacolate di-anion (Scheme 9, route 2). On the basis of relative base strengths the hydroxide ion thus formed would not be expected to abstract a proton from the solvent, although rapid removal of the cyanomethyl anion by reaction with acetophenone may displace this equilibrium. However, the low water content of the solvent suggests that the major pathway for protonation of the pinacolate must involve direct abstraction from the solvent (Scheme 9, route 3).





Once produced by one of the processes indicated above the cyanomethyl anion will be continuously regenerated during the subsequent steps of the reaction to be discussed.

Addition of the Cyanomethyl Anion to Acetophenone - Formation of the β -Hydroxynitrile

The addition of the cyanomethyl anion to carbonyl compounds to form β -hydroxynitriles has been frequently observed. The method has been used to prepare, chemically, an authentic sample of 3-hydroxy-3-phenylbutyronitrile, as will be discussed later. There is also electrochemical evidence for this reaction occurring during the electro-reduction of acetophenone in acetonitrile. The hydroxynitrile was isolated from a reduction of acetophenone in acetonitrile/liquid ammonia, presumably due to a slowing down of the subsequent dehydration step at the lower reaction temperature. Also the electrogeneration of the cyanomethyl anion, following the reduction of azobenzene to its di-anion, has been used^{56, 57} to demonstrate addition to the carbonyl group of ketones.

The initial addition of $^-\text{CH}_2\text{CN}$ to acetophenone affords an anion. Protonation or solvation of this species is subject to the same comments as used previously for the acetophenone radical anion and pinacol di-anion. Assuming that the major pathway for protonation is abstraction from the solvent, the cyanomethyl anion would be regenerated as indicated below.

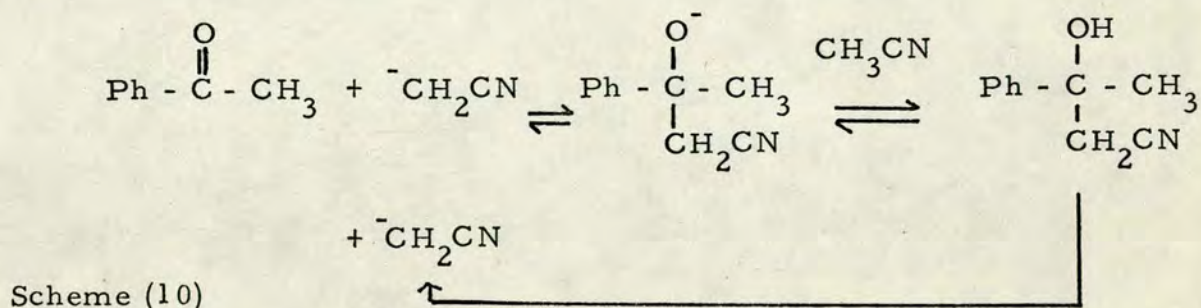


FIGURE 5.5

PhCOCH_3 (7mM) in CH_3CN ($10^{-1}\text{M Et}_4\text{NBF}_4$) vs. $\text{Ag}/10^{-1}\text{M Ag}^+$; DME.

(a) Prior to electrolysis $i_d = 43.5\mu\text{A}$.

(b) After passing 48C $i_d = 9.5\mu\text{A}$.

(c) After passing 86C.

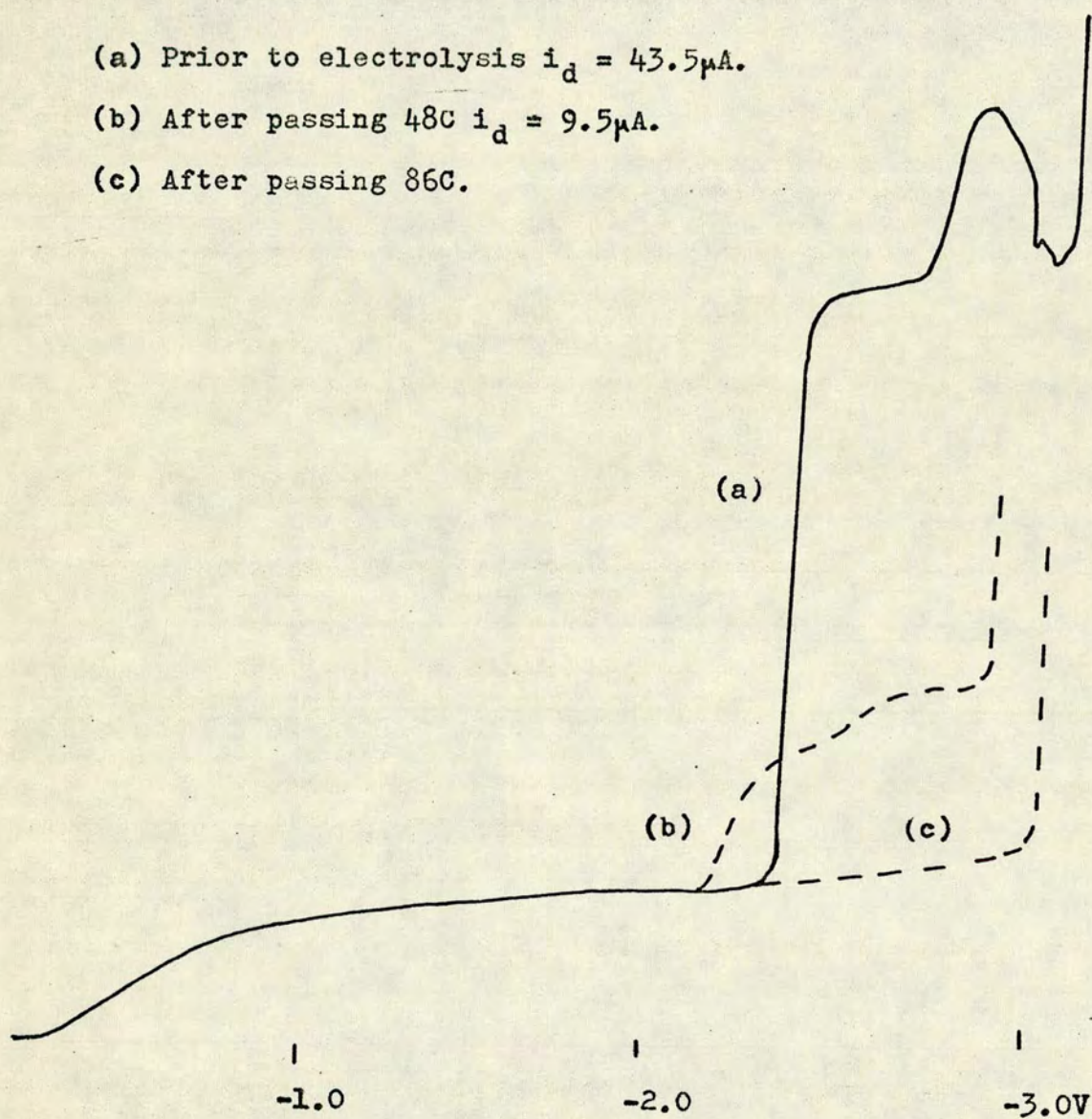
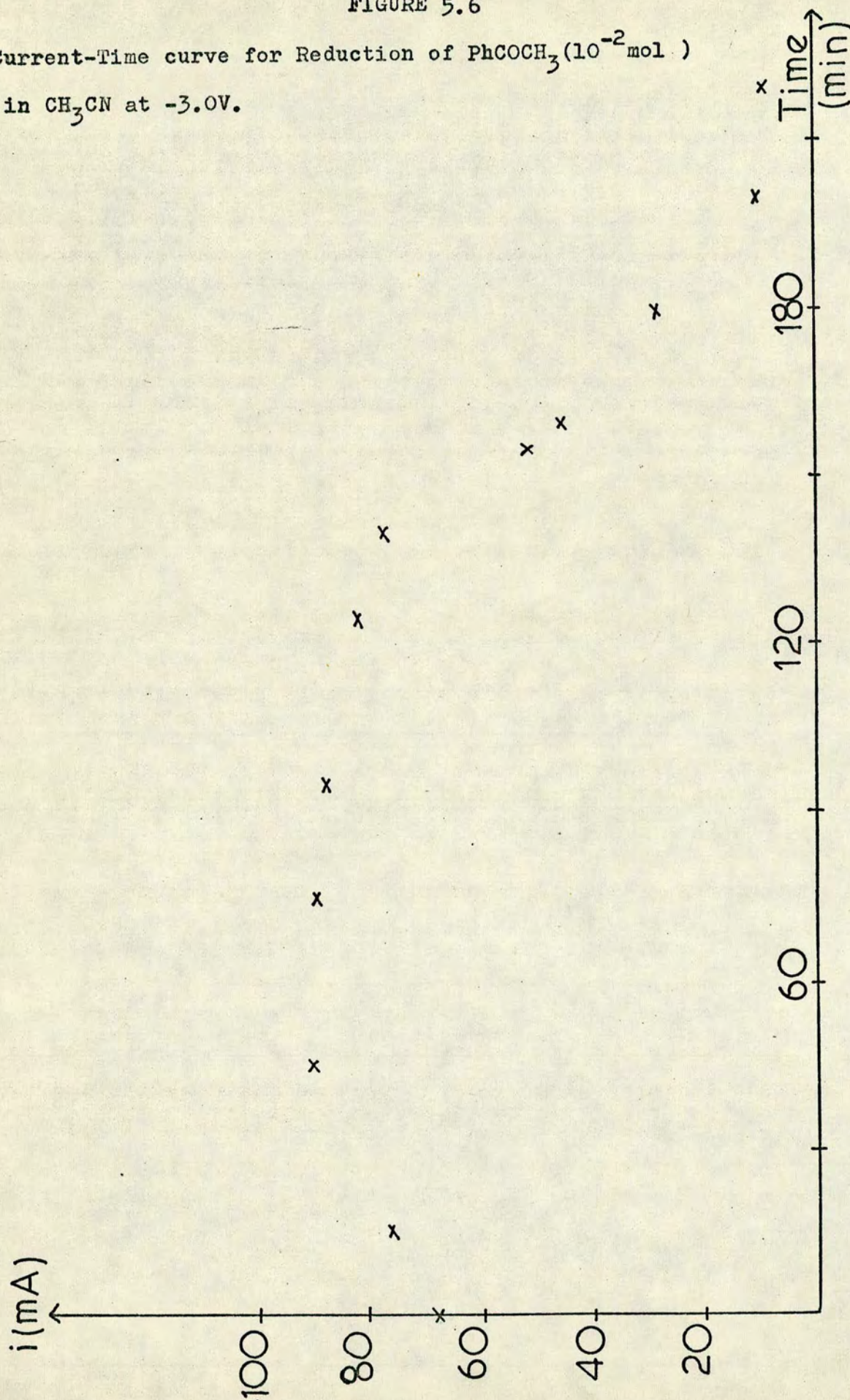


FIGURE 5.6

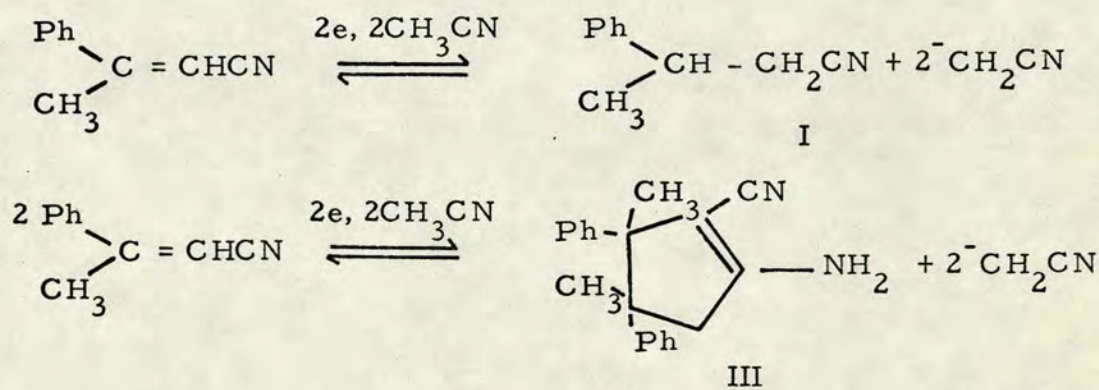
Current-Time curve for Reduction of PhCOCH_3 (10^{-2} mol)
in CH_3CN at -3.0V .



the concentration of electro-active substrate had occurred, accompanied by an anodic shift of 100-200 mV in the position of the waves and the anodic limit. The second wave of the polarogram (Fig. 5. 5b) was considerably more defined than usually observed for acetophenone, showing more similarity in shape to the polarogram of 3-methylcinnamionitrile (Fig. 6. 3). The observation suggests that at an intermediate stage in the electrolysis the electro-active species may be 3-methylcinnamionitrile rather than acetophenone. No waves were observed when $2F \text{ mol}^{-1}$ had been passed.

Reduction of 3-Methylcinnamionitrile to 3-Phenylbutyronitrile (I) and 1-Amino-2-cyano-3, 4-dimethyl-3, 4-diphenylcyclopent-1-ene (III).

The reduction of 3-methylcinnamionitrile as substrate in acetonitrile will be discussed in greater detail later. The dihydroproduct (I) and the cyclised hydrodimer (III) result from the transfer of two and one electrons per mole respectively, both products being of the type expected for the reduction of an activated olefin.⁵⁹ Protonation of the intermediate anions would result in the generation of the cyanomethyl anion as indicated below.



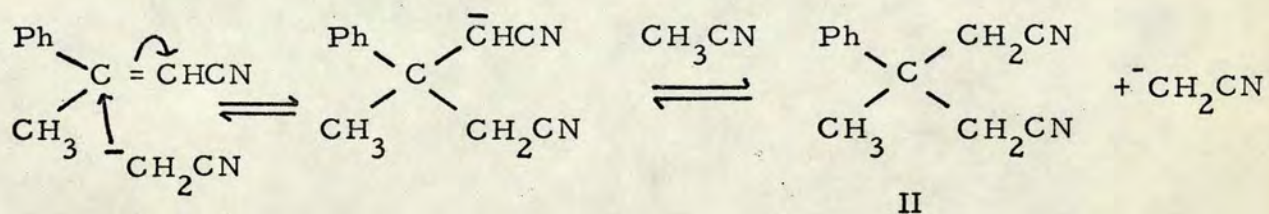
Scheme (12)

Analysis of a 10% completed reduction of acetophenone ($0.2F \text{ mol}^{-1}$ passed) indicated that products I and III had not been produced at that stage in the reduction. This is surprising, since the chemical steps previously discussed, which result in formation of 3-methylcinnamionitrile, are believed to occur rapidly and near to the electrode. Also the initial increase in the shape of the current-time graph (Fig. 5. 6) (a continuous

decrease in current is usually observed) may reflect a transition from a 1e reduction of acetophenone to a 2e reduction of 3-methylcinnamionitrile during the early stages of the reduction. However it is perhaps more likely that the initial increase in current is due to electrical heating of the solution and the failure to observe I and III reflects the insensitive method used for their detection (separation by column chromatography).

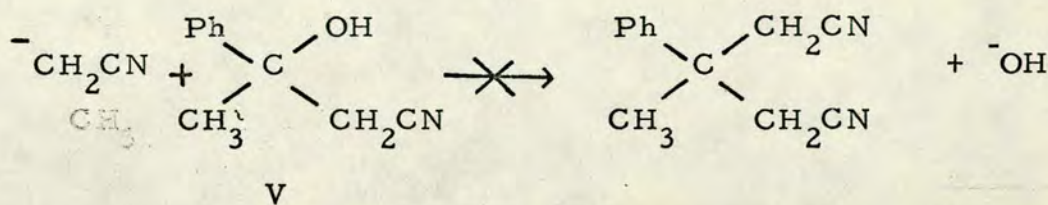
Formation of 3-Methyl-3-phenylglutaronitrile

As already indicated, reduction of 3-methylcinnamionitrile affords compounds I and III. An alternative pathway for reaction of IV in the presence of the cyanomethyl anion involves Michael addition to give 3-methyl-3-phenylglutaronitrile, II. The reaction involves the nucleophilic addition of the anion to the double bond of the α, β -unsaturated nitrile, the latter being capable of stabilizing the carbanionic intermediate. The reaction has numerous analogies in synthetic organic chemistry.⁶⁰ Protonation of the intermediate carbanion by solvent completes the reaction. (Scheme 13).



Scheme (13)

An alternative route to compound II might involve nucleophilic displacement of hydroxide ion from 3-hydroxy-3-phenylbutyronitrile, V, by cyanomethyl anion, as indicated below, but an attempt to promote this reaction chemically by treating V with a solution of the cyanomethyl anion in acetonitrile (formed by dissolution of sodium in acetonitrile) overnight at room temperature gave only unreacted starting material.



(ii) Product Yields and Effect of Potential

A summary of the product yields from various electrolyses is given in Table II. 3-Phenylbutyronitrile was estimated either from g. l. c. peak integration (following standardisation of an authentic sample against n-octadecane) or after separation by column chromatography. Failure to separate 3-methyl-3-phenylglutaronitrile, II, from the cyclised hydrodimer by column chromatography or fractional distillation did not allow an accurate measurement of their respective yields. The combined yield is calculated on the assumption that II is the major product, as estimated by n. m. r. spectroscopy. Pinacol, 1-phenylethanol and 3-methylcinnamionitrile were all formed in relatively small amounts (<10%), as indicated by the n. m. r. spectra of the crude reaction mixtures and column chromatography, although the pinacol was not readily eluted and may be present in greater yields than suggested.

The highest yield of 3-phenylbutyronitrile (51%, Table II, expt. 3) was obtained on continued electrolysis. During this experiment the final cell current of 20mA was maintained and not found to decrease further even when electrolysis was continued overnight. The high yield may reflect a slow reversion of initially formed pinacol to acetophenone (as discussed previously) thereby allowing further conversion of the latter to nitrile products. A similar reduction (Table II, expt. 4) was terminated when the current fell to its minimum value and in this case only 34% of I was obtained.

The initial experiments (Table II, expts. 1-4) were carried out in a cell whose reference electrode was positioned some distance from the surface of the mercury pool cathode. The associated iR drop suggests that the actual cathode potential would be considerably lower than the set value of -3.0V. The yield of nitriles (80-90%) is considerably higher than in subsequent experiments (Table II, expts. 5-7) when yields of about 50% were obtained. These latter electrolyses were conducted using a more accurately applied voltage, by placing the reference and working electrodes closer together. (A subsequent decrease in the electrode area was necessary to avoid overloading the potentiostat and this resulted in lower initial cell currents). The higher yield of nitriles obtained at the lower

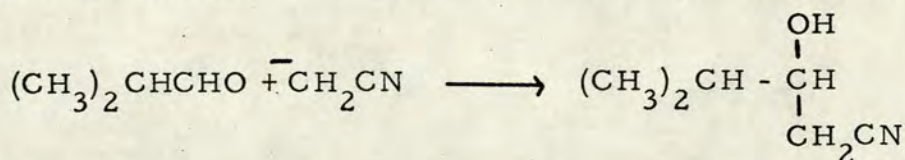
potential may be rationalised in terms of a slower rate of electron transfer to acetophenone to form pinacol, thereby allowing more extensive conversion to 3-methylcinnamionitrile to take place at the electrode.

(iii) Related Chemical Reactions

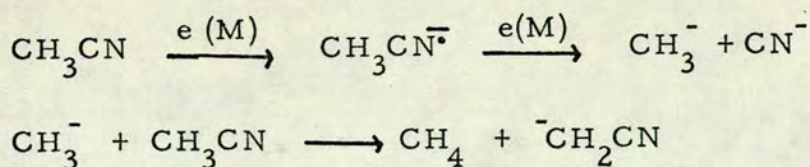
Steps (1), (2) and (5) in the reaction pathway for reduction of acetophenone in acetonitrile (Scheme 7) are purely chemical in nature and do not result in the formation of a reduced species. Their close analogies may be found in synthetic organic chemistry.

Preparation of the cyanomethyl anion by the action of a base on acetonitrile, when carried out in the presence of a ketone generally affords the corresponding β -hydroxy nitrile. The base may be metallic sodium,⁶¹ n-butyl lithium in THF/hexane,⁶² sodamide or lithamide,⁶³ and potassium hydroxide.⁵⁸ Reaction of lithamide with acetonitrile in the presence of acetophenone allowed preparation of an authentic sample of 3-hydroxy-3-phenylbutyronitrile.

An interesting connection between the chemically and electrochemically initiated generation of the cyanomethyl anion is afforded by the cathodic decomposition of acetonitrile using alkali metal salt electrolytes.⁶⁴ Reduction of the electrolyte resulted in deposition of the alkali metal on the platinum electrode. Subsequent cleavage of the solvent by the metal afforded methane and the cyanomethyl anion, the latter being trapped by isobutyraldehyde to yield 3-hydroxy-4-methylpentanonitrile.

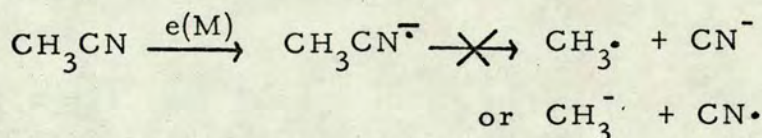


Evidence is presented to show that the mechanism of cleavage of acetonitrile probably involves electron transfer from the metal to the solvent, producing the radical anion of acetonitrile, which then reductively cleaves to the methyl and cyanide anions. The former is then believed to abstract a proton from the solvent to give methane and CH_2CN^- . The sequence may be written:

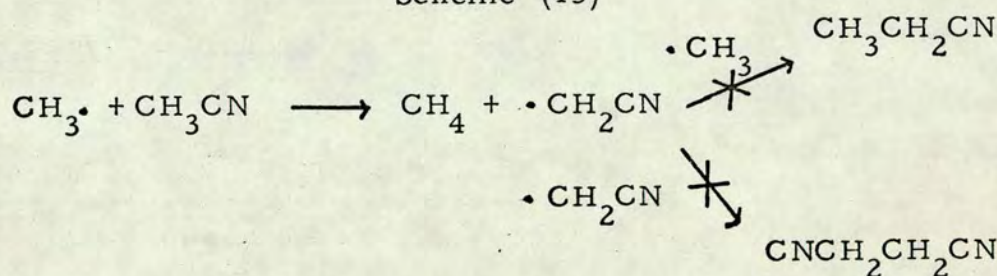


Scheme (14)

The rapid transfer of a second electron to the cyanomethyl radical anion was indicated by the absence of any 2,3-butanediimine (from dimerisation) or its hydrolysis product diacetyl. Evidence that cleavage of the cyanomethyl radical anion to a methyl or cyano radical did not take place (Scheme 15) was the failure to identify any cyanogen (from dimerisation of $\text{CN}\cdot$) or succinonitrile and propionitrile (from further reaction of a methyl radical). (Scheme 16).



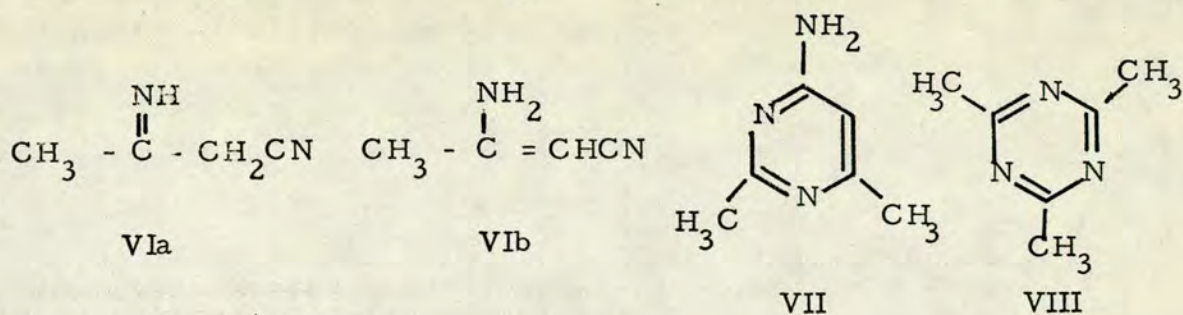
Scheme (15)



Scheme (16)

However rapid further reduction of the cyanomethyl radical has been postulated by other workers⁶⁵ as a possible route to the cyanomethyl anion.

The chemical generation of the cyanomethyl anion in the presence of ketones does not generally result in production of the dimer and trimer of acetonitrile, suggesting that addition to the carbonyl group is rapid. However in the absence of ketones, the dimer, 3-iminobutyronitrile (VIa), its tautomer 3-aminocrotonitrile (VIb), and the trimers 4-amino-2,6-dimethylpyrimidine (VII) and 2,4,6-trimethyl-1,3,5-triazine (VII) are formed.^{64, 65, 66}



Failure to quench anions present at the end of an electrolysis, and the use of an excess of sodium when preparing 3-methylcinnamionitrile by the method of Matsuda et al.⁶¹ (see Experimental section) resulted in the formation of the trimer VII identified by comparison with an authentic sample prepared by the method of Ronzio and Cook.⁶⁷

Spontaneous dehydration of 3-hydroxy-3-phenylbutyronitrile, V, does not usually occur during the reaction of bases with acetonitrile in the presence of ketones, although the use of potassium hydroxide⁵⁸ is reported to afford the α, β -unsaturated nitrile directly. In one case,⁶¹ reaction at reflux temperatures was reported to yield 3-methylcinnamionitrile IV, but when this reaction was duplicated incomplete dehydration occurred. The more usual method involves acid catalysed dehydration using a mixture of glacial acetic acid and sulphuric acid.⁶³ Phosphoric acid has also been used.⁶²

An authentic sample of 3-methyl-3-phenylglutaronitrile (II) was prepared by reaction of 3-methylcinnamionitrile (IV) with a solution of CH_2CN^- (prepared from sodium in acetonitrile) at reflux temperatures. Using these conditions a 2:1 mixture of II:IV was obtained. The reaction at room temperature afforded only unreacted IV, suggesting that more extreme reaction conditions operate to promote a similar reaction in the electrolysis cell. The addition of tetraethylammonium chloride to displace sodium chloride allowed complete conversion to II to take place, suggesting that ion-pairing with sodium ions may inhibit the nucleophilicity of the cyanomethyl anion. A similar reaction of lithamide in liquid ammonia with acetonitrile has been used to prepare 3,3-diphenylglutaronitrile from 3-phenylcinnamionitrile.⁶⁸

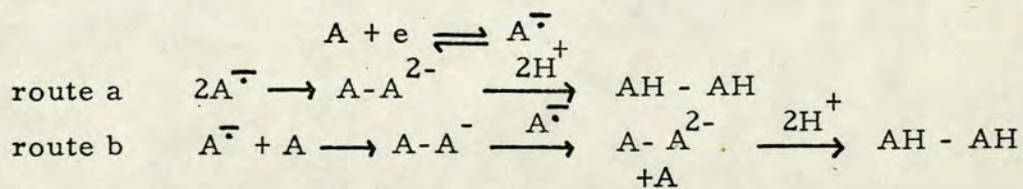
3. The Reduction of 3-Methylcinnamionitrile in Acetonitrile.

Introduction

The observation that electrolysis of acetophenone in acetonitrile afforded reduction products of 3-methylcinnamionitrile suggested that a study of this compound might be useful.

In recent years the reductive coupling of activated olefins (where the activating group may be CN, COOR, COR, Ar etc) has been of particular interest to electrochemists due to the successful commercial application of the electrohydrodimerisation of acrylonitrile, as originated by Baizer and developed by Monsanto.^{69, 70, 71} Despite the discouraging 2e reduction of acrylonitrile in water, Baizer was able to produce adiponitrile in almost quantitative yield by the use of high concentrations of acrylonitrile and large quantities of tetraalkylammonium p-toluene-sulphonates. The latter served to raise the solubility of the acrylonitrile and was believed to maintain a region of relatively low proton availability at the electrode.

Considerable efforts have been made to determine the mechanism of hydrodimerisation. Of the many possible pathways two mechanisms are most favoured - a simple dimerisation of radical anions (Scheme 17, route a) and an addition of the radical anion to the substrate followed by a second electron transfer, probably in solution (Scheme 17, route b). For substrate A:



Scheme (17)

Studies in aprotic solvents using rotating ring-disc voltammetry,⁷² chronopotentiometry⁷³ and linear sweep voltammetry³⁴ have shown that route (a) predominates for a variety of activated olefins. The observation⁷⁴ that a 5% aqueous solution of DMF is roughly equivalent to the water $R_4N^+ \bar{O}TS$ system used by Baizer with respect to proton availability in the medium surrounding the electrode suggests that the above conclusion can

FIGURE 6.1

$\text{Ph}(\text{CH}_3)\text{C}=\text{CHCN}(5\text{mM})$ in CH_3CN (10^{-1}M Bu_4NBF_4) vs. $\text{Ag}/10^{-1}\text{M}$ Ag^+ ;
Pt wire; 300mVs^{-1} .

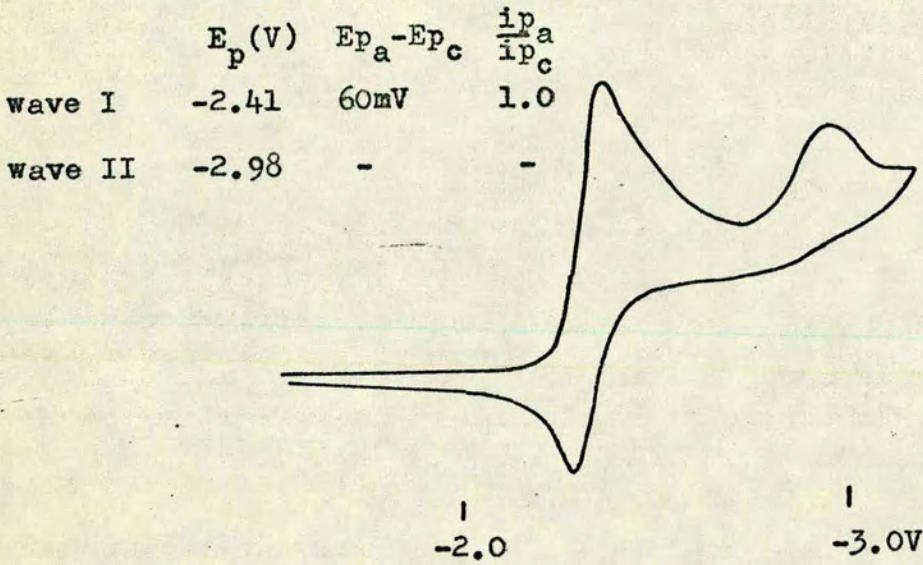


FIGURE 6.2

$\text{Ph}(\text{CH}_3)\text{C}=\text{CHCN}(5\text{mM})$ in CH_3CN (10^{-1}M Bu_4NBF_4) vs. $\text{Ag}/10^{-1}\text{M}$ Ag^+ ;
DME.

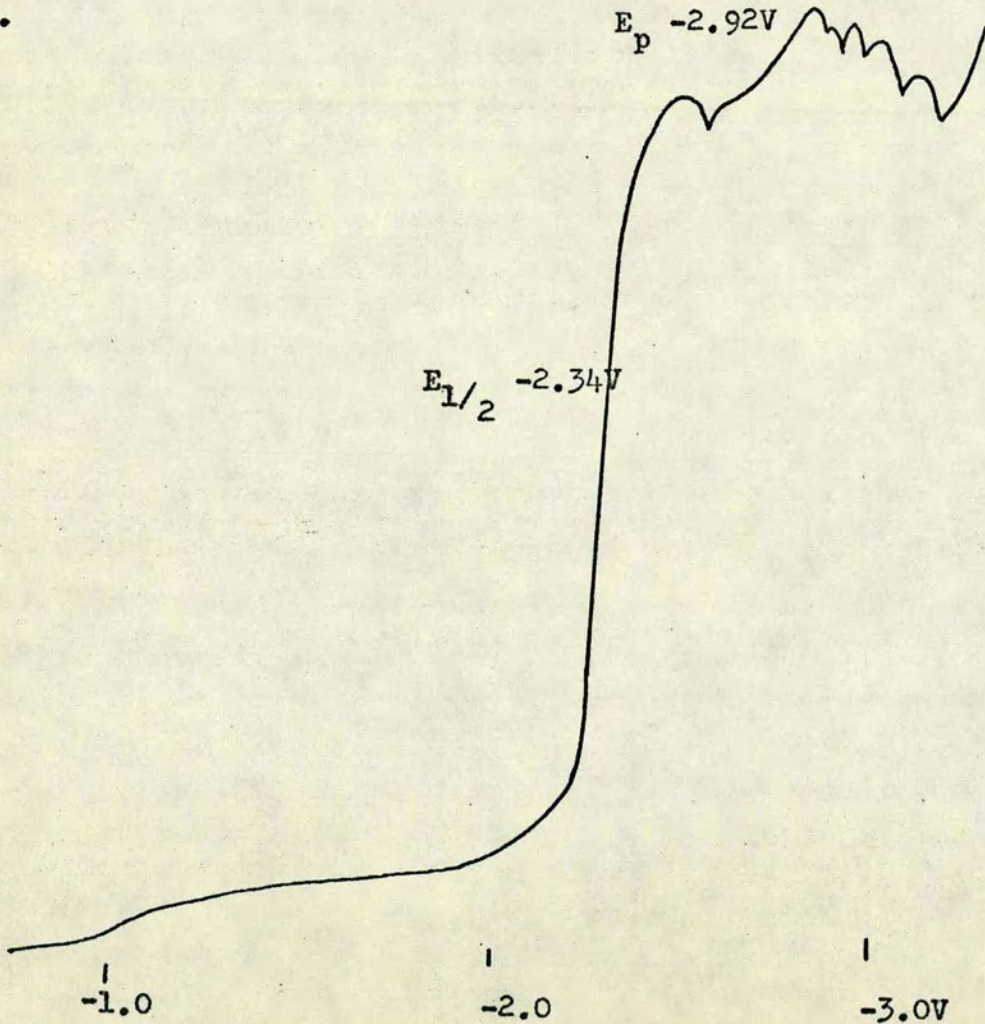


FIGURE 6.3

E_p -2.94V

$\text{Ph}(\text{CH}_3)\text{C}=\text{CHCN}$ in CH_3CN ($10^{-1}\text{M Et}_4\text{NBF}_4$)
vs. $\text{Ag}/10^{-1}\text{M Ag}^+$; DME.

(a) ca. 2.5mM

(b) ca. 5mM

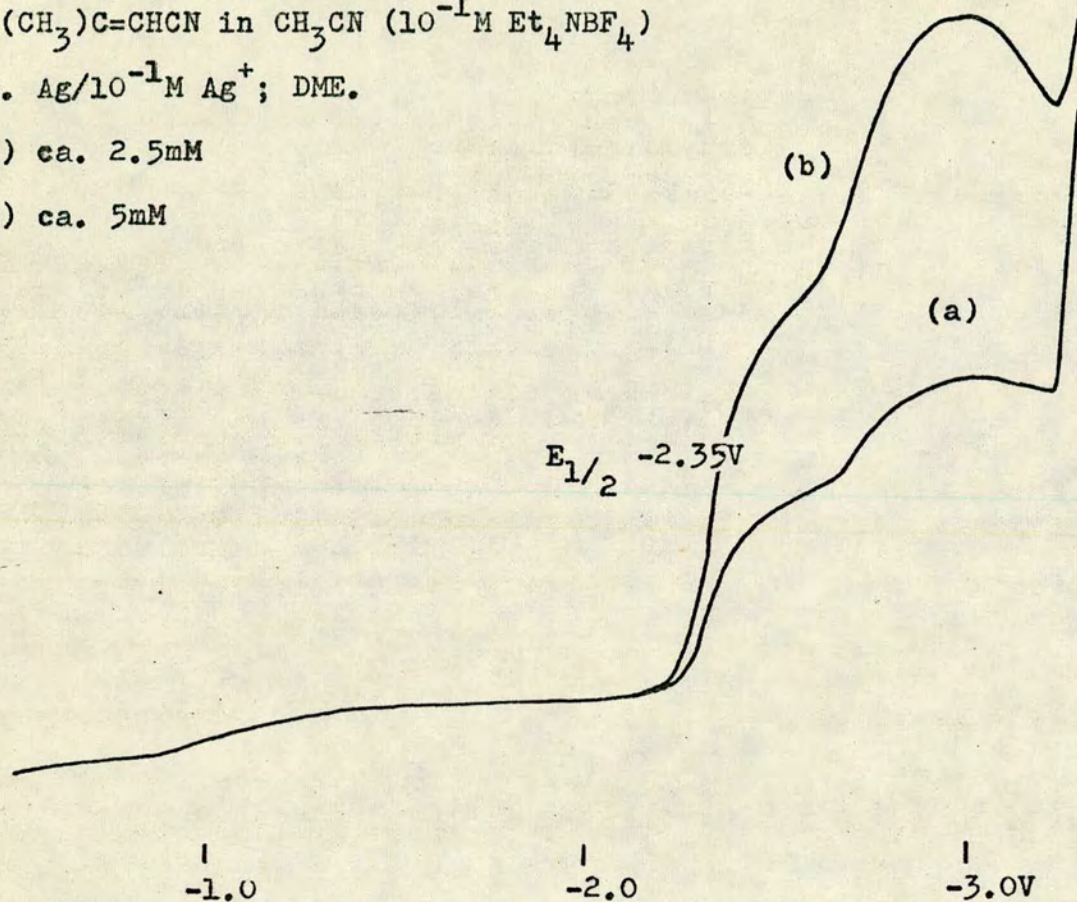
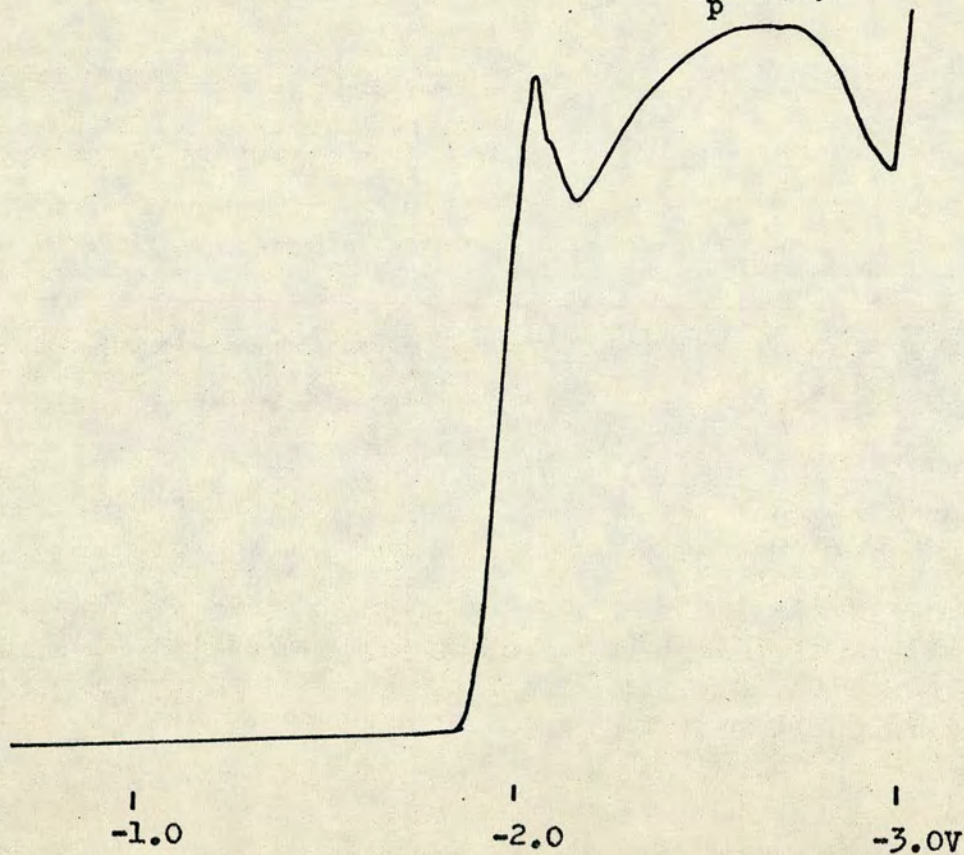


FIGURE 6.4

$\text{Ph}(\text{CH}_3)\text{C}=\text{CHCN}$ in 80% aqueous CH_3CN vs. $\text{Ag}/10^{-1}\text{M Ag}^+$; DME.

E_p -2.65V



fruitfully be applied to the hydrodimerisation of acrylonitrile. There is also evidence⁷⁵ that a similar pathway operates at the higher substrate concentrations used in electrosynthesis.

Discussion

(a) Polarography and Cyclic Voltammetry of 3-Methylcinnamionitrile in Acetonitrile.

Two waves for the reduction of 3-methylcinnamionitrile were observed on polarography and CV in acetonitrile. The radical anion is stable on the CV time-scale, as indicated by the reversibility of the first wave (Fig. 6.1). The second wave in both CV and polarography (Fig. 6.2) was considerably smaller than the first when recorded in the presence of tetrabutylammonium fluoroborate; this is surprising in view of the reversibility of the first wave and may be associated with the nature of the supporting electrolyte. When recorded in a solution of tetraethylammonium fluoroborate the polarogram (Fig. 6.3a) exhibited two waves of equal height, suggesting that electron transfer between the di-anion and substrate does not occur to a great extent (cf. acetophenone). At higher concentrations of substrate (Fig. 6.3b) the second wave showed a maximum. A polarogram was also recorded (Fig. 6.4) prior to electrolysis in 80% aqueous acetonitrile; only one wave was observed (with marked maxima, probably a result of the high concentration of substrate) which was considerably shifted anodically.

The voltammetric behaviour described above is similar to that reported for cinnamionitrile in aprotic solvents. Savéant et al.³⁴ observed a merging of the two polarographic waves in a 10% aqueous solution in acetonitrile, although in DMF the two waves were still apparent at a 20% concentration of water, suggesting that water is a better proton donor in the former solvent. The authors estimated that a reversible first wave would be observed at sweep rates of $> 500 \text{ mV s}^{-1}$ for this compound in the anhydrous solvent, the stability of the radical anion decreasing with increased water content.* A reversible wave for 3-methylcinnamionitrile

* The CV of cinnamionitrile was also studied by Hazelrigg and Bard⁷⁶ in DMF, and similarly suggested an unstable radical anion; a ratio of peak currents, $\frac{i_{p_a}}{i_{p_c}}$ of 0.41 was obtained for the first wave at sweep rates of 200 mV s^{-1} .

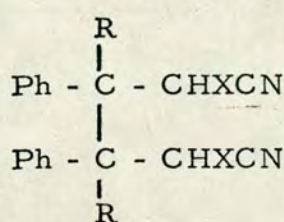
was however observed at 300 mV s^{-1} (Fig. 6.1), suggesting that the radical anion of the methyl-substituted compound is more stable than cinnamonnitrile itself. This probably reflects a steric inhibition to dimerisation.

(b) The Controlled Potential Electrolysis of 3-Methylcinnamonnitrile in Acetonitrile.

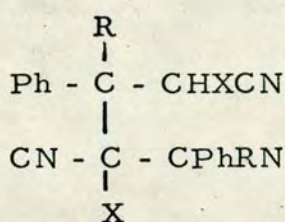
The reduction of 3-methylcinnamonnitrile was conducted at the potential of the second wave in dry acetonitrile. A mixture of three products was obtained, consisting of 3-phenylbutyronitrile, (I, ca. 12%), 3-methyl-3-phenylglutaronitrile (II, ca. 30%) and 1-amino-2-cyano-3,4-dimethylcyclopent-1-ene (III, ca. 10%), which were identified following separation by column chromatography. The relative yields of II and III were estimated from the n.m.r. spectrum of a mixture of the two compounds obtained from the column. Approximately one half of the crude product was unidentified and probably consisted of polymerised material owing to the aprotic conditions employed. The formation of trimers and oligomers of activated olefins has been shown to be reduced by the addition of water to an aprotic system.⁷⁷ Additional evidence for polymerisation is the low current yield for the formation of I and III; only 300-400 C are required for their formation, representing a current efficiency of about 25% for the 1200 C total. Polymers probably result from nucleophilic attack by anions on the substrate. When conducted in an 80% aqueous solution of acetonitrile, electrolysis of 3-methylcinnamonnitrile afforded only the dihydro reduction product, I. The formation of this product could involve either an ece mechanism or a disproportionation mechanism as discussed previously for acetophenone.

The ratio of dihydro product to hydrodimer from the reduction of activated olefins is difficult to rationalise. The olefin, Ph(R)C=CXCN , ($\text{R}=\text{Ph}$, $t\text{-Bu}$; $\text{X}=\text{CN}$) has been reported⁷⁸ to give only dihydro product when reduced in DMF containing acetic acid, whereas the olefin ($\text{R}=\text{CH}_3$, H ; $\text{X}=\text{CN}$) yielded only hydrodimer under similar conditions. The reluctance of the former to dimerise presumably reflects steric inhibition and a stable radical anion. On the other hand when reduced in 3% aqueous DMF cinnamonnitrile ($\text{R}=\text{H}$; $\text{X}=\text{H}$) gave a 1:4 ratio of

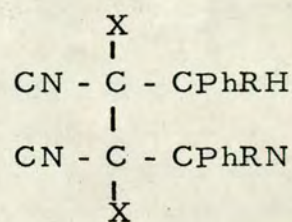
dihydro product : hydrodimer while 2-phenylcinnamionitrile (R=H, X=Ph) gave only hydrodimer.³⁷ Hydrodimerisation must be assumed to involve coupling of two radical anions in the 1, 1-, 1, 2- or 2, 2-positions to afford the linear products IX, X and XI on protonation. In addition, a product XII resulting from intramolecular cyclisation of the 1, 1-coupled product is also possible.



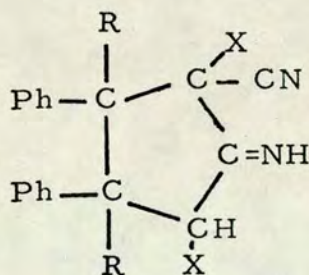
1, 1- IX



1, 2- X



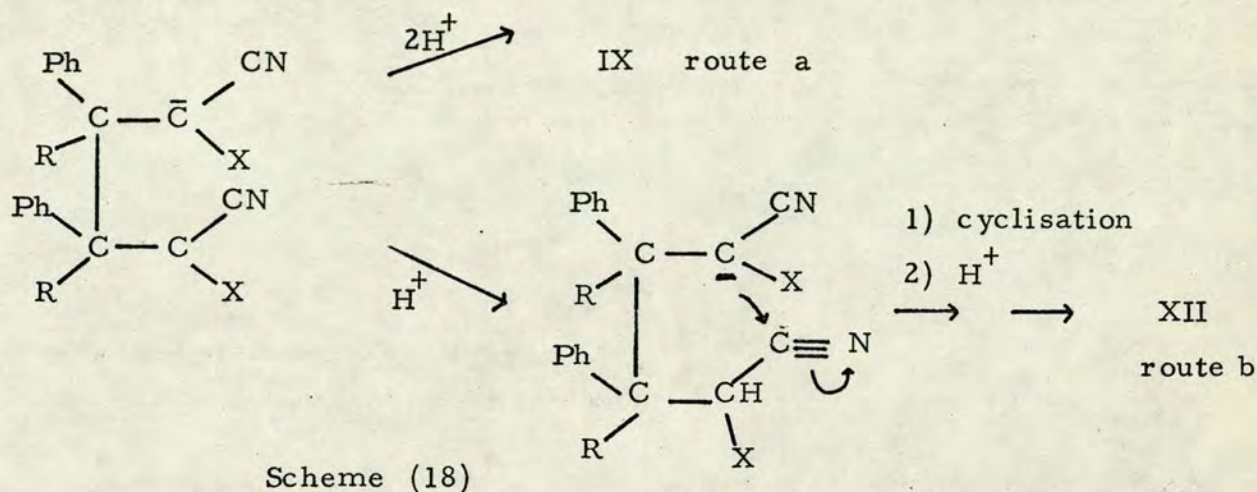
2, 2- XI



XII

1-Amino-2-cyano-3, 4-dimethylpent-1-ene (III) is the tautomer of the cyclised hydrodimer XII (R=CH₃, X=H). There was no evidence for the formation of the corresponding linear hydrodimers from the reduction of 3-methylcinnamionitrile in acetonitrile. The formation of linear and/or cyclised products appears from the literature to be unpredictable. For example reduction of cinnamionitrile in aqueous DMF afforded only linear products (primarily 1, 2-coupled),⁷⁷ whereas 2-phenylcinnamionitrile afforded 86% of the cyclised product under similar conditions.⁷⁷ The yield of cyclised product was markedly decreased in the presence of alkali metal cations, an observation which was rationalised in terms of increased proton availability. On the other hand the dinitrile compounds (R=CH₃, H; X=CN) have been reported⁷⁸ as affording only cyclised product both in the presence of alkali metal and quaternary ammonium cations. Coupling of radical anions in the 1, 1-position yields a di-anion which could either

protonate (Scheme 18, route a) or cyclise (Scheme 18, route b). The ratio of linear to cyclised products must depend on the proton availability and the relative basicity and nucleophilicity of the mono-protonated species.



The formation of reduction products of 3-methylcinnamionitrile in acetonitrile in the absence of proton donors must result in proton abstraction from the solvent to generate the cyanomethyl anion. This can then add nucleophilically to 3-methylcinnamionitrile to give 3-methyl-3-phenylglutaronitrile, as already discussed. It is perhaps not surprising that when an electrolysis was conducted in 80% aqueous acetonitrile no dinitrile product was formed.

Attempted Preparation of the Hydrodimers of 3-Methylcinnamionitrile

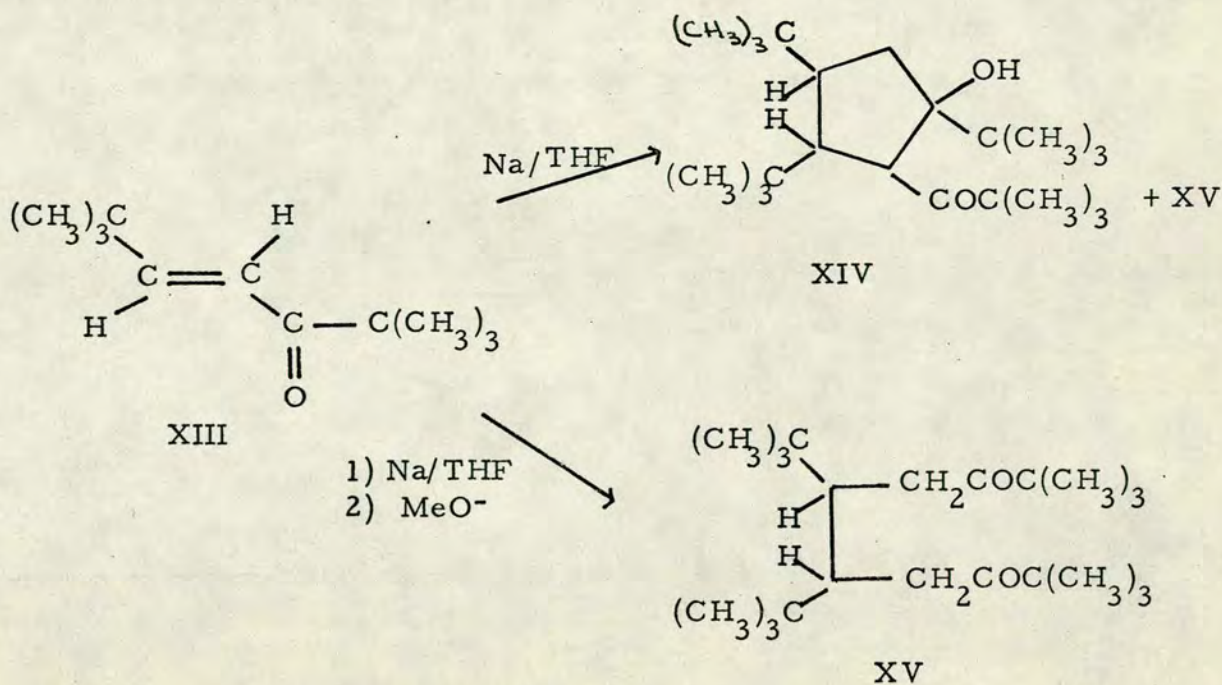
(i) By Electrochemical Reduction of 3-Methylcinnamionitrile in DMF

The reduction of this compound in DMF was carried out in an attempt to prepare samples of hydrodimers, either linear or cyclic, for comparison with the reaction mixtures obtained from reduction in acetonitrile. The method was based on that described by Petrovich and Baizer³⁷ who successfully prepared 96% hydrodimers (14% 1,1-linear coupled product and 86% cyclised product) by electrochemical reduction of cinnamionitrile in DMF (150 ml) containing water (5 ml). The supporting electrolyte consisted of tetraethylammonium tosylate and reduction was conducted using a high

concentration of substrate and high current density. However, an n. m. r. spectrum of the crude reaction mixture obtained from a similar reduction of 3-methylcinnamionitrile indicated that only 3-phenylbutyronitrile, the dihydro product, had been formed. This presumably results from a steric inhibition to dimerisation of the 3-methyl substituted compound compared to the unsubstituted compound. Possibly hydrodimerisation would in this case be better promoted by reduction at the first wave in the presence of an alkali metal cation such as a lithium salt, which has been shown⁷⁶ to increase the rate of dimerisation of cinnamionitrile by ion-pairing with the radical anion, thereby decreasing coulombic repulsion of the negative charges.

(ii) By Reduction of 3-Methylcinnamionitrile using Sodium in THF

House and co-workers⁷⁹ prepared the hydrodimers of α, β -unsaturated ketones using the reducing media sodium/THF/hexamethylphosphoramide or sodium/THF. Reduction of trans-2, 2, 6, 6-tetramethylhept-4-ene-3-one (XIII) using sodium in THF at 0°C afforded either a mixture of the cyclised hydrodimer (XIV) and linear dimer (XV) (if the reaction mixture was decanted from excess sodium) or the linear dimer XV alone (if the reaction mixture was quenched with methanol to afford sodium methoxide).



Scheme (19)

An analogous reaction was carried out on 3-methylcinnamionitrile. A small amount of a crystalline product, identified by spectroscopy as 1-amino-2-cyano-3,4-dimethyl-3,4-cyclopent-1-ene was obtained when the crude reaction mixture was quenched with methanol. Failure to quench the reaction resulted in an unidentified mixture.

FIGURE 7.1

$(\text{CH}_3)_2\text{C}=\text{CHCN}$ in CH_3CN ($10^{-1}\text{M Et}_4\text{NBF}_4$) vs. $\text{Ag}/10^{-1}\text{M Ag}^+$; DME.

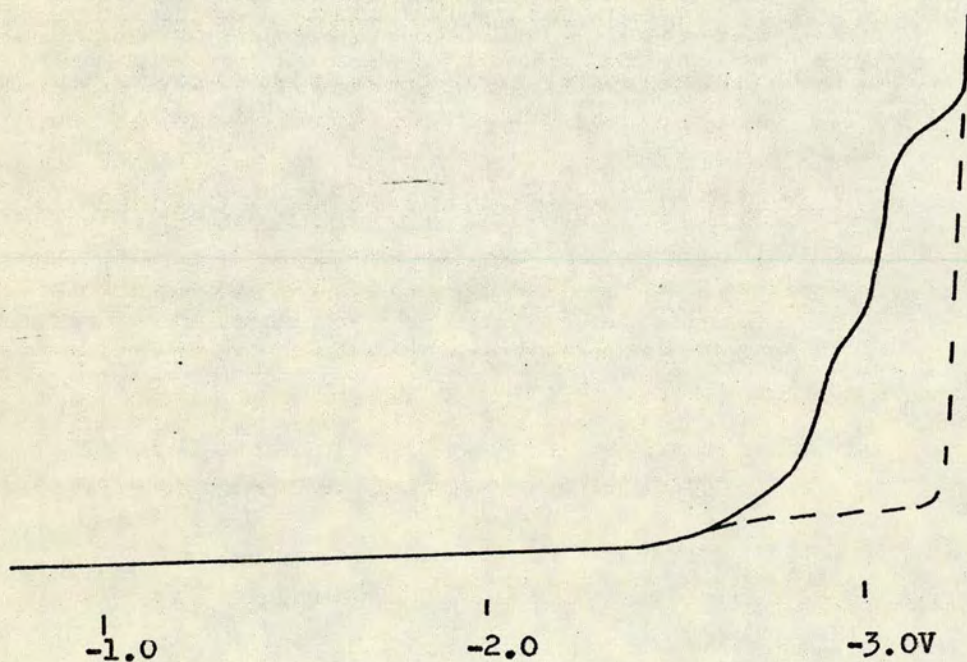
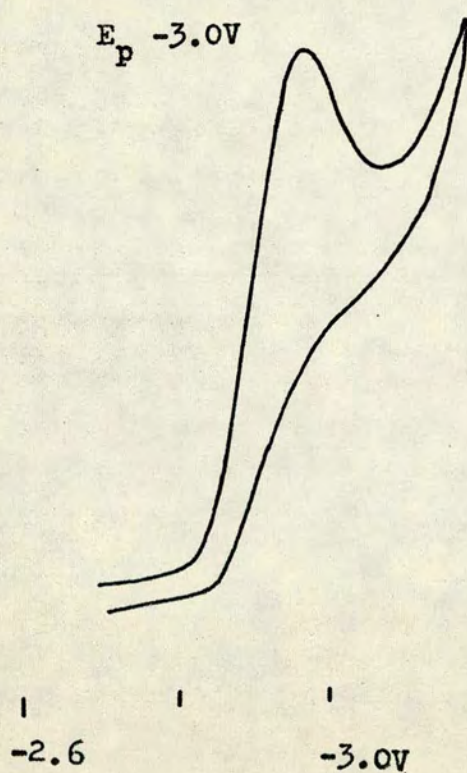


FIGURE 7.2

$(\text{CH}_3)_2\text{C}=\text{CHCN}$ in CH_3CN ($10^{-1}\text{M Et}_4\text{NBF}_4$) vs. $\text{Ag}/10^{-1}\text{M Ag}^+$;
Pt wire; 100mVs^{-1} .



4. The Reduction of Acetone (in the Presence of Azobenzene) and 3, 3-Dimethylacrylonitrile in Acetonitrile.

(a) Polarography and Cyclic Voltammetry of 3, 3-Dimethylacrylonitrile in Acetonitrile.

Acetone showed no reduction waves in acetonitrile. However polarography and CV of 3, 3-dimethylacrylonitrile indicated that this compound was reduced just prior to the cathodic limit. The polarogram (Fig. 7.1) showed two closely spaced waves, presumably to afford the radical anion and di-anion. The behaviour is similar to that observed by Savéant et al³⁴ for reduction of acrylonitrile in acetonitrile. The 3, 3-dimethyl substituted compound [$E_{\frac{1}{2}}$ (wave I) = -3.0V] is however considerably more difficult to reduce than the parent acrylonitrile [$E_{\frac{1}{2}}$ (wave I) = -2.3V approx.]. The rapid dimerisation of the radical anion was indicated by the absence during cyclic voltammetry of an anodic peak for the first wave on the reverse sweep (Fig. 7.2).

(b) The Controlled Potential Electrolysis of Acetone (in the Presence of Azobenzene) in Acetonitrile.

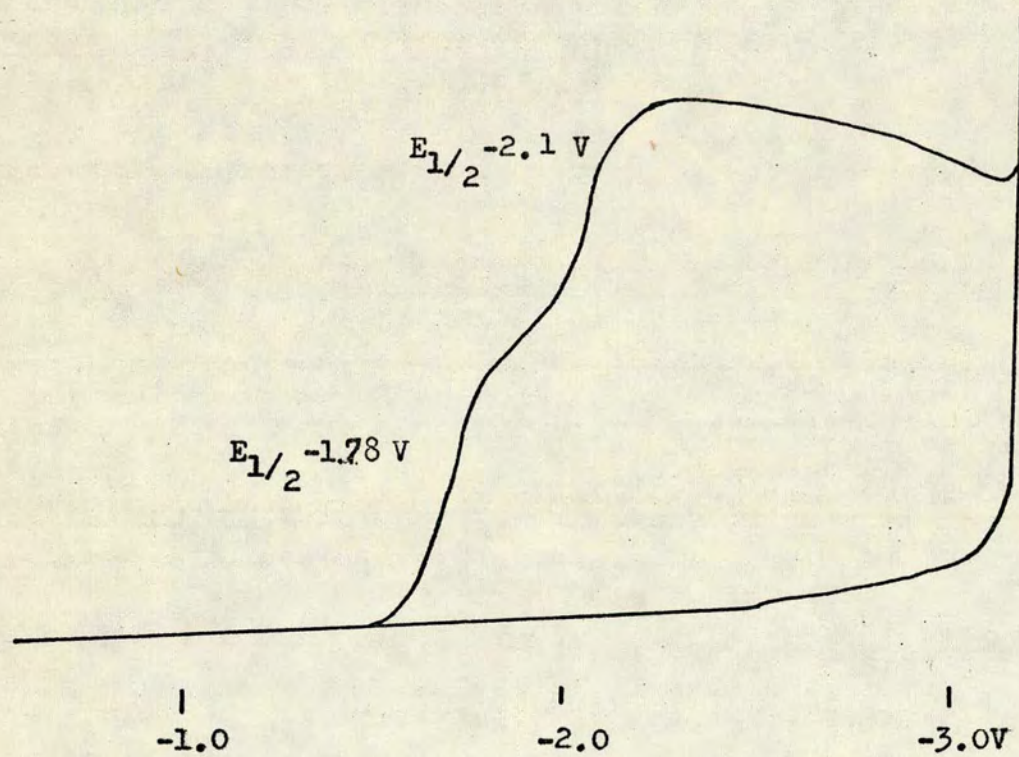
The voltammetric observations described above suggested that reduction of acetone in acetonitrile might afford nitrile products providing the reaction was initiated by generation of the cyanomethyl anion. Once the chemical reactions, previously described for acetophenone, were established to produce 3, 3-dimethylacrylonitrile, reduction of the latter should provide a further continuous source of the cyanomethyl anion.

An attempt was made to observe reduction waves for 3, 3-dimethylacrylonitrile by carrying the cathodic sweep in the cyclic voltammogram of a solution containing acetone to beyond the cathodic limit. At these negative potentials one might expect reduction of the solvent to the cyanomethyl anion to take place, thereby producing 3, 3-dimethylacrylonitrile which should be observed on subsequent sweeps. Unfortunately the procedure caused an anodic shift in the cathodic limit, thereby obscuring any possible waves for the unsaturated nitrile.

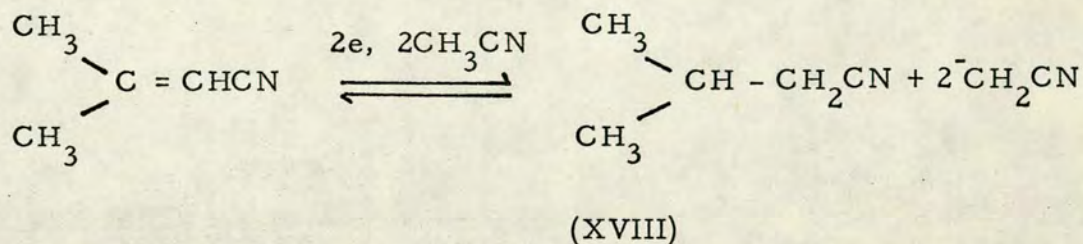
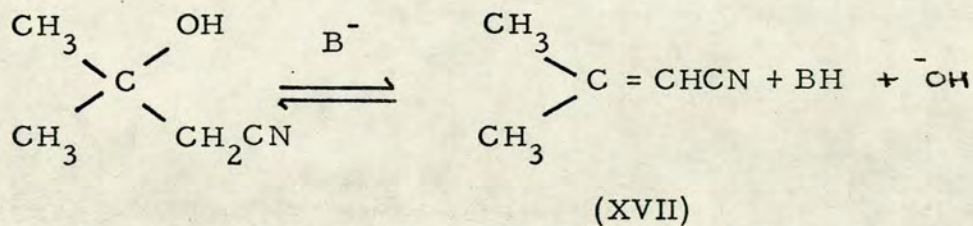
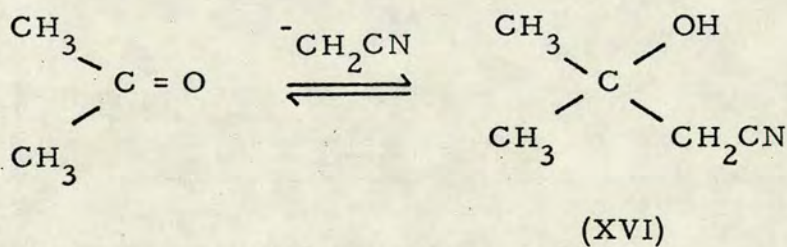
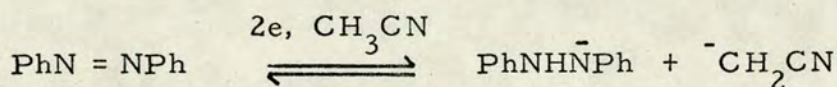
In order to provide a suitable source of the cyanomethyl anion the

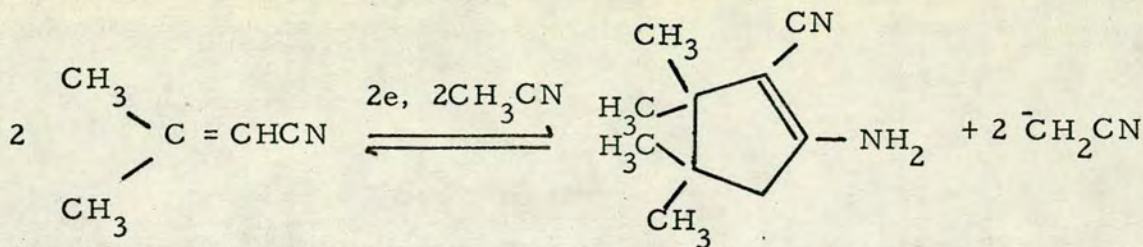
FIGURE 7.3

PhN=NPh in CH_3CN ($10^{-1}\text{M Et}_4\text{NBF}_4$) vs. $\text{Ag}/10^{-1}\text{M Ag}^+$; DME.



electrolysis of acetone was conducted in the presence of azobenzene. The latter showed two waves on polarography (Fig. 7. 3) and, as indicated previously, protonation of the di-anion by the solvent produces CH_2CN^- . Subsequent addition of acetone to the catholyte and continued electrolysis just anodic of the cathodic limit afforded a crude product which was shown to contain 3-hydroxy-3-methylbutyronitrile (XVI), 3, 3-dimethylacrylonitrile (XVII) and 3, 3-dimethylglutaronitrile (XX), by comparison of the n. m. r. spectrum of the reaction mixture with the spectra of authentic samples. Mass spectral evidence for 3-methylbutyronitrile (XVIII) was also obtained, and a low frequency nitrile signal at 2185 cm^{-1} in the i. r. spectrum indicated the presence of 1-amino-2-cyano-3, 3, 4, 4-tetramethylcyclopent-1-ene (XIX). No attempt was made to separate these products. By analogy with the reduction sequence previously discussed for acetophenone, the probable origin of these compounds is indicated below:





(XIX)



(XX)

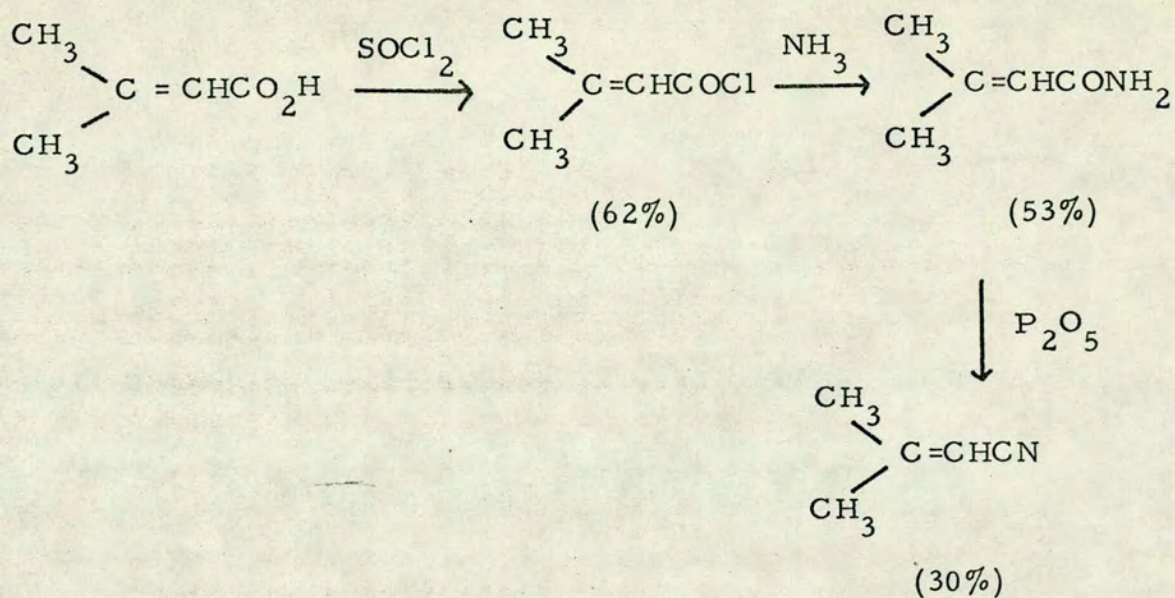
Scheme (20)

The identification of the hydroxynitrile (XVI) in the reaction mixture suggests perhaps that the base catalysed dehydration of the 3-methyl derivative is slower than that of the 3-phenyl derivative obtained from acetophenone.

As expected, controlled potential electrolysis of 3,3-dimethylacrylonitrile in anhydrous acetonitrile afforded a mixture of nitrile products believed to consist of compounds XVIII, XIX and XX on spectral evidence. In a 10% aqueous solution, however, only the dihydro compound, XVIII, was identified.

(c) The Preparation of Authentic Samples

3-Hydroxy-3-methylbutyronitrile (XVI) was prepared using a method analogous to that described for the 3-phenyl derivative. Dehydration was most effectively conducted by the action of acetic acid/sulphuric acid. Phosphorus pentachloride was believed to afford a mixture of XVII and the 3-chloro derivative and the use of phosphoric acid was unsuccessful. An alternative synthesis of XVII involved the route described below, but the overall yield (ca. 10%) gave little advantage over the former method.

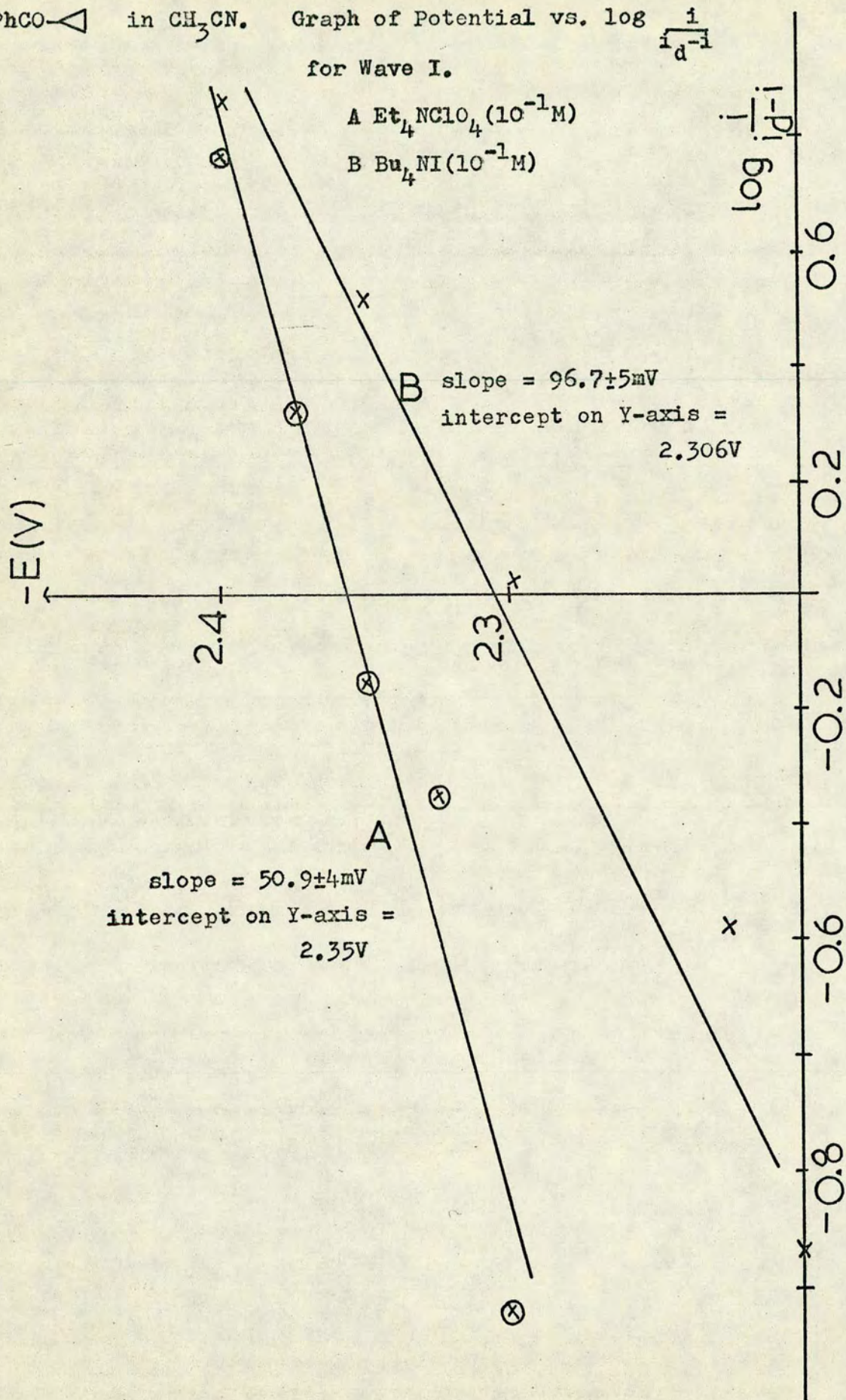


Scheme (21)

The conversion of XVII to the dinitrile (XX) was achieved as previously described by addition of the cyanomethyl anion to the olefin in the presence of the tetraethylammonium cation. Catalytic hydrogenation of 3, 3-dimethylacrylonitrile afforded 3-methylbutyronitrile (XVIII).

FIGURE 8.2

PhCO \triangleleft in CH_3CN . Graph of Potential vs. $\log \frac{i}{i_d - i}$
for Wave I.



5. Polarography and Cyclic Voltammetry of Benzoylcyclopropane in Acetonitrile

A comparison was made of the polarograms for benzoylcyclopropane when recorded in the presence of quaternary ammonium salts of varying cation size, (Figs. 8.1a, 8.1b, 8.1c). In the presence of tetramethyl- and tetraethyl-ammonium salts (Figs 8.1a and 8.1b), two successive 1e transfers were observed. A graph of \sqrt{h} versus i_d for both waves in the presence of tetraethylammonium perchlorate indicated a diffusion controlled process in each case. The application of Tomes' criterion to the first wave gave a value of $E_{1/4} - E_{3/4} = 60\text{mV}$ in the presence of both salts, suggesting an electrochemically reversible first wave. This was confirmed in the tetraethylammonium case by a plot of potential vs. $\log \frac{i}{i_d - i}$ which gave a slope of 50.9 mV (Fig 8.2) and CV (Fig. 8.3) which exhibited an anodic wave on reverse sweep, although the peak separation was somewhat larger ($E_{p_a} - E_{p_c} = 85\text{ mV}$) than the theoretical value for a reversible electron transfer. The polarographic wave observed in a solution of tetrabutylammonium ions (Fig. 8.1c) however appeared less reversible as indicated by Tomes' criterion ($E_{1/4} - E_{3/4} = 80\text{ mV}$) and the graph of potential vs. $\log \frac{i}{i_d - i}$ (Fig. 8.2) which gave a slope of 96.7 mV.

The effects of quaternary ammonium cation size on the rate of electron transfer have been noted by other workers. For example, Jensen and Parker^{80, 81} observed an irreversible second wave for the formation of the 9,10-diphenylanthracene di-anion in DMF in the presence of tetrabutylammonium ions, although the wave became reversible on addition of small amounts of the tetraethylammonium salt. A similar observation³⁵ was made following studies on the reduction of cyclooctatetraene in DMF; the estimated rate constant for the first electron transfer being 10^3 times faster in the presence of the tetramethylammonium cation compared to the tetrabutylammonium cation. Similar conclusions were reached by Fry and Krieger⁸² who found that reduction waves for alkyl halides in DMSO were shifted cathodically in the presence of large cations. The effects have been explained in terms of ion-pairing. For example the irreversible second wave for diphenylanthracene in the presence of the tetrabutylammonium

FIGURE 8.3

PhCO \triangleleft (ca. 2mM) in CH₃CN (10⁻¹M Et₄NClO₄) vs. Ag/10⁻¹M Ag⁺;

Pt wire; — 30mVs⁻¹ E_p -2.92V
 - - - 100mVs⁻¹

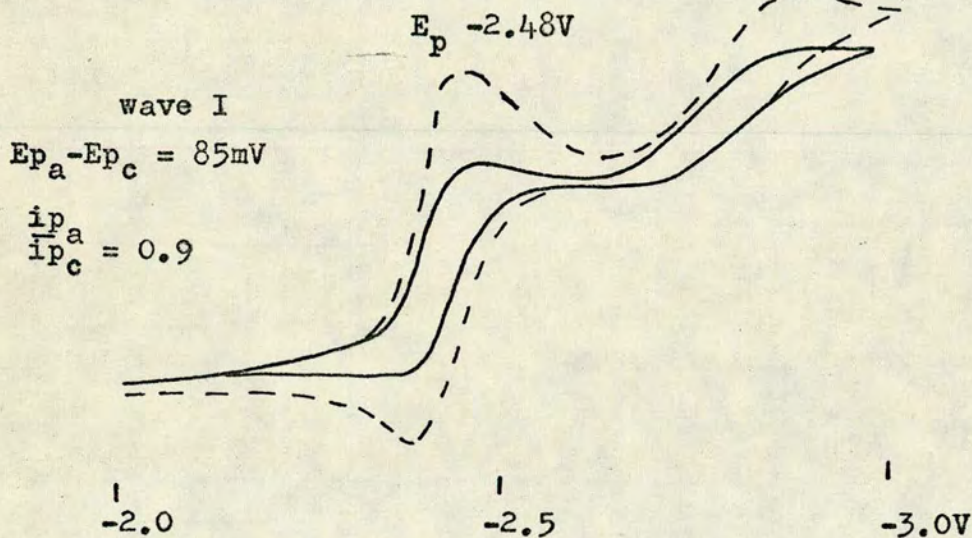
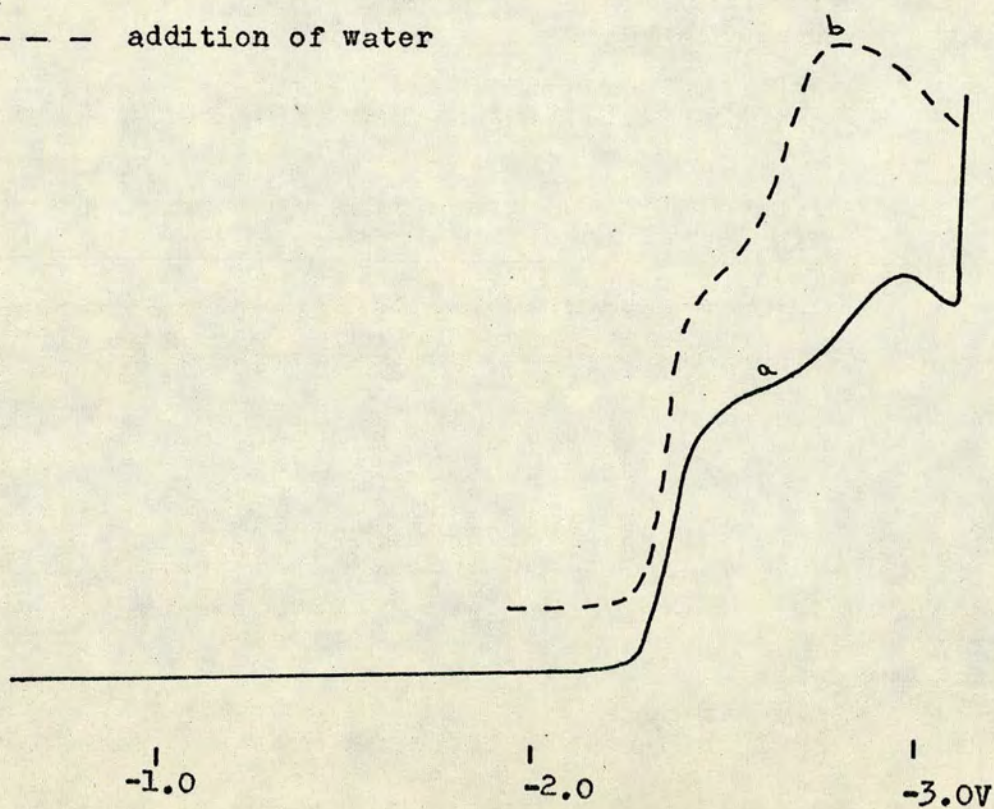


FIGURE 8.4

PhCO \triangleleft (ca. 8mM) in CH₃CN (10⁻¹M Et₄NClO₄) vs. Ag/10⁻¹M Ag⁺;

DME.

- - - - - addition of water



salt was believed to result from the steric inaccessibility of the negative charges to approach by the large cations on the same side.

Examination of the polarograms for benzoylcyclopropane also indicates a variance in the peak separation between the first and second waves $[E_{\frac{1}{2}}(2) - E_{\frac{1}{2}}(1)]$ with supporting electrolyte cation. The polarographic waves observed in a solution of tetramethylammonium cations $[E_{\frac{1}{2}}(2) - E_{\frac{1}{2}}(1) = 240 \text{ mV}]$ are considerably closer together than those obtained in a solution of tetraethylammonium cations $[E_{\frac{1}{2}}(2) - E_{\frac{1}{2}}(1) = 400 \text{ mV}]$. In the presence of tetrabutylammonium iodide the second wave is not even visible. This may be also due to ion-pairing effects. Jensen and Parker,⁸¹ for example, observed a good correlation between ΔE° values and the size of the supporting electrolyte cation. The polarographic second wave for benzoylcyclopropane is slightly smaller than the first (Fig. 8.4a) and probably reflects a solution electron transfer to the substrate as previously discussed for acetophenone. In the presence of water (Fig. 8.4b) the second wave increased in height and shifted anodically, behaviour attributable to protonation of the di-anion. The second CV wave (Fig. 8.3) showed no anodic current on scan reversal indicating the instability of the di-anion under these conditions.



B Electrochemistry in Liquid Ammonia

I Liquid Ammonia as an Electrochemical Solvent.

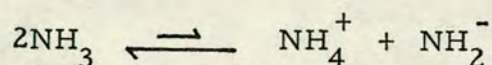
Liquid ammonia is a basic, protic solvent [b. p. -33.4°C ; $\epsilon = 23$ (at -33.4°C); $\text{p}K_{\text{a}}$ ca. 34] which shows considerable potential as a solvent for organic electrochemistry, particularly in the field of reductions owing to its ability to withstand strongly cathodic conditions at low temperatures. The usefulness of liquid ammonia as a solvent for synthetic organic chemistry has frequently been demonstrated. In particular, solutions of alkali metals in ammonia have been used to reduce numerous unsaturated compounds. The medium is suitable for the reaction and preparation of many compounds which would be labile at room temperature and the low boiling point of the solvent facilitates its removal and the reaction work-up. These features are equally attractive to the organic electrochemist.

The solvent is manufactured in large quantities at a reasonable price and is available as the anhydrous solvent in pressurised cylinders. This allows its purification to be readily achieved by distillation. It has, however, received little attention from organic electrochemists and only one review on electrode reactions in liquid ammonia has been published.⁸³ This is probably due to its low b. p. which requires the use of specialised equipment to allow operation at either low temperature or increased pressure.

Those features of the solvent which relate to its use as a solvent for electrochemistry will first be considered.

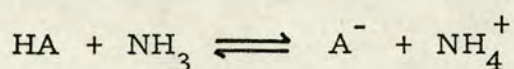
1. Acid-Base Properties in Liquid Ammonia

Liquid ammonia undergoes auto-ionisation, as indicated below, in a manner analogous to that of water but to a lesser extent.



This is reflected in its low specific conductance and ensures that the ammonium ion concentration will be extremely low. It follows that the

ammonium and amide ions are the strongest possible acid and base respectively that can exist in liquid ammonia. All acids of aqueous $pK_a < 12$ (e. g. acetic and mineral acids) are levelled to the acidity of the ammonium ion and all bases of aqueous $pK_a > \text{ca. } 39$ (e. g. potassium hydride) undergo ammonolysis to the amide ion. However the acidity of the medium can often be controlled by the addition of proton donors such as acidic hydrocarbons, alcohols and water. The reaction of such acids (HA) with the solvent is generally much slower than protonation of a reduced species and proton transfer to ammonia is strongly suppressed as the concentration of the base (A^-) increases:



The pK_a values of some weak acids at -60°C in liquid ammonia have been determined;⁸⁴ ethanol ($17 < pK_a < 19$) and t-butanol (pK_a 28) have been found to act as weaker acids than water (pK_a 16) in ammonia. In general, pK_a values in ammonia are 12 units lower than those in water,⁸⁵ due to the higher basicity of the solvent.

2. Solubilities of Ionic and Covalent Compounds in Liquid Ammonia

Hildebrand⁸⁶ has discussed the properties of liquid ammonia which are significant in comparing solubilities in ammonia with those in other solvents. The dielectric constant of ammonia is considerably lower than that of water leading, in general, to a lower solubility of ionic salts in liquid ammonia compared to water. Salts with polynegative ions e. g. sulphates, carbonates and phosphates are practically insoluble in liquid ammonia owing to their high lattice energies. Salts with highly polarizable anions e. g. thiosulphate and iodide tend to be more soluble than those with less polarizable anions e. g. sulphate, chloride. This is due to the relatively large polarizability of ammonia compared to water.

The solubilities of covalent organic compounds in liquid ammonia are usually considerably higher than in water, probably owing to the greater dispersion energy interaction which results from the polarizability mentioned above. Substances capable of hydrogen-bonding or ionising

e. g. sugars, esters, amines, alcohols, carboxylic acids or phenols, have high solubilities due to the basic character of liquid ammonia. However many organic compounds have low solubility in liquid ammonia; this necessitates the use of co-solvents such as ether, THF or dioxan.

A summary of the published solubilities of inorganic salts and general trends in the solubilities of organic compounds are given in Table III.

3. Practical Aspects of Electrochemistry in Liquid Ammonia

(a) Solvent Purification and Cell Design.

During these studies vacuum techniques were used to purify the ammonia and transfer it to the cell, the main purpose being to avoid the presence of oxygen and eliminate water from the solvent and cell. Once the apparatus was assembled, every effort was made to prevent exposure of the purified ammonia or cell to the atmosphere. When this was unavoidable, for example when adding electrolyte or changing the electrode, a flow of dry nitrogen gas was maintained through the apparatus during the procedure.

The final cell design, described in the experimental section, was found to be more reliable, convenient to use and versatile than the more conventional H-type cell design originally constructed.

The major problem encountered resulted from evaporation of solvent from the cell, which did not permit accurate concentrations of depolariser to be measured. This was particularly marked when mercury cathodes were used, since the minimum operating temperature was limited by the freezing point of the mercury (-39°C). However lower temperatures and hence less evaporation could be achieved by using solid electrodes.

As a result of the low dielectric constant of liquid ammonia, solution resistances are high and iR compensation must be employed for accurate potential measurements. However, as scan rates were $\dagger 250 \text{ mV s}^{-1}$, this was not considered a serious problem.

(b) Reference Electrodes in Liquid Ammonia.

The working and secondary electrodes employed in liquid ammonia are conventional in design. Reference electrodes, however, constitute more of a problem as they have to be prepared in situ prior to each experiment. A survey of the topic is presented in the review by Brown.⁸³ The simplest reference electrode is the mercury pool anode as used by Laitinen and Shoemaker,⁸⁷ which is in effect the mercury-mercuric ion couple. A silver wire immersed in the electrolyte solution has also served as a suitable pseudo reference.⁸⁸ Other reference electrodes which have been used include Ag/AgNO₃ (10⁻² M)/KI (10⁻¹ M)^{88, 89, 90}, Pb/PbCl₂ (satd.)/KCl (satd.)⁹¹, Pb/Pb(NO₃)₂ (5x10⁻² M)⁹², and Ag/AgCl (satd.)/KCl (satd.)⁹³. The latter two were both used during these studies. A 5 x 10⁻² M solution of lead nitrate is readily prepared owing to the high solubility of the salt (7M at -36°C) as estimated using the technique described for quaternary ammonium salts. In some cases a Ag/AgCl (satd.)/BuMe₃NBF₄ (10⁻¹ M) reference was used, in which the estimated solubility of the silver chloride was 3 x 10⁻² M, as measured by controlled potential coulometry. The Pb/Pb(NO₃)₂ electrode is 0.31V negative of the N. H. E.⁹⁴ and the Ag/AgCl (satd.)/KCl (satd.) and Ag/AgCl (satd.)/BuMe₃NBF₄ (10⁻¹ M) references were estimated as about 0.2 and 0.3V more negative respectively than the Pb/Pb(NO₃)₂ electrode. Unless otherwise indicated potentials are hereafter quoted versus the latter reference electrode.

(c) Supporting Electrolytes in Liquid Ammonia.(i) The Solubilities of Quaternary Ammonium Salts in Liquid Ammonia.

Previous studies in liquid ammonia utilised tetrabutylammonium iodide as the supporting electrolyte,⁹⁵ but the low solubility of this salt (ca. 4 x 10⁻³ M at -36°C) precluded its use as a suitable electrolyte for anything but very low concentrations of substrate, and a more soluble electrolyte was required for preparative electrochemistry. Several

quaternary ammonium fluoroborates were therefore synthesised and their solubilities measured at -36°C by determining the weight of the salt which dissolved in a known volume of solution. Likely cations were selected by reference to the available data for solubility of quaternary ammonium iodides in liquid ammonia at -78°C .⁹⁶ The experimental results have been summarised together with the published solubilities (Table IV).

As expected, the solubilities at -36°C are considerably greater than at the lower temperature, and in general the fluoroborates are more soluble than the corresponding iodides. The tetraethylammonium salt, particularly the fluoroborate, shows considerably higher solubility than the other symmetric salts. This may be due to the relatively large polarizability of this cation which falls between the small unpolarizable tetramethylammonium cation and the sterically crowded large tetrapropyl- and tetrabutylammonium cations. However the fluoroborates of asymmetric quaternary ammonium cations which contain three identical alkyl groups are, in general, considerably more soluble than the symmetric salts. This may be due to less effective packing in the crystal structure of the asymmetric salts and consequently lower lattice energies. As a result of the solubility studies tetraethyl- and butyltrimethylammonium salts were selected as being the most useful. Bard et al.¹⁷¹ have used methyltributylammonium iodide. However, the use of quaternary ammonium halides was avoided whenever possible during these studies, owing to the hazardous formation of nitrogen trihalides as a black deposit on the anode during preparative electrolyses. These compounds are formed by reaction between ammonia and halogens and are highly explosive, as discovered to the expense of Dulong (1811)⁹⁸, who lost an eye and three fingers in the process of preparing nitrogen trichloride.

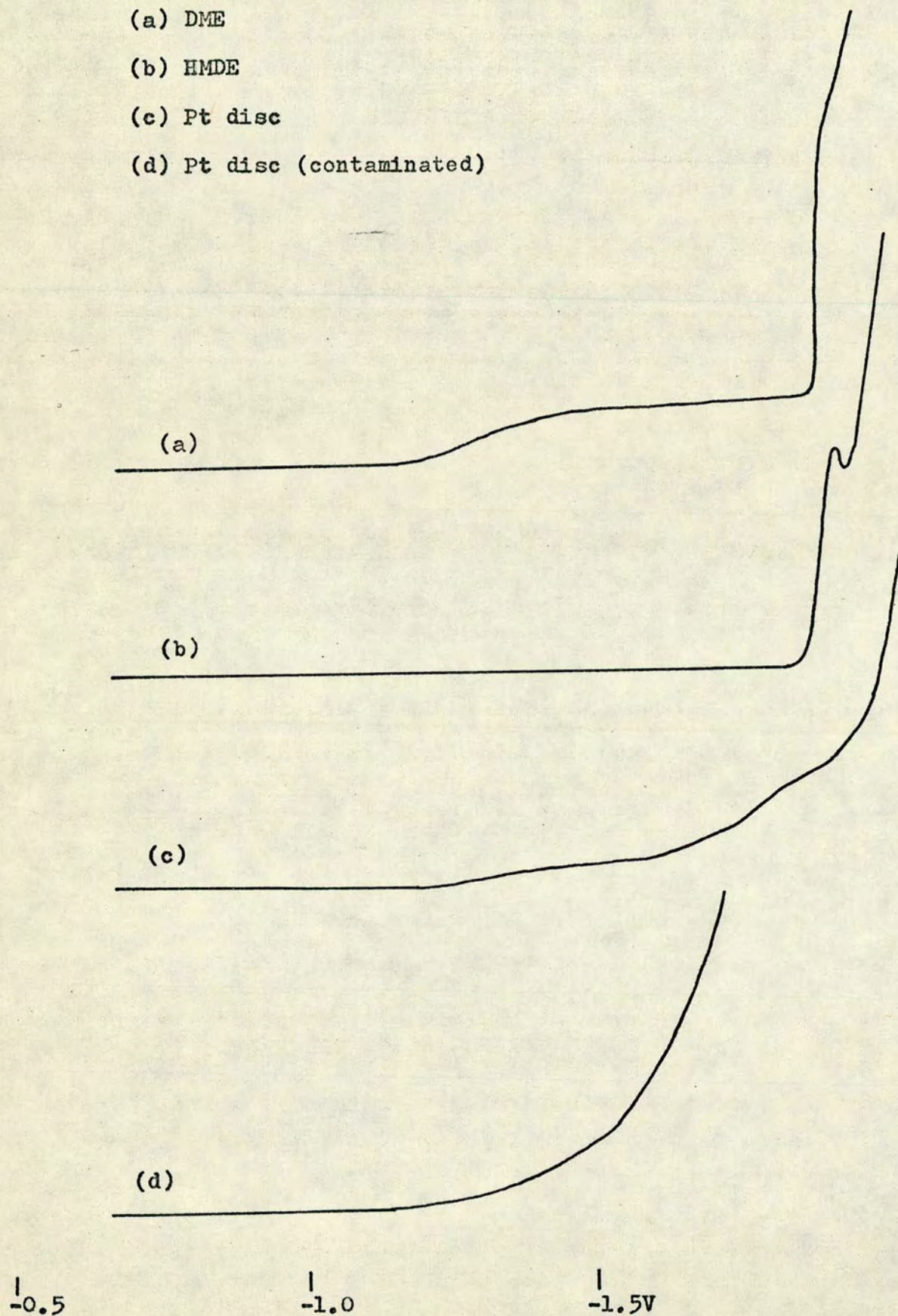
Following the successful application of tetraalkylammonium *p*-toluenesulphonates as supporting electrolytes in aqueous media, particularly their ability to increase the solubility of organic compounds, two tosylates were synthesised with a view to use in liquid ammonia.

Preliminary solubility measurements indicated that tetraethylammonium

FIGURE 9

$\text{Et}_4\text{NBF}_4 (10^{-1}\text{M})$ in liquid ammonia vs. $\text{Pb}/\text{Pb}^{2+} (0.05\text{M})$.

- (a) DME
- (b) HMDE
- (c) Pt disc
- (d) Pt disc (contaminated)



tosylate (solubility 0.39M) may be suitable but further studies were not made.

(ii) Potential Ranges in Liquid Ammonia

The thermodynamically controlled potential range in liquid ammonia is only 0.04V as governed by the standard potentials of the $\text{NH}_3\text{-N}_2$ and $\text{H}_2\text{-NH}_3$ couples. Fortunately, however, both couples usually exhibit overvoltages of about 1V and in practice the available potential range may exceed 2V. Generally the anodically and cathodically limiting reactions are oxidation of the solvent to nitrogen and protons and the transfer of electrons to the solvent respectively.

Cathodic Limits

During the course of these studies the cathodic limit was measured at mercury and platinum in the presence of various quaternary ammonium salts. The values are summarised in Table V. A carbon-paste electrode was found to be unsuitable for reductions owing to the poor range (ca. -1.0V). The DME showed slightly extended ranges compared to the HMDE; for example, in a solution of tetraethylammonium fluoroborate at the HMDE, an impurity peak was frequently present just prior to the cathodic limit (Fig. 9b). In general, the limit at platinum was less well defined than at mercury and a gradual increase in current was frequently observed beyond -1.6V (Figs. 9c and 10b), although the final sharp increase in current occurred at a similar potential for mercury and platinum. During later studies the high background currents at platinum were particularly troublesome (Figs. 9c and 10c), and could not be remedied by the usual cleaning and pre-treatment methods e. g. immersion in aqua regia, cathodic pre-treatment and mechanical polishing. It is possible that reduction of residual water is responsible for the behaviour observed, although the same procedure for purification of the solvent/supporting electrolyte was used throughout. The low overpotential for hydrogen evolution on platinum may result in a cathodic process:

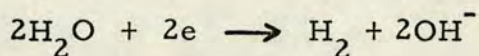


FIGURE 10

$\text{BuMe}_3\text{NBF}_4 (10^{-1}\text{M})$ in liquid ammonia vs. $\text{Pb}/\text{Pb}^{2+} (0.05\text{M})$.

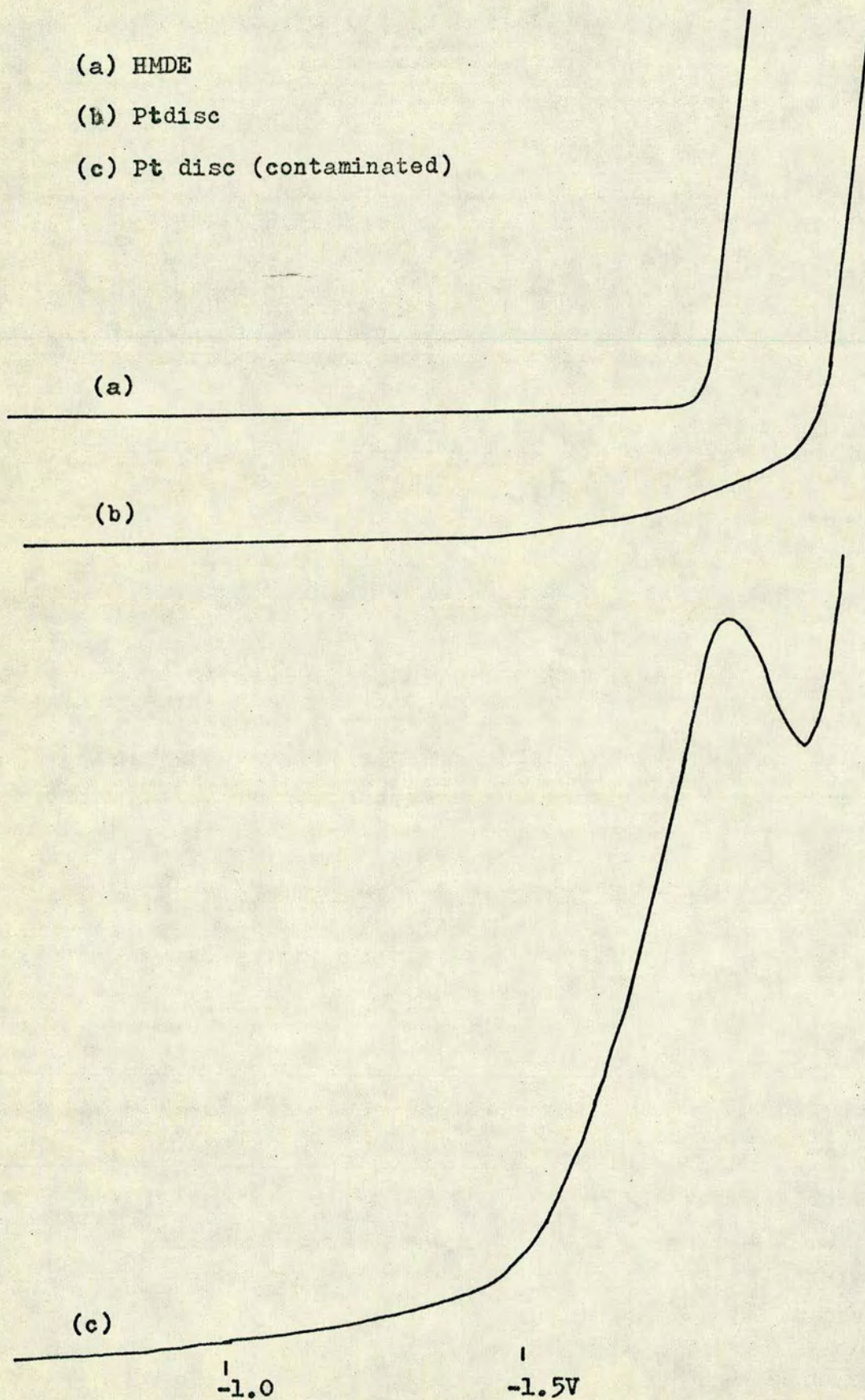


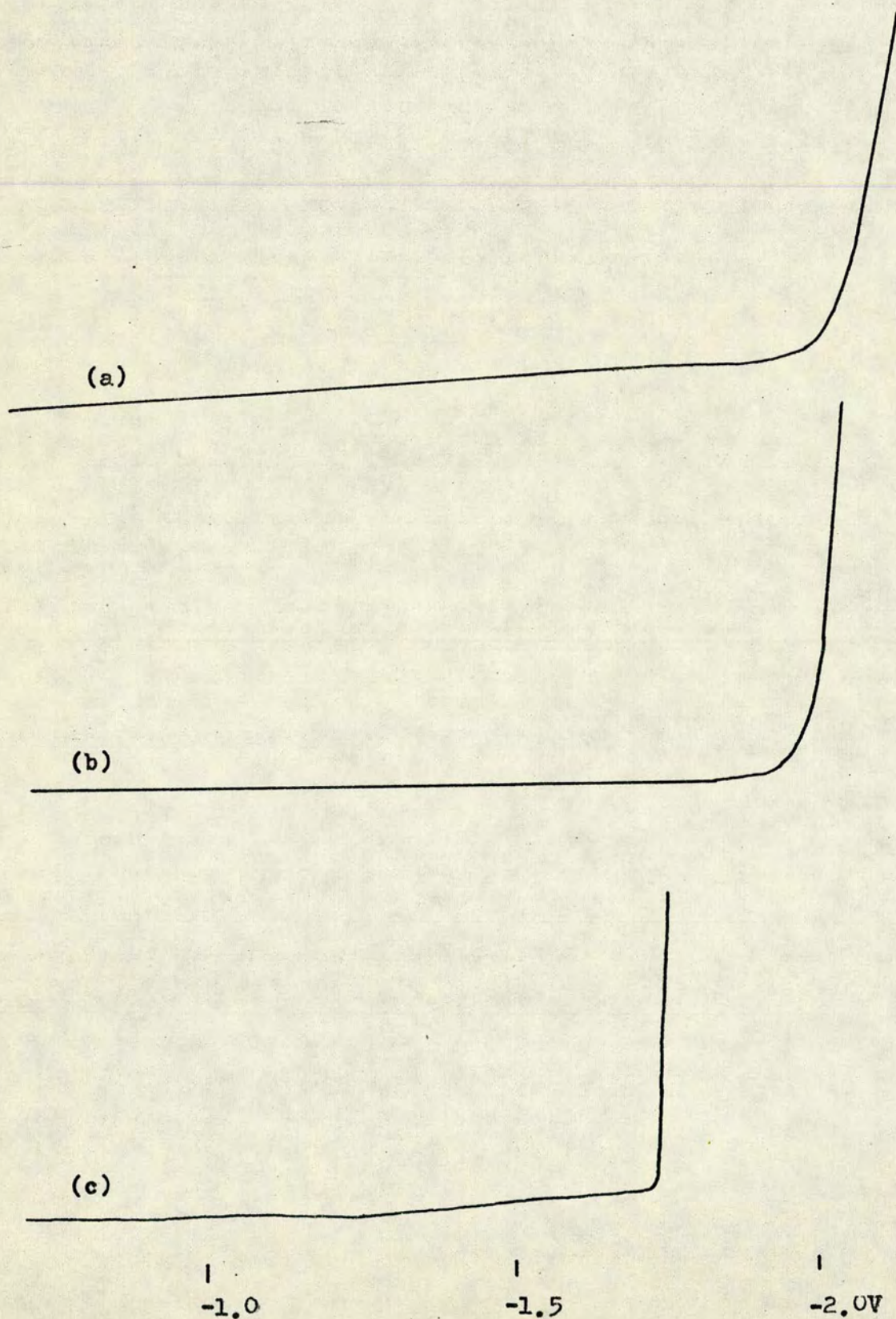
FIGURE 11

(a) Bu_4NI (satd. ca. 0.006M)

(b) Pr_4NBF_4 (satd. ca. 0.02M)

(c) Me_4NBF_4 (satd. < 0.1M)

in liquid ammonia vs. Pb/Pb^{2+} (0.05M); DME.



and is supported by the observation that bubbles of gas formed on the electrode surface at potentials negative of -1.5V. The relatively high overpotential of mercury compared to platinum may result in suppression of hydrogen evolution, thereby explaining why similar high currents were not observed using a mercury electrode. Herlem⁸⁹ has observed a similar wave for reduction of water [$E_{\frac{1}{2}} -1.7V$ vs. Ag/Ag^+ ($10^{-2}M$) at water concn. = $5 \times 10^{-3}M$] in liquid ammonia using potassium iodide as supporting electrolyte and a platinised platinum or silver electrode, although the reduction was said not to take place at a polished platinum electrode. A later report⁹⁹ however indicated that reduction of water at polished platinum did occur.

A comparison of the cathodic limits at mercury in the presence of different quaternary ammonium salts (Figs. 9a, 10a, 11a, 11b and 11c) shows an increase in the order $Me_4N^+ < Et_4N^+$, $BuMe_3N^+ < Pr_4N^+ < Bu_4N^+$. The limit is frequently associated with the production of solvated electrons, which will be discussed in greater depth later.

Cathodic limits were also measured in the presence of lithium and potassium salts (Figs. 12 and 13). The range was less at mercury than at platinum, particularly in the case of potassium, due to amalgam formation.¹⁰⁰ Pre-treatment by the discharge of solvated electrons on electrolysis beyond the cathodic limit in the presence of potassium iodide resulted in an improved range at platinum (Fig. 13b), although at mercury a large cathodic peak was present ($E_p -0.83V$) after the pre-treatment. The most cathodic range obtainable (ca. -2.1V) was at a platinum electrode in the presence of lithium ions (Fig. 12b).

Anodic Limits

As indicated previously, the anodic range in liquid ammonia is limited by oxidation of the solvent to nitrogen and hydrogen ions, the latter reacting with the solvent to form ammonium ions:

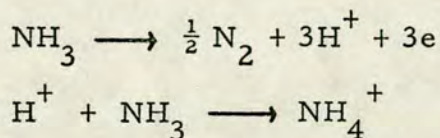


FIGURE 14.1

$\text{BuMe}_3\text{NBF}_4$ (0.5M) in liquid ammonia vs. Pb/Pb^{2+} (0.05M); Pt wire.

(a) sweep of +1.5 to -1.5V

(b) sweep of +0.5 to -1.5V

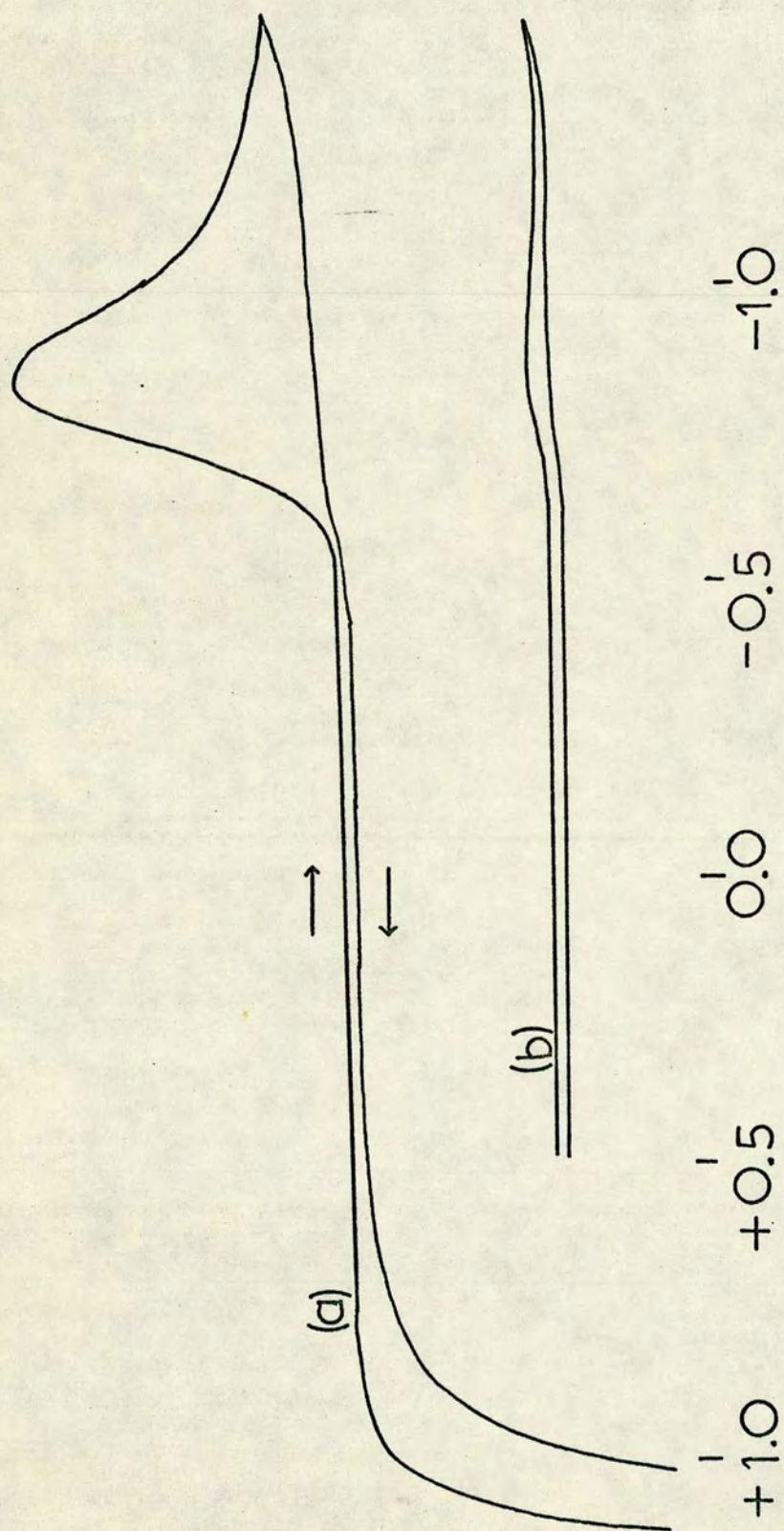


FIGURE 14.2

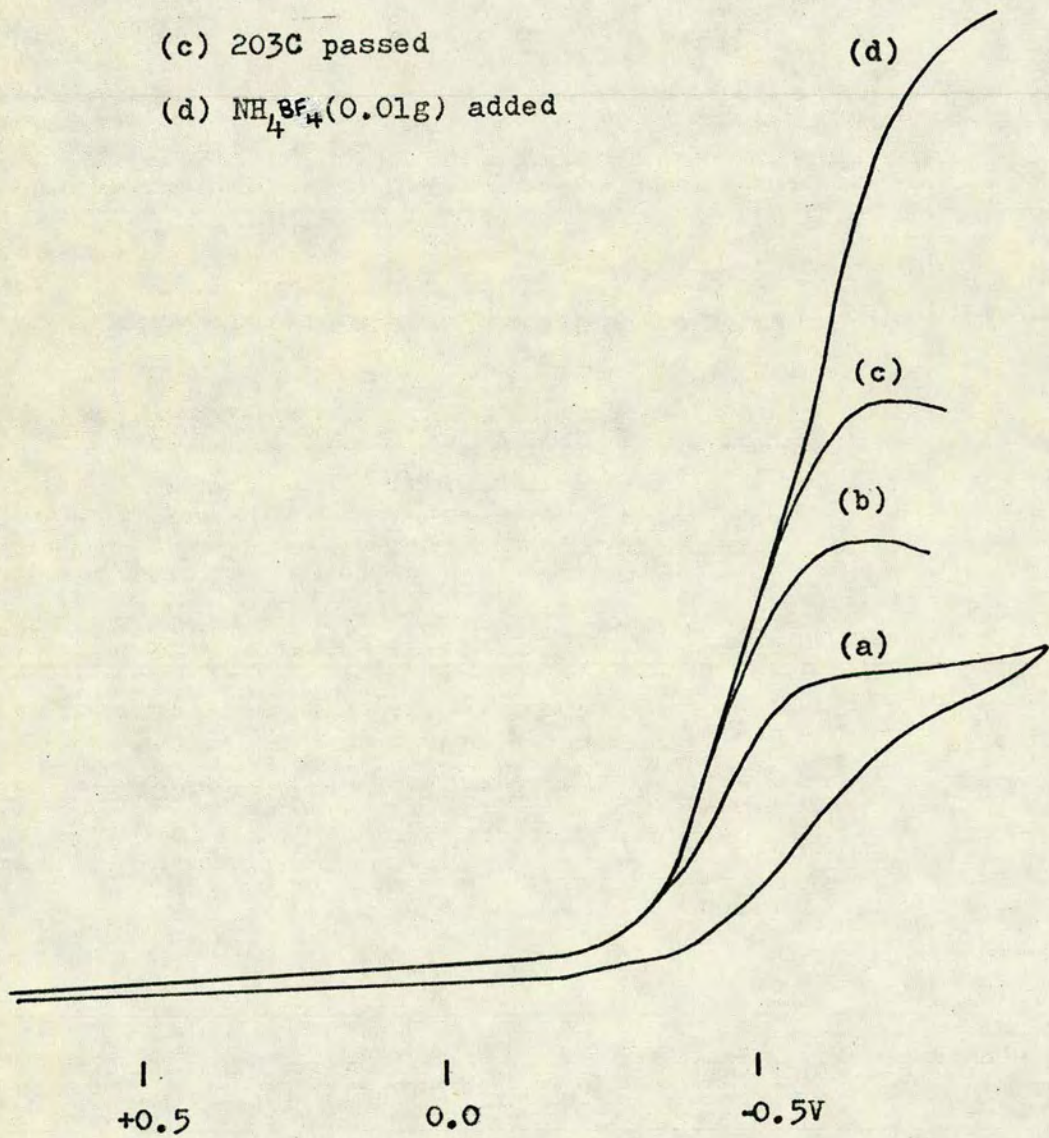
$\text{BuMe}_3\text{NBF}_4$ (0.5M) in liquid ammonia vs. Pb/Pb^{2+} (0.05M); Pt wire.

CPE at +1.2V (a) 57C passed

(b) 94C passed

(c) 203C passed

(d) NH_4BF_4 (0.01g) added



This is supported by voltammetry in the presence of different supporting electrolyte anions (BF_4^- , ClO_4^- and NO_3^-) which showed a similar cut-off potential (ca. +0.9V) at a platinum wire electrode in each case (e. g. Fig. 14.1a). At the anodic limit, gas evolution occurred and, by controlled potential electrolysis at +1.0V under an atmosphere of helium, a sufficient volume of the gas was collected to analyse by g.l.c., thus confirming its identity. Complete evaporation of the solvent from the anode compartment after electrolysis, and treatment of the residue with sodium hydroxide solution resulted in a strong smell of ammonia, suggesting that ammonium ions had been formed during the oxidation. CV studies involving sweep reversal following an anodic scan beyond the cut-off potential exhibited a cathodic wave (E_p -0.8V, Fig. 14.1a) which was attributed to ammonium ion reduction. The symmetric shape of the wave suggested that adsorption had occurred. The wave was not present if sweep reversal was effected prior to the anodic limit (Fig. 14.1b) indicating that the ammonium ions are formed as a result of solvent oxidation. By carrying out cathodic sweeps at a platinum electrode following controlled potential oxidation at +1.2V, it was shown (Fig. 14.2) that the height of the reduction wave increased with the number of coulombs passed (although the increase was not as great as expected). Addition of ammonium fluoroborate also caused an increase in the wave height, thereby confirming that the wave was attributable to ammonium ion reduction. The potential of this wave is somewhat anodic of the value suggested by Laitinen and Shoemaker⁹⁴ who reported the $E_{\frac{1}{2}}$ -1.37V vs. Pb/Pb^{2+} (5×10^{-2} M) for ammonium ion reduction. However the reduction potential may be expected to vary with electrode material, particularly if adsorption is occurring at the platinum electrode. Studies by Herlem and co-workers⁹⁹ on the oxidation of amide ions in liquid ammonia at polished platinum, indicated that reduction of hydrogen ions occurred at about -1.5V vs. Hg/Hg^{2+} (5×10^{-3} M). A comparison of the reported anodic and cathodic limiting potentials for oxidation and reduction of the solvent with the values obtained in the present studies indicated that the Hg/Hg^{2+} reference was about 0.5V positive of the Pb/Pb^{2+} couple.

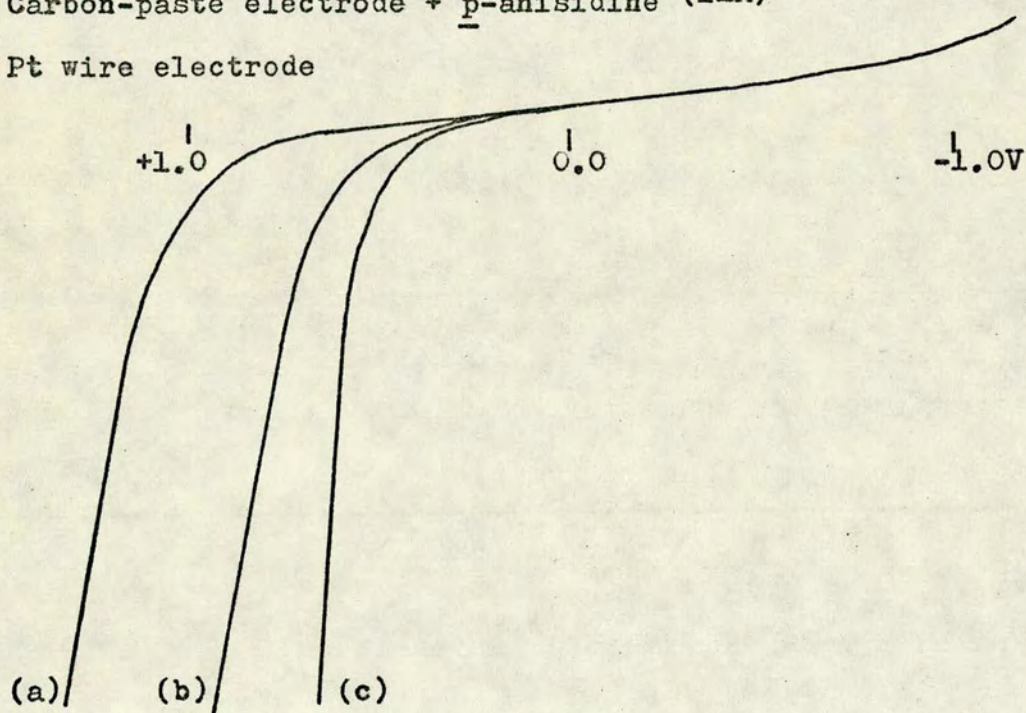
FIGURE 14.3

Et_4NBF_4 (10^{-1}M) in liquid ammonia vs. Ag/satd. AgCl; satd. KCl.

(a) Carbon-paste electrode

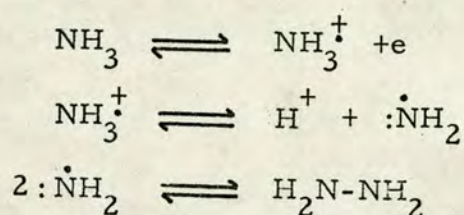
(b) Carbon-paste electrode + p-anisidine (1mM)

(c) Pt wire electrode



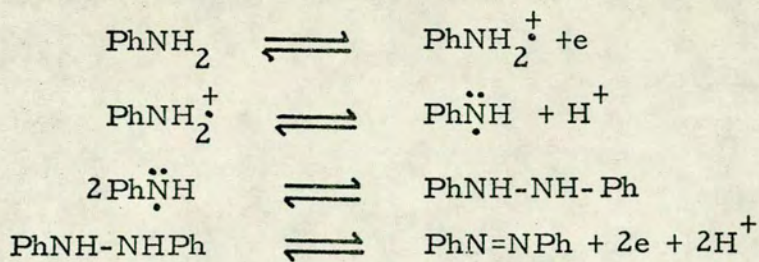
Barnes and Mann¹⁰¹ have also studied the oxidation of ammonia and other amines in acetonitrile by CV and controlled potential electrolysis. An n value of 0.75 was obtained for ammonia and the theoretical yields of ammonium ions and nitrogen gas were obtained for the number of coulombs passed.

Attempts to prepare hydrazine by incomplete oxidation of ammonia to the amino-radical have generally proved unsuccessful due to the fact that hydrazine is itself more easily oxidised than ammonia. The sequence of steps would be:

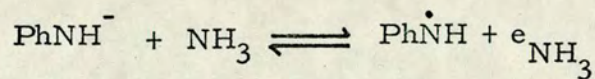


A survey of this topic is given in the review by Brown.⁸³ During these studies preliminary experiments were carried out involving oxidation of ammonia in the presence of radical trapping agents e. g. cyclohexene, butadiene, but no evidence for amination was obtained suggesting that oxidation or dimerisation of the amino radical (if formed) occurs rapidly. The trapping agents were however fairly insoluble in ammonia.

A comparison of the anodic limits obtained at a platinum and carbon-paste electrode indicated that a considerably extended range was obtained in the latter case (Figs.14.3c and 14.3a). The result suggested that carbon may be a suitable electrode for conducting electro-oxidations, and indeed an oxidation wave for *p*-anisidine was clearly visible prior to the anodic limit at a carbon-paste electrode (Fig.14.3b) The inability to observe oxidation waves for aromatic amines at platinum was reported by Herlem and co-workers¹¹¹ in their studies on aniline and *p*-bromoaniline in liquid ammonia. Controlled potential oxidation of *p*-anisidine at +0.9V vs. Ag/AgCl (satd.)/KCl (satd.) using a carbon rod electrode gave 4,4'-dimethoxyazobenzene (18% yield; 55% current yield), together with other higher azo- and hydrazo-derivatives. A possible mechanism for formation of this compound might be:



A similar oxidation¹⁰² of several p-substituted anilines in acetonitrile in the presence of pyridine has been studied at the rotating platinum electrode, as well as by product isolation. Two electron oxidations were observed accompanied by the formation of substituted azobenzenes. The oxidation of the conjugate bases of aniline and p-bromoaniline in liquid ammonia at platinum similarly afforded azo- and hydrazo-products in low chemical yields.¹⁶¹ However current yields exceeded 100% and this was attributed to the simultaneous occurrence of a chemical oxidation:



II. The Electrochemical Reduction of Acetylcyclopropanes and Pentan-2-one by Solvated Electrons in Liquid Ammonia.

1. Introduction

The Solvated Electron

The solvated electron has been defined¹⁰³ as an electron in a liquid which is non-ionised, or only very weakly so, such as water, ammonia, amines, ethers, alcohols and hydrocarbons.

Solutions of solvated electrons may be produced in different ways, the most well documented¹⁰⁴ being the dissolution of metals in suitable polar solvents, such as ammonia (the Birch reduction), low molecular weight amines (the Benkeser reduction) and hexamethylphosphoramide.

The nature of metal-ammonia solutions has been the subject of a large number of physico-chemical studies and it is now generally agreed that different models have to be formulated, depending on the concentration of the metal.¹⁰⁵ Two models are postulated for solutions which are 0.005 M or less. The 'cavity' model theory considers the solutions to consist of essentially independent ammoniated metal cations and solvated electrons, the 'free' electrons occupying cavities surrounded by ammonia molecules having their protons orientated towards the cavity. The 'expanded metal' model, on the other hand, depicts the electron as occupying an 'expanded orbital' defined by the hydrogen atoms of the first solvent sphere about the cation. As the concentration is increased to the 0.005-1.0M range, species of stoichiometry M , M^- and M_2 appear to become important, and are thought to arise by simple electrostatic interactions of solvated electrons and cations. On the basis of spectral studies it has been concluded that the characteristics of the electrons and cations are essentially the same in these ion-paired species as they are in the species involved in very dilute solutions.¹⁰⁶ More concentrated solutions (1.0M or greater) are considered to be composed mainly of solvated cations held together by electrons, a situation closely akin to that of the metallic state of the metal.^{105a}

From an electrochemist's point of view, Ebersson and Nyberg¹⁰⁷ prefer

that the terminology solvated electrons be dropped in favour of radical anions of solvent molecules. In some cases the solvent radical anions are stable (e.g. ammonia, amines, HMPA), in some they are not (e.g. protic solvents), exactly the same kind of behaviour exhibited by more conventional radical anions.¹⁰⁸

The electrochemical production of solvated electrons in liquid ammonia containing quaternary ammonium salts was first carried out by Palmaer,¹⁰⁹ who produced blue solutions characteristic of solvated electrons in ammonia by electrolysis of tetramethyl- and tetraethyl-ammonium salts at platinum electrodes. Kraus¹¹⁰ confirmed this finding and Forbes and Norton⁹⁶ extended the work to the ammonia solutions of ten different quaternary ammonium iodides. More detailed studies were carried out by Laitinen and Nyman¹¹² on solutions containing symmetric quaternary ammonium salts at mercury electrodes. In these cases amalgamation of the cation was an alternative cathodic reaction to electron dissolution. Identical cathodic ranges were shown by solutions containing tetrabutyl- and tetrapropyl-ammonium salts and the associated currents did not show limiting values, indicating that electron dissolution was the cathodic reaction in both cases. Tetramethylammonium solutions however showed a reduced potential range attributed to amalgam formation, the associated current being limited in value due to removal of cations from the solution surrounding the electrode. Solutions containing tetraethylammonium cations were thought to exhibit both types of behaviour.

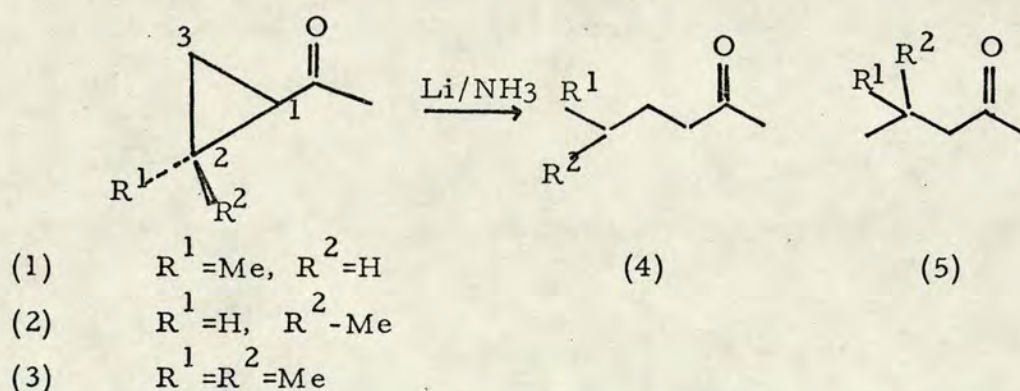
Absorption and EPR spectroscopy have shown, at least for dilute solutions, that the properties of solutions of electrons produced electrochemically in ammonia are strictly similar to those produced chemically.¹¹³ Quinn and Lagowski¹¹⁴ electrochemically prepared solutions of electrons in liquid ammonia in the presence of quaternary ammonium cations of varying size and found the position of the absorption band at 1440 m μ to be constant and independent of the cation. This, they concluded, gave support to the 'cavity' model theory in the concentration range used (2 - 200 x 10⁻⁵ M). The 'expanded metal' model was discounted on the grounds that it should show a more marked dependence on the size of the cation.

2. The Reduction of Acetylcyclopropanes by Solvated Electrons.

(a) Introduction

The reductive ring cleavage of conjugated acetylcyclopropanes has been carried out using solutions of dissolved metals in liquid ammonia.^{115, 116, 117}

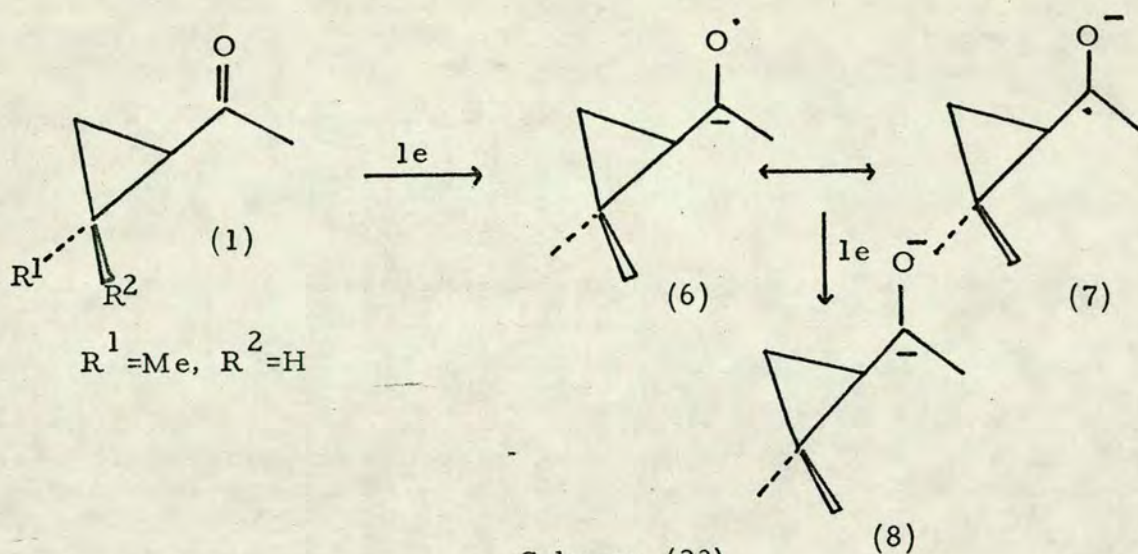
It is generally assumed that the reduction occurs by initial addition of one or two electrons to the carbonyl group, followed by cleavage of the cyclopropyl bond in the resulting intermediate species. Reduction of acetylcyclopropanes substituted in the 2-position could lead to products resulting from C₁-C₃ or C₁-C₂ bond cleavage (Scheme 22).



Scheme (22)

In order to distinguish between a radical or a carbanion intermediate in the ring opening, studies were made¹¹⁵ on trans-1-acetyl-2-methylcyclopropane (1), which has no steric interaction between the substituent and the acetyl group. A carbanionic species would be expected to open preferentially towards the unsubstituted position forming a primary rather than a secondary carbanion, whereas a radical species would be expected to open preferentially towards the 2-methyl forming a secondary rather than a primary radical. Cleavage occurred predominantly away from the 2-methyl group, the behaviour expected for a carbanionic intermediate, indicating either species (6) or (8) is involved in the cleavage step.

(Scheme 23). Compounds (2) and (3), however, showed predominant cleavage towards the more substituted centre. Rather than postulate a change over to a radical mechanism, the result was explained in terms of the steric effect of the cis-2-methyl group on the conformation of the side chain.



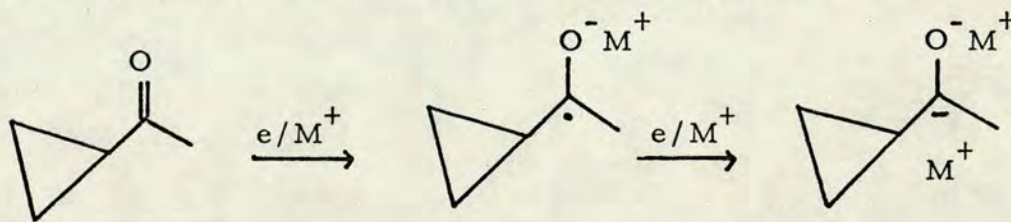
Further evidence against a radical type intermediate was the absence of dimer formation during normal reduction (excess lithium) and the fact that the authentic radical ring-opening gave a much higher proportion of product (4) [(4)/(5) = 41] than that observed from the lithium/ammonia reduction [(4)/(5) = 2.05 - 4.5].

The original objective of the work described in the following pages was to determine whether a radical anion or di-anion species was involved in the ring cleavage step and, in the case of the latter, whether the addition of two electrons occurred stepwise or simultaneously. This could be established by polarographic studies coupled with controlled potential electrolysis in liquid ammonia. A 2e wave might suggest a species such as (8) as an intermediate, while two consecutive 1e transfers might enable one to determine whether cleaved product was produced at the potential of the first or second waves. Similar studies for several alkyl- and aryl-substituted enones have been determined in DMF.⁷⁹

Unfortunately acetylcyclopropanes were found to be electro-inactive in the available cathodic range in liquid ammonia when butyltrimethyl- and tetraethyl-ammonium salts were used as supporting electrolytes. A polarographic wave was just visible in a solution of tetrapropylammonium fluoroborate but was too close to the cathodic limit to be of diagnostic value.

The acetylcyclopropanes also failed to give reduction waves in dry

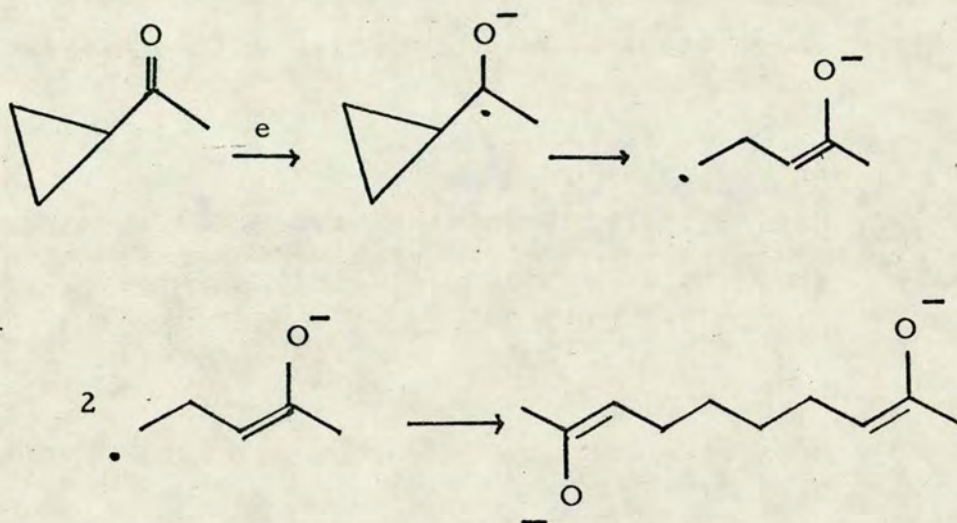
acetonitrile and dimethylformamide when a stationary mercury drop electrode was used, although polarography in acetonitrile suggested that reduction of acetylcyclopropane occurs just prior to the cathodic limit [ca. $E_{\frac{1}{2}} - 3.0\text{V vs. Ag/AgNO}_3 (10^{-1}\text{M})$ in CH_3CN], when tetraethylammonium fluoroborate was used as supporting electrolyte. It therefore appears that acetylcyclopropanes are even more difficult to reduce than the similar aliphatic enones, which show a single one electron wave in the region (0.0 to -2.7V vs. sce) accessible for measurements in these solvents. By comparison with phenyl-substituted enones, for which a second reduction wave is visible, one can postulate that the formation of the dianion of an aliphatic enone would require a reduction potential more negative than -3.0V vs. sce .^{118a} Since potentials of only -2.2 to -2.3V vs. sce have been reported for solutions of sodium in liquid ammonia at -33°C ,^{118b} it would appear that free di-anion intermediates are seldom, if ever, involved in reductions of aliphatic enones or acetylcyclopropanes under these conditions. However it is possible that the formation of tight ion-pairs (or covalent bonds) between the metal cation and oxygen could cause sufficient neutralisation of the negative charge to allow addition of a second electron. (Scheme 24).



Scheme (24)

To support this, there is polarographic evidence¹¹⁹ that for the reduction of aromatic ketones in aprotic media the second electron transfer occurs at less negative potential in the presence of metal cations. Disproportionation also provides a possible pathway for di-anion formation^{105e} and would be facilitated by stabilisation of the di-anion by lithium ions. Thus, at present, there appears to be no firm evidence to allow one to rule in favour of a radical anion or di-anion intermediate in the reductive ring cleavage of acetylcyclopropanes by metal/ammonia solutions. The suggestion that conditions which favour tight ion-pair formation (for example the presence

of small cations such as lithium) should favour the formation of di-anionic species such as (8) is however supported by experiments involving the titration of lithium-ammonia solutions with acetylcyclopropane.¹¹⁵ In addition to the normal ring-cleaved compounds a new product, decan-2, 9-dione, was produced and its formation was presumed to involve dimerisation after ring cleavage of a radical species. (Scheme 25).



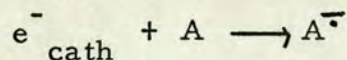
Scheme (25)

These observations were accounted for by the suggestion that in the presence of an excess of reducing metal (at the beginning of a titration) $2e^-$ addition to the carbonyl group occurred leading to 'normal' cleavage products. In the presence of a much lower concentration of metal (near the end-point of a titration) the addition of the second electron would be slower, thus giving the radical anion a chance to rearrange and form dimeric products.

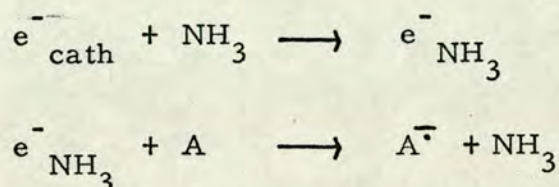
(b) The Electro-reduction of Acetylcyclopropanes

As already indicated, acetylcyclopropanes proved to be electro-inactive in liquid ammonia. However it was observed that beyond the cathodic limit solvated electrons formed at the electrode. These were visible as a blue stream which diffused from the cathode surface into the bulk of the solution. It was therefore decided to carry out reduction beyond the point of electron dissolution, and compare the results with similar chemical reductions.

Under these conditions, electron transfer from electrode to substrate could be either direct or indirect. The direct process involves electron transfer without any intermediate electron carriers,



whereas in the indirect situation electrons are transferred from the electrode to a species, in this case ammonia, which then chemically reduces the substrate.



The distinction between these types of reaction may not be clear cut, since in some cases of so-called 'direct' electron transfer, a layer of solvent molecules may be found between the electrode and the substrate. However under the experimental conditions employed, (Tables VI, VII and VIII), it is likely that reduction by solvated electrons predominates.

In addition to the production of solvated electrons, quaternary ammonium amalgam formation occurred at the mercury cathode. In most cases, this took place simultaneously with electron dissolution, and was apparent as a grey, crusty solid which formed on the mercury surface. Similar observations have been made by Littlehailes and Woodhall.¹²⁰ No attempt was made to isolate the amalgams, owing to their reported instability. Their decomposition occurred on addition of ammonium chloride to the electrolyte solution during work-up. Amalgam formation did not appear to alter the course of reduction, since similar products were formed at a platinum electrode. However it is probable that in most cases electron dissolution occurred at an amalgam rather than a mercury cathode.

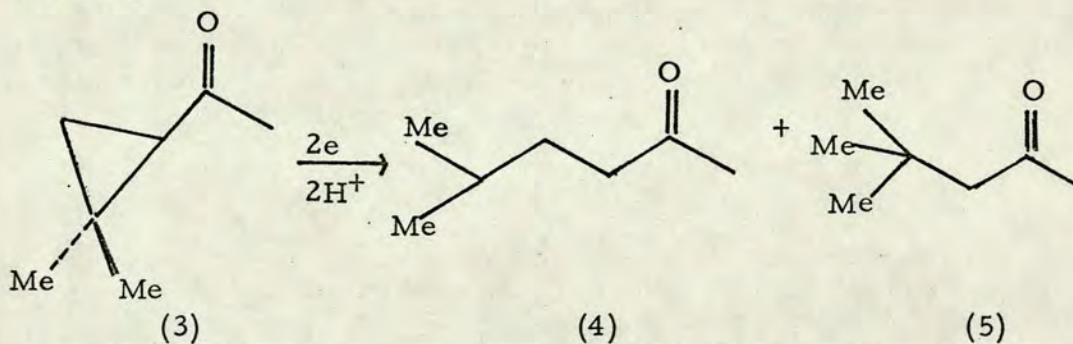
(i) Butyltrimethylammonium Fluoroborate as Supporting Electrolyte.

Reduction of 1-acetyl-2, 2-dimethylcyclopropane was carried out beyond the cathodic limit in a solution of butyltrimethylammonium fluoroborate in liquid ammonia. A summary of the products obtained under varying reduction conditions is given in Table VI. 1-Acetyl-2, 2-dimethylcyclo-

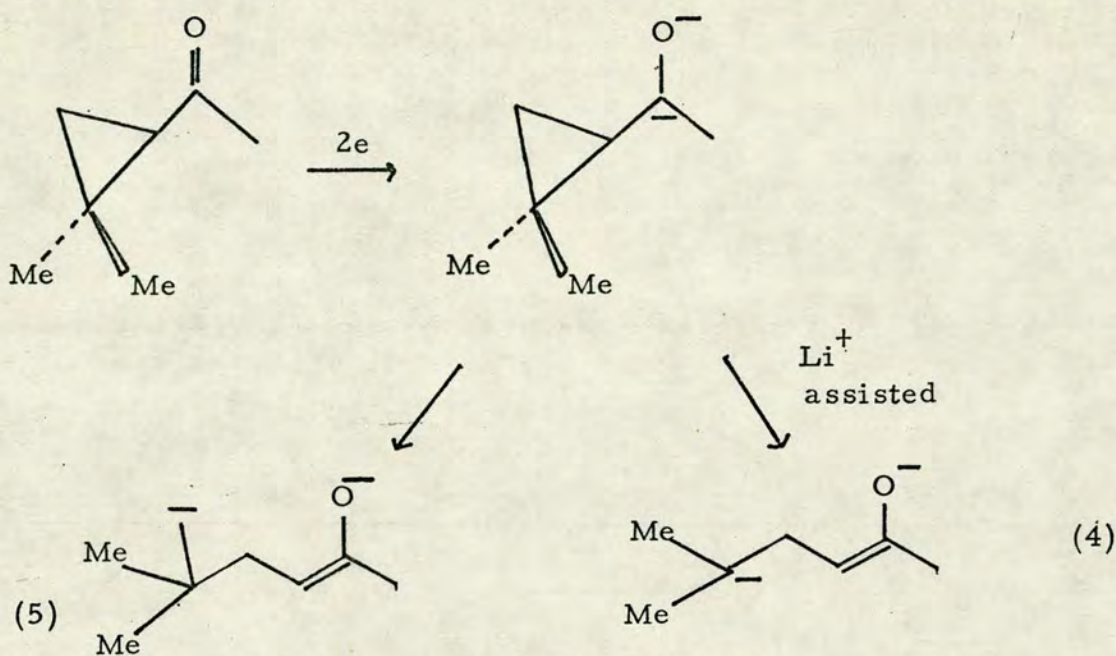
propane was chosen for study as it is relatively easy to prepare compared to the cis- and trans-2-methyl derivatives. The supporting electrolyte was selected by virtue of its high solubility in liquid ammonia, solubility in water and insolubility in ether.

Solvated electrons were visibly formed at the electrode (usually a mercury pool) but, even in the absence of substrate, they immediately decomposed and at no time was a blue solution formed. This was attributed to reaction of the solvated electrons with supporting electrolyte and will be discussed further later. However, in the presence of substrate, passage of current slightly in excess of the number of coulombs required for a 2e reduction resulted typically in 80-90% ring-cleaved products at a mercury cathode (Table VI), indicating that electron transfer to the acetylcyclopropane occurs faster than to the supporting electrolyte. Alternatively, since quaternary ammonium amalgam formation also occurred to a considerable extent with this supporting electrolyte, it is possible that reduction of ketone by the amalgam also took place.

As previously indicated, the lithium/ammonia reduction of 1-acetyl-2,2-dimethylcyclopropane gave predominantly 5-methylhexan-2-one (4), the direction of ring-opening being governed by the steric interaction between the cis-methyl group and the acetyl group. [Scheme (22) $R^1 = R^2 = \text{Me}$].



The ratio of (4)/(5) was reported¹¹⁵ to increase from 2.05 to 4.5 as the lithium concentration was increased. This effect was attributed to the cleavage towards the more substituted position of ketone (3) (tertiary carbanion formation) being catalysed by lithium ions. (Scheme 26).

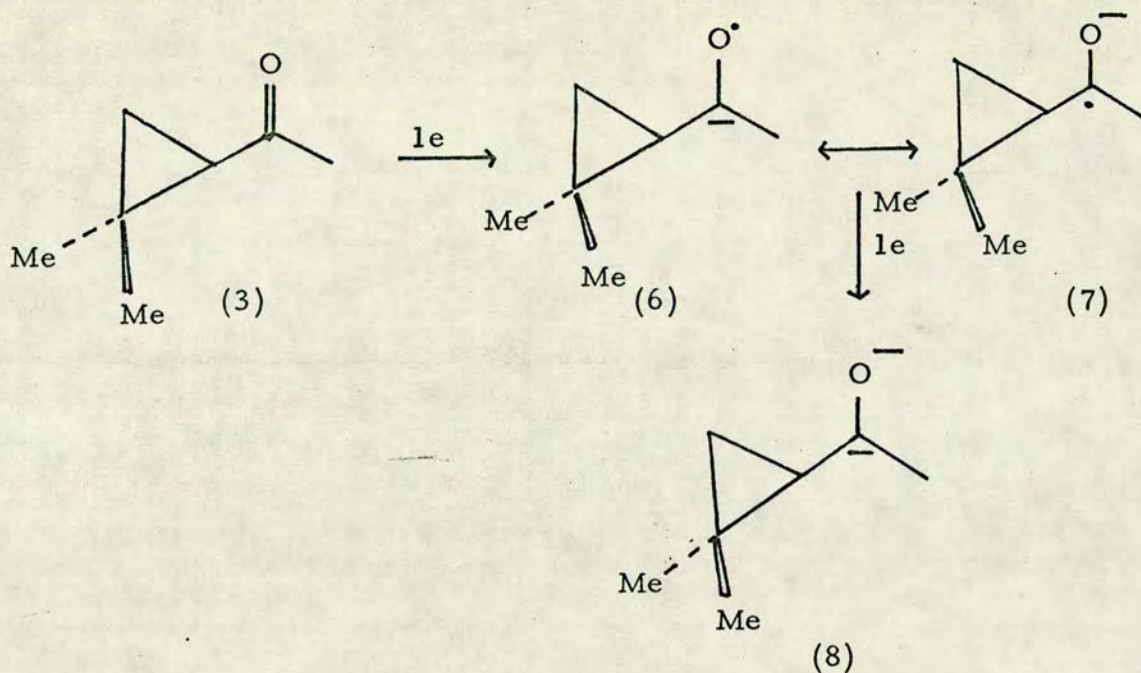


Scheme (26)

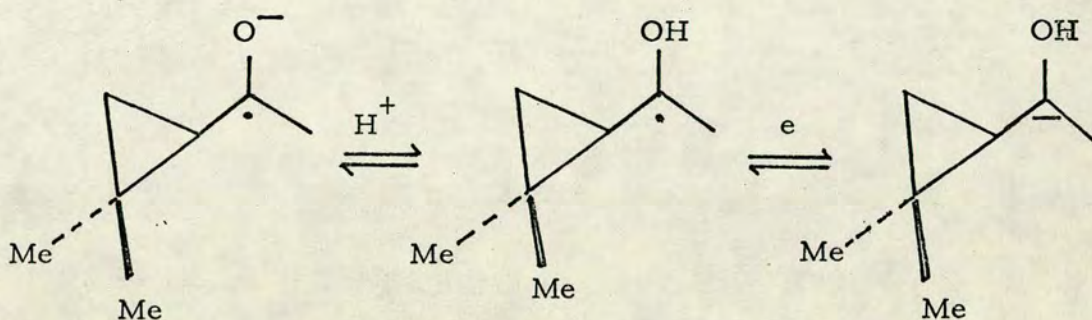
This was supported by the fact that addition of lithium iodide to the reaction mixture resulted in an increased ratio, whereas removal of lithium ions from the solution by addition of tetraethylammonium chloride (lithium chloride was precipitated) resulted in a decreased ratio of (4)/(5) of 1.47 - 2.00.

The electrochemical reduction using a mercury pool cathode (Table VI) gave a product ratio (4)/(5) of 1.9-2.1. The ratio was measured after first oxidising product alcohols to ketones using chromic acid. The value was independent of current density and electrode potential. This ratio is somewhat larger than that expected in the total absence of lithium ions but is sufficiently close to the value obtained by chemical reduction to suggest a parallel mechanism, that is a carbanion intermediate in the ring cleavage step. (Scheme 23 is repeated overpage for convenience).

Additional evidence against the participation of a radical anion intermediate such as (7) is the absence of any dimerisation products in the electrochemical reduction. The carbanion intermediate (6) is also unlikely since radical anions of carbonyl groups are known to preferentially accommodate the negative charge on the oxygen atom.¹²¹ On the other hand since the standard potential of the electron electrode at -36°C in a saturated



solution of tetrabutylammonium iodide in liquid ammonia has been estimated at about $-1.9\text{V vs. NHE}^{112}$ (-2.14V vs. SCE), and since, by comparison with results for the reduction of aliphatic enones, one would expect a potential of at least -3.0V vs. SCE to be required for the formation of di-anion (8), it seems unlikely that a second electron transfer occurs to an appreciable extent. Also, under electrochemical conditions, stabilisation of the di-anion by ion-pairing would not be likely and disproportionation would not be favoured. However even a trace of di-anion, in equilibrium with radical anion may be sufficient to provide a reaction pathway via this type of intermediate, provided the follow-up chemical reaction i. e. ring cleavage is sufficiently fast. An alternative intermediate may be the anion formed from an ece type mechanism, resulting from protonation of the radical anion (7) and further electron transfer:



However, since protonation of (7) by solvent or supporting electrolyte is probably unlikely, a di-anionic intermediate will be hereafter considered as participating in the ring-cleavage step.

The Influence of Electrode Material

By comparison with reduction at mercury, ~~a similar product ratio was obtained at a carbon rod electrode but~~ a reduced product ratio, (4)/(5), was observed at platinum/^{carbon,} and lead cathodes (Table VI). The decrease at carbon and platinum was slight, the ratio (4)/(5) being about 1.8, but at lead the ratio fell to about 1.2. The influence of electrode material on the course of an electrochemical reaction has frequently been observed but seldom rationalised. The result at the lead electrode is perhaps surprising in that lead and mercury are generally observed to exhibit similar behaviour as electrodes.

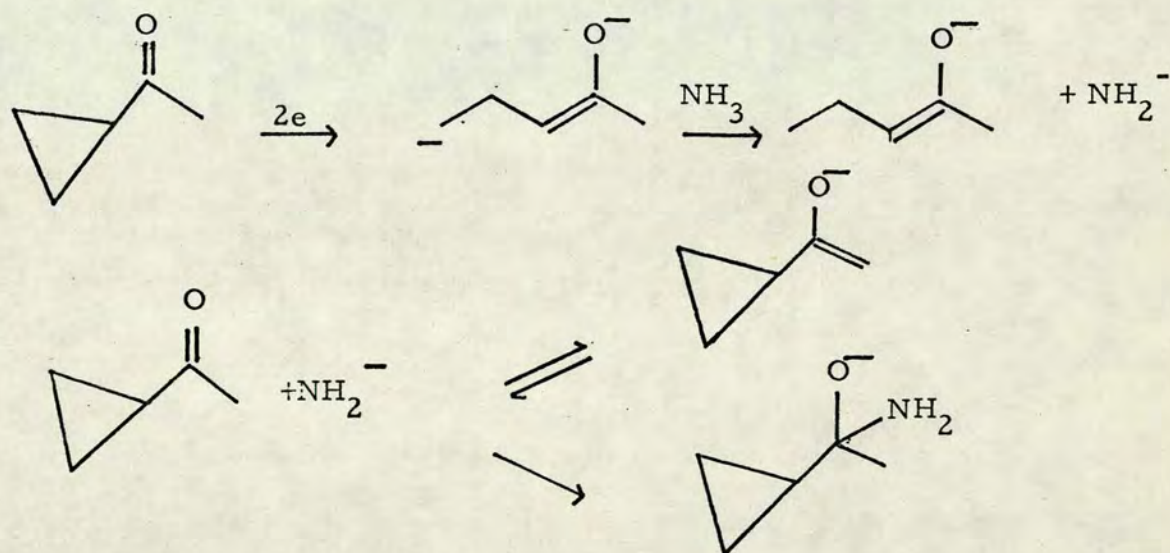
The efficiency of reduction also varied with electrode material. A more negative potential was required to give the same current at carbon, platinum and lead electrodes compared to the mercury pool cathode, an observation which could not be explained in terms of electrode area and geometry. The carbon rod and lead wire electrodes were also inferior due to corrosion and contamination respectively. Reduction appeared to be less efficient at platinum; under similar conditions 60% cleaved product was obtained at platinum compared to 84% at mercury (Table VI). A similar observation was made in the case of unsubstituted acetylcyclopropane (Table VIII).^{*} Taking all these factors into consideration, mercury proved to be the best electrode material for these reductions.

Recovered Starting Ketone

The electrochemical reduction of acetylcyclopropanes appeared to be more efficient than the dissolved metal reduction with regard to conversion of starting ketone to the cleaved product. Passage of a slight excess of coulombs at a mercury cathode resulted in about 80% ring cleavage of 1-acetyl-2, 2-dimethylacetylcyclopropane in the presence of butyltrimethyl-

* This may possibly be due to some additional amalgam reduction of the ketone occurring at a mercury cathode.

ammonium cation (Table VI), and the efficiency was even higher in the presence of tetraethylammonium fluoroborate (see later). However from the observations of Bellamy and co-workers,¹¹⁵ when acetylcyclopropane was left in the presence of an excess of lithium for 2 hours the amount of lithium remaining after this time, (determined by back titration) indicated that only 1 atom equivalent of lithium had been consumed in the reduction, and the products contained equal amounts of starting ketone and cleaved product. This led to the conclusion that for each molecule of starting ketone which is converted into the saturated ketone, another molecule of starting ketone must be converted into a form which cannot be reduced. The following explanation was put forward to account for this observation. Protonation of the carbanion-enolate ion by ammonia would lead to amide ion, which could either convert the starting ketone into its enolate ion (a process shown to be in equilibrium by deuterium labelling) or add to the carbonyl group of the starting ketone. (Scheme 27).



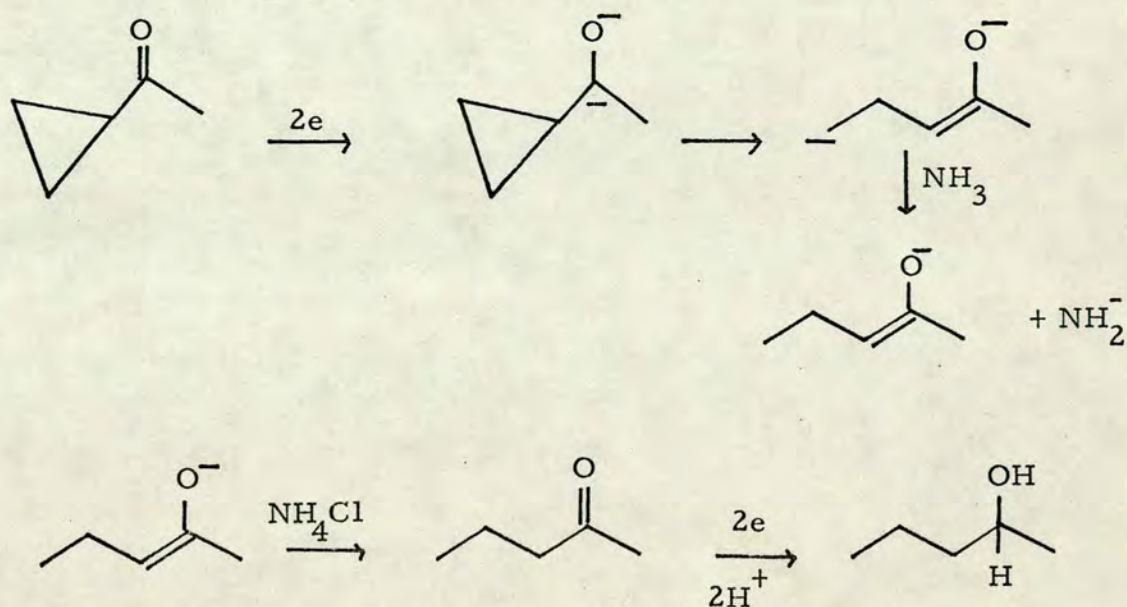
Scheme (27)

A similar removal of acidic hydrogen atoms by amide ion has been observed in the reduction of aliphatic enones and is probably the primary reason why it is necessary to add alcohols to the reaction mixture in order to obtain high yields of reduced products.⁷⁹ If protonation of the

carbanion-enolate ion by ammonia occurred in the electrochemical studies, one would expect a similar high percentage of recovered starting material due to reaction with amide ion. If however the supporting electrolyte acted as a proton donor, the reduction would go to completion, as is observed in the presence of tetraethylammonium cations. The small amount of recovered starting ketone (10-15%) obtained in the presence of the butyltrimethylammonium cation after the transfer of $2F \text{ mol}^{-1}$ could be due to some protonation by ammonia, since proton abstraction from the butyltrimethyl group is likely to be more sterically hindered compared to the tetraethylammonium group. Alternatively, it is possible that insufficient current was passed for complete cleavage, due to reaction of some of the electrons with supporting electrolyte.

Product Alcohol Formation

The lithium/ammonia reduction of acetylcyclopropanes resulted in the formation of ring-cleaved alcohols as well as the corresponding ketones.¹¹⁵ As already indicated, protonation of the carbanion-enolate ion ($\text{pK}_a > 50$) by ammonia ($\text{pK}_a \text{ } 34$) rapidly occurred, resulting in an enolate ion, which was considered insufficiently basic to abstract a proton and remained in solution until work-up. Alcohol formation was believed to result from protonation of the enolate ion during work-up occurring in the presence of excess solvated electrons, which immediately further reduced the ring-cleaved ketones to alcohols. (Scheme 28).



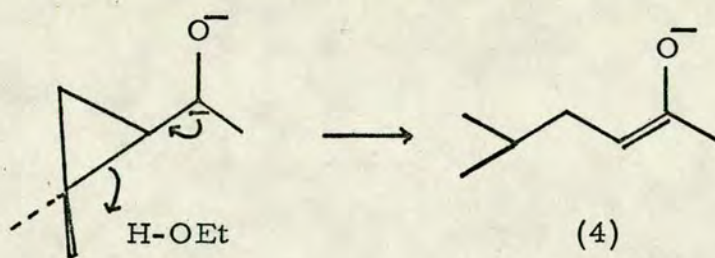
This was supported by the fact that the alcohol yield appeared to depend on the rate of addition of ammonium chloride to the reaction mixture i. e. the rate of quenching of anions and electrons. Gradual addition resulted in a high (60%) yield of alcohol, whereas rapid addition reduced the alcohol yield considerably (5%). In the electrochemical experiment, however, there is no possibility of reduction to alcohol occurring after the addition of ammonium chloride, since an excess of electrons is never formed, due to their reaction with supporting electrolyte. However 4e reduction of acetylcyclopropane (Table VIII) yielded up to 20% product alcohol. This suggests that some protonation of the enolate ion may occur during the electrochemical reduction. An alternative explanation for product alcohol formation may involve reduction of the cleaved ketone by quaternary ammonium amalgam taking place after quenching with ammonium chloride.

The Effect of Ethanol Addition

The lithium/ammonia reduction of 1-acetyl-2, 2-dimethylcyclopropane in the presence of ethanol¹¹⁵ resulted in a decreased ratio of (4)/(5) (from 2.998 to 1.8) and a decrease in the yield of recovered ketone (from 13.3 to 3.4%). The latter observation was in accordance with the postulated mechanism involving the reversible removal of starting material as enolate ion by amide ion. In the presence of ethanol this would not occur. The effect on the ratio of (4)/(5) was equivalent to a decrease in the lithium concentration and was thought possibly to be due to solvation of lithium ions by ethanol, which would reduce the amount of lithium ion catalysed ring cleavage of the C₁-C₂ bond as previously described.

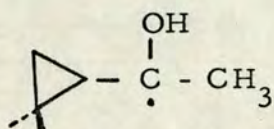
Addition of ethanol to the catholyte during the electrochemical reduction on the other hand increased the ratio of (4)/(5) from 2.1 to 4.5 (Table VI). Ethanol (pK_a 18) is considerably more acidic than either ammonia or supporting electrolyte. It is possible that the cleavage step may be assisted by the proton donating ability of ethanol. This would be more effective if cleavage were via the less stable tertiary carbanion i. e. a situation similar to that postulated to explain the effect of increased

lithium ion concentration on the product ratio (4)/(5) (Scheme 29).



Scheme (29)

A further explanation might involve ring cleavage via a radical intermediate,



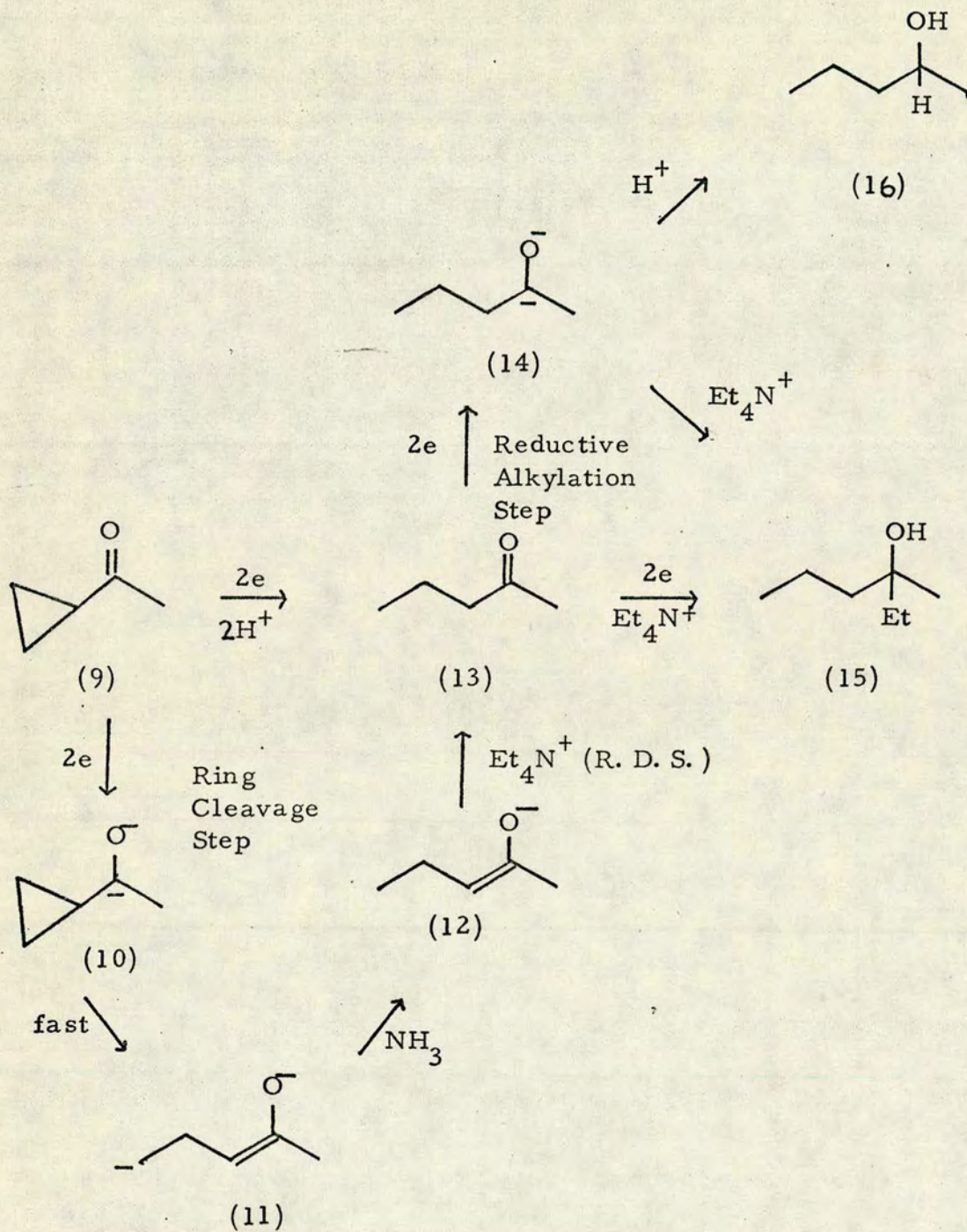
formed by protonation by ethanol of the initially formed radical anion.

This would require that ring cleavage occurred faster than addition of a second electron. Also since the product ratio [(4)/(5) = 4.5] is considerably lower than that observed for the authentic radical ring-opening of the corresponding alcohol [(4)/(5) = 21],¹¹⁵ this is perhaps a less likely explanation.

(ii) Tetraethylammonium Fluoroborate as Supporting Electrolyte.

The reduction of 1-acetyl-2,2-dimethylacetylcyclopropane was carried out in liquid ammonia containing tetraethylammonium fluoroborate as supporting electrolyte. The objective was to determine whether a change in the nature of the supporting electrolyte cation affected the cleaved product ratio (4)/(5) [Scheme (22); $R^1 = R^2 = \text{Me}$]. Analysis of the reaction mixture after the passage of a slight excess of electrons (for a 2e reduction) and oxidation by chromic acid, indicated, however, that two new products had been formed in addition to the products (4) and (5) already discussed.

Identification of the new products as 3,6-dimethylheptan-3-ol and 3,5,5-trimethylhexan-3-ol was complicated by the fact that these tertiary alcohols failed to show a parent ion (m/e 144) in the mass spectrum. The highest mass peak P-Me (129) resulted from fragmentation β to the O-atom, a mode of cleavage commonly observed in the mass spectrum of alcohols. Fragmentation with loss of the largest group is favoured, resulting in a base peak P - C_5H_{11} (73).



Scheme (30)

The yield of the new products was increased by a larger electrolysis time and complete conversion was achieved after a 4e reduction. As was observed in the presence of the butyltrimethylammonium cation, the major product, 3,6-dimethylheptan-3-ol, resulted from cleavage towards the more highly substituted C atom.

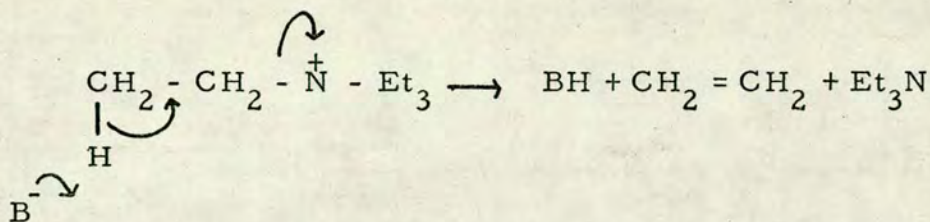
The 4e reduction of unsubstituted acetylcyclopropane (9) resulted in the analogous formation of 3-methylhexan-3-ol (15) and, as this reaction gave a more readily resolved product mixture, it was selected for more detailed study. The non-alkylated alcohol pentan-2-ol (16) was also formed. The formation of (15) can be considered as taking place in two stages, the first involving 2e reductive cleavage of the cyclopropyl ring to pentan-2-one (13) and the second involving 2e reductive alkylation of (13), affording 3-methylhexan-3-ol (15). The intermediate steps involved in these transformations are summarised in Scheme (30).

The Ring Cleavage Step

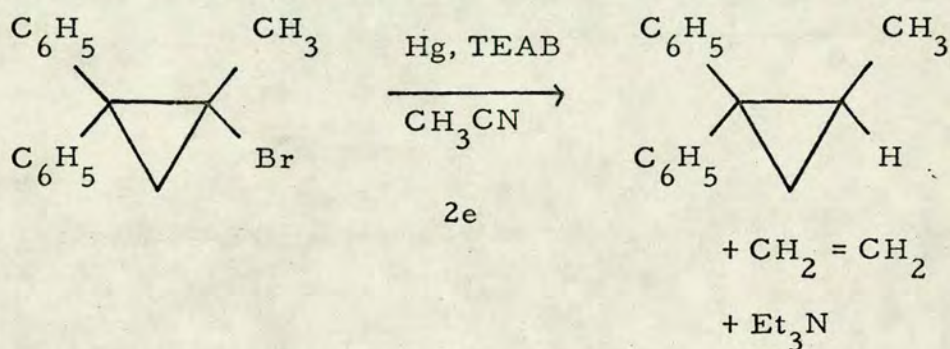
The ring cleavage step of the reduction is analogous to that described previously for the reduction of 1-acetyl-2,2-dimethylcyclopropane in the presence of butyltrimethylammonium fluoroborate. For simplicity in Scheme (30) a di-anionic intermediate (10) is written as involved in the ring cleavage step. However, as one might expect the tetraethylammonium cation to behave as a better proton donor than the butyltrimethylammonium cation (less steric hindrance), it is possible that under these conditions a greater proportion of the reductive cleavage involves an anionic rather than a di-anionic intermediate. No alkylation of the acetylcyclopropane di-anion (10) occurs, supporting the consideration that ring cleavage to the carbanion-enolate anion (11) is rapid. As described previously, protonation of the carbanion-enolate anion to enolate-anion (12) by ammonia would be expected. Also, in order that further reduction may take place, protonation of the enolate-anion to pentan-2-one (13) by supporting electrolyte must occur.

The role of the tetraethylammonium cation as a proton donor during electrochemical reductions has frequently been observed. The mechanism

is thought to involve a Hofmann type elimination yielding ethylene and triethylamine.



In some cases the products of elimination have been recovered as, for example,¹²² in the reductive dehalogenation of 1-halo-1-methylcyclopropanes in acetonitrile containing tetraethylammonium bromide (Scheme 31).



Scheme (31)

During the 4e reduction of acetylcyclopropane the catholyte was observed to turn blue, due to an excess of solvated electrons, after the transfer of only two electron equivalents. This can be explained in terms of the rate determining step being protonation of the enolate-anion (12) to pentan-2-one (13) (Scheme 30). Until this has occurred transfer of electrons to (13) cannot take place. The observation is not due to slow electron transfer to (13) since, when pentan-2-one is used as substrate, a blue solution is not obtained until two electron equivalents have been passed.

The Reductive Alkylation Step

The reductive alkylation step could be studied using either acetylcyclopropane (in a 4e reduction) or pentan-2-one (in a 2e reduction). By analogy with the reductive cleavage step and from the absence of any dimerisation products which may be expected to result from a radical intermediate, it seems likely that alkylation involves nucleophilic attack

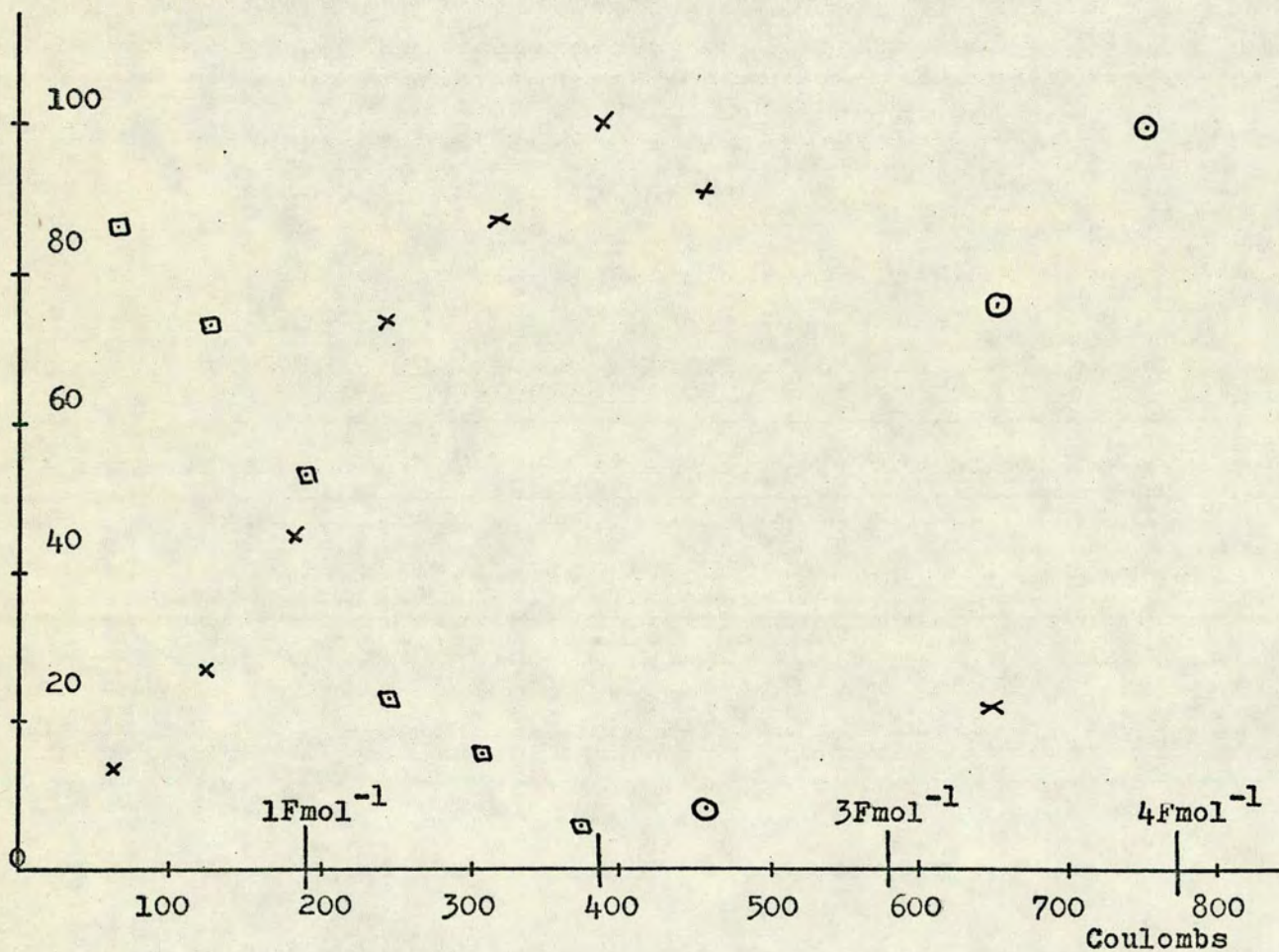
GRAPH I

Electrolytic Reduction of MeCO Δ by Solvated Electrons in the

Presence of Et₄NBF₄

MeCO Δ (0.002 mol) in 0.1M Et₄NBF₄ (100 ml); galvanostatic redn. (100 mA) ca. 60mAcm⁻²Hg.

Relative %



□ MeCO Δ

x MeCOPr

○ {
 $\begin{matrix} \text{OH} \\ | \\ \text{Me}-\text{C}-\text{Pr} \\ | \\ \text{Et} \end{matrix}$
 $\begin{matrix} \text{OH} \\ | \\ \text{Me}-\text{C}-\text{Pr} \\ | \\ \text{H} \end{matrix}$

of an anion, on the supporting electrolyte, rather than a mechanism involving a radical intermediate. As already discussed, the nucleophile may be a di-anion or an anion, the latter being formed if protonation occurs between electron transfers. As discussed previously for the reduction of acetylcyclopropane, formation of a free di-anion would be energetically unfavourable but may provide a reduction pathway providing the alkylation step is fast. For simplicity a di-anion (14) is written as the intermediate in Scheme 30.

Information Obtained by Sampling the Reaction Mixture during the Course of Reduction.

In order to gain more information on the ratios of reactants, intermediates and products at any one time during the reduction, an experiment was carried out which involved monitoring the reaction mixture obtained from the galvanostatic reduction of acetylcyclopropane. Each sample was analysed by g.l.c. and graphs of the concentration of acetylcyclopropane (9), pentan-2-one (13), pentan-2-ol (16) and 3-methylhexan-3-ol (15) against the number of electrons transferred were plotted. The concentrations of pentan-2-one and pentan-2-ol, as estimated by g.l.c., will include any enolate anion (12) and di-anion (14) respectively, present in the reaction mixture at that time.

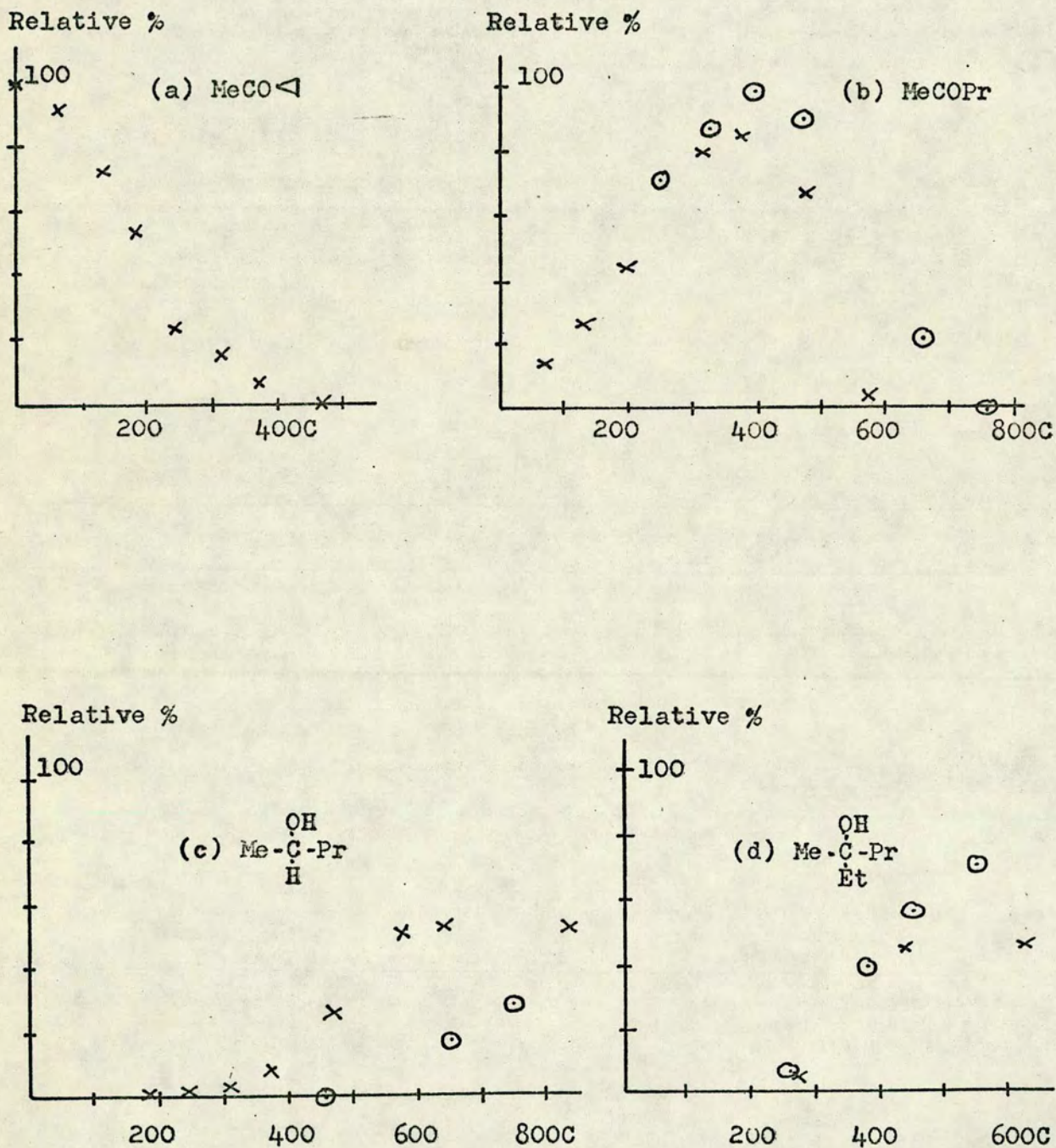
The results, (Graph I) show that complete cleavage of acetylcyclopropane has taken place after the transfer of two electron equivalents. During this period virtually no 3-methylhexan-3-ol (or pentan-2-ol) are formed; this may be due to a slow protonation of the enolate anion (12), or to the transfer of electrons to pentan-2-one occurring less readily than to acetylcyclopropane. After the transfer of the first two electron equivalents, further reduction results in a decrease in the pentan-2-one concentration and increasing alcohol formation, complete reduction having occurred after the transfer of four electron equivalents.

In Graph I the alcohol concentration is taken as the sum of alkylated and non-alkylated products (15) and (16) respectively. A plot of the concentration of pentan-2-ol alone against the number of coulombs (Graph IIc) shows no maximum. This suggests that pentan-2-ol is formed in

GRAPH II

Electrolytic Reduction of MeCO Δ by Solvated Electrons in the Presence of Et₄NBF₄.

Conditions as in Graph I.



x sampling commenced at beginning of electrolysis
 o sampling commenced after ca. 2Fmol⁻¹ transferred

the reaction and does not result from protonation of the pentan-2-one di-anion during work-up. A maximum in the curve would suggest a build-up of pentan-2-one di-anion due to slow alkylation.

The Effect of Proton Donors on the Reaction

The ratio of pentan-2-ol to 3-methylhexan-3-ol was found to be considerably higher in the sampled experiment compared to the normal reduction, and this was considered to be a direct result of the sampling technique. During the sampling procedure the catholyte level fell, causing a leakage of the anodic solution into the catholyte. Since the anodic reaction involves oxidation of ammonia resulting in ammonium ion formation, it is likely that protonation of di-anion (14) to pentan-2-ol (16) would be in direct competition with alkylation (Scheme 30). This is supported by the fact that, when sampling was not commenced until between one and two electron equivalents had been passed, the ratio of pentan-2-ol to 3-methylhexan-3-ol was much lower (1:1 vs. 1:2.3). (Graphs IIc and IIId).

Reduction of pentan-2-one in the presence of ethanol (10^{-1} M) afforded no alkylated product (15). Only pentan-2-ol (16) was isolated (Table VII), suggesting that protonation by ethanol occurs faster than alkylation.

It was also observed that the highest yields of 3-methylhexan-3-ol were obtained for large scale reductions of acetylcyclopropane. Small scale reductions of pentan-2-one resulted in a considerably higher yield of pentan-2-ol. For example a two electron reduction of pentan-2-one afforded only 34% alkylated product, whereas a four electron reduction of acetylcyclopropane under similar conditions yielded 62% of 3-methylhexan-3-ol. (Tables VII and VIII). This observation was attributed to the intermediates formed during the ring cleavage of acetylcyclopropane acting as proton scavengers, thereby removing any protic impurities in the catholyte which would protonate the pentan-2-one di-anion (14) to give pentan-2-ol. This effect would be more marked during a large scale reduction, resulting in a higher yield of alkylated product (a 90%^{yield} of (15) was obtained from the reduction of 0.005 mole of acetylcyclopropane). During the reduction of pentan-2-one, alkylation would not commence until all the

protic impurities had been scavenged by the di-anion (14) to produce pentan-2-ol.

The Influence of Electrode Material.

Reductions were normally carried out at a mercury pool cathode. Under these conditions the reaction was much cleaner than in the presence of butyltrimethylammonium fluoroborate and amalgam formation did not occur to a visible extent although the surface of the mercury became tarnished.

The same products were observed at a platinum electrode, although the current efficiency was lower. Under otherwise similar conditions galvanostatic reduction of pentan-2-one at mercury resulted in 63% 3-methylhexan-3-ol (plus 10% pentan-2-ol), whereas at platinum only 45% alkylated alcohol was formed (plus 5% pentan-2-ol) (Table VII). Similarly, reduction of acetylcyclopropane at mercury afforded 62% alkylated and 29% non-alkylated alcohols, compared to 43% and 12% respectively at platinum (Table VIII). Current efficiencies at mercury were high. For example a 4e reduction of acetylcyclopropane (0.001 mole) gave an 80% yield of a product mixture consisting of pentan-2-one (9%), pentan-2-ol (29%) and 3-methylhexan-3-ol (62%), representing an overall current efficiency of 76%.

The Influence of Supporting Electrolyte Concentration.

A 0.1M solution of supporting electrolyte was normally employed. For comparison a reduction of pentan-2-one in a 0.02M solution of tetraethylammonium fluoroborate was performed. In the more dilute solution the proportion of recovered starting ketone was increased (18% vs. 0%) (Table VII). This is perhaps due to a higher cell resistance in the 0.02M case, resulting in a more negative potential for the galvanostatic conditions employed. This in turn may lead to more amalgamation at the electrode and a lower current efficiency for ketone reduction. However the relative proportion of 3-methylhexan-3-ol produced was only slightly lower in the 0.02M solution, suggesting that perhaps the alkylation step is unaffected by the concentration of electrolyte in the bulk of the solution.

In a further experiment, acetylcyclopropane was reduced in a solution containing a mixture of tetraethylammonium fluoroborate (0.05M) and butyltrimethylammonium fluoroborate (0.05M). Although 4e equivalents were passed, a considerable proportion of pentan-2-one (37% vs. 9% in the presence of Et_4N^+ alone) was recovered in the product mixture (Table VIII). This possibly results from destruction of some of the solvated electrons by the butyltrimethylammonium cation during the reduction (see later). The presence of butyltrimethylammonium fluoroborate, however, did not prevent formation of the alkylated alcohol, 3-methylhexan-3-ol. In fact in this experiment the relative proportion of pentan-2-ol was particularly low.

Attempted Alkylation using Chemically Generated Solvated Electrons.

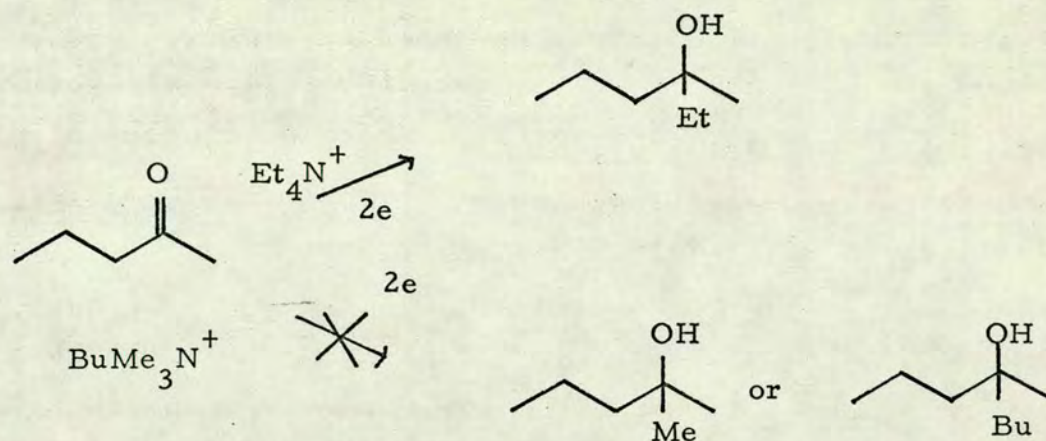
An attempt to carry out an analogous alkylation of acetylcyclopropane and pentan-2-one by alkali metal/ammonia solutions in the presence of tetraethylammonium fluoroborate resulted in the formation of pentan-2-one and pentan-2-ol. In order to detect any possible ion-pairing effects between the pentan-2-one di-anion and lithium ions which might reduce its nucleophilic character, the reduction was also carried out using sodium and potassium metals, and in a further experiment lithium ions were precipitated from the solution as lithium chloride by addition of tetraethylammonium chloride. No 3-methylhexan-3-ol was produced in any of these experiments.

Since, as has already been indicated, the nature of solutions of solvated electrons produced by metals dissolved in ammonia is believed to be identical to those produced electrochemically, it appears that the alkylation reaction is dependent on the electrode surface or on the conditions in the solution in the vicinity of the electrode.

Attempted Alkylation using other Supporting Electrolytes

The previous discussion involves the reductive alkylation of acetylcyclopropane and pentan-2-one in the presence of tetraethylammonium fluoroborate. No equivalent alkylated products were observed from the

reduction of pentan-2-one in the presence of the butyltrimethylammonium cation on the passage of 2e equivalents. (Scheme 32).



Scheme (32)

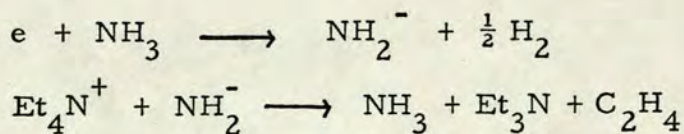
The absence of methyl- and butyl-alkylated products was verified by the synthesis of authentic samples and examination of their g. l. c. behaviour.

In a search to find other supporting electrolytes which would function as alkylating agents, a series of reductions of pentan-2-one were carried out in the presence of diethyldimethyl- and triethylmethyl-ammonium iodides, and tributylethyl-, tributylmethyl-, ethyltripropyl-, tetramethyl- and tetrapropyl-ammonium fluoroborates. These reductions were performed using solvated electrons produced at a mercury pool cathode, except in the case of tetramethylammonium fluoroborate when a platinum electrode was used owing to extensive amalgam formation at mercury with this salt. During the reduction of solutions containing iodides a black solid was observed to deposit on the platinum anode and at the end of the electrolysis removal of the anode from its compartment resulted in detonation of the solid with production of iodine. The solid was believed to be nitrogen triiodide mono-ammoniate NI_3NH_3 , as discussed previously.

Analysis of product mixtures from the above reductions showed

that only tributylethylammonium fluoroborate afforded an ethyl alkylated product in high yield but there was no evidence for butyl alkylation, which may be attributed to steric inhibition to nucleophilic attack on the butyl side chain. Reduction in the presence of diethyldimethylammonium iodide gave only trace amounts of ethyl- and methyl-alkylated products. It therefore appears that tetraethyl- and tributylethylammonium fluoroborates behave differently from the other supporting electrolytes tried. Another feature that distinguishes these cations, and may be associated with their ability to alkylate the pentan-2-one di-anion, is their high stability in the presence of solvated electrons. This stability was demonstrated by the immediate formation of blue solutions at potentials beyond the point of electron dissolution, suggesting that the life-time of the solvated electrons in the presence of the tetraethyl- and tributylethylammonium salts is greater than the time required for their diffusion from the electrode through the solution. In the presence of the other supporting electrolytes a blue solution was not produced.

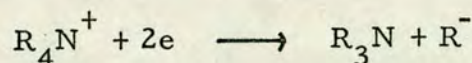
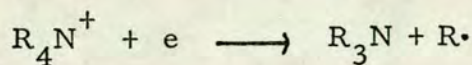
The exceptionally high stability of the tetraethylammonium cation has been observed by other workers. It has been suggested¹²³ that solvated electrons do not react with the tetraethylammonium cation but with ammonia to form amide ions which decompose the cation.



The diphenylamide ion $\text{N}(\text{Ph})_2^-$ was a weak enough base to form stable salts with tetraethylammonium ions.

Hazlehurst et al¹²⁴ studied the reaction of symmetric and asymmetric tetraalkylammonium halides with potassium in liquid ammonia at -78°C . The precipitation of potassium halide gave a solution of R_4N^+ and solvated electrons and the subsequent cleavage of the ammonium salt was studied. The ease with which C-N bond fission occurred increased in the order $\text{Pr}^n > \text{Me} > \text{Et}$ for the symmetric ions while the asymmetric ions, R_3MeN^+ , reacted very rapidly giving methane. Similarly the cleavage of tetraalkylammonium halides by sodium/ammonia at -33°C have

been investigated,¹²⁵ the products being alkanes, tertiary amines and alkenes. The cleavage could involve either 1e or 2e transfer.



In order to explain the relative rates of cleavage of different R groups, it was postulated that secondary and tertiary groups cleave as radicals, while methyl and higher primary groups cleave as carbanions. The effects of relief of steric strain were also taken into consideration.

Wrobel and Krawczyk¹²⁶ have also observed that the ease of reduction of C-N bonds decreased in the order $E_{N-C_{aryl}} > E_{N-C_{benzyl}} > E_{N-C_{alkyl}}$.

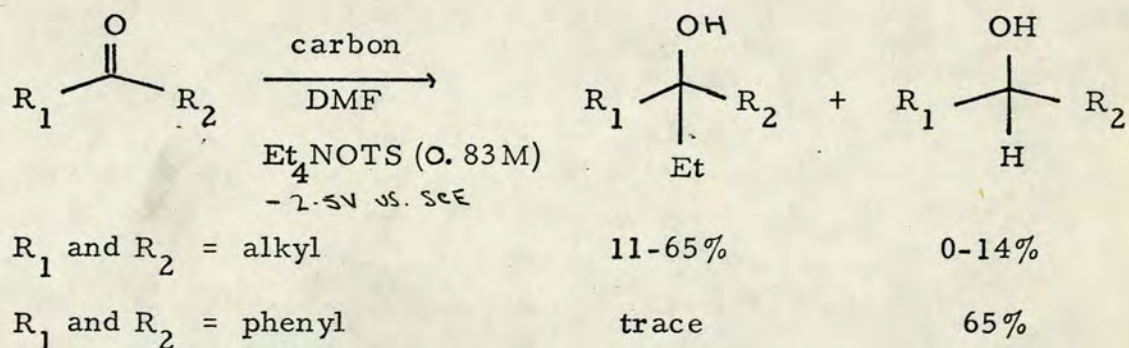
From the results of all these studies, and from our own observations, it appears that the stability of the N-Et bond in the presence of solvated electrons in liquid ammonia, particularly in the case of the tetraethylammonium cation, is almost unique. It appears that the N-Me bond is particularly labile presumably resulting from its availability, and cleavage of higher alkyl groups will be associated with relief of steric strain. The N-Et bond must be relatively free from both these considerations. It is interesting to note also that tetraethylammonium fluoroborate shows a much higher solubility in liquid ammonia (ca. 0.6M) compared to the other symmetric salts (<0.05M).

The Role of the Electrode in Alkylation

In order to explain the failure of the attempted alkylation of pentan-2-one by chemically generated solvated electrons, it is suggested that the electrode must play an important role in the alkylation. As discussed in the previous section, it also appears that the reaction requires a quaternary ammonium salt which is relatively stable in the presence of solvated

electrons. These facts together suggest that incorporation of the tetraethylammonium cation into the electrified interface (or even adsorption of the cation onto the electrode) may be essential before the alkylation step can take place. The formation of 3-methyl-hexan-3-ol may be explained by assuming that the majority of electron transfer to pentan-2-one, and subsequent alkylation, occurs near the electrode, where the concentration of solvated electrons and abundance of tetraethylammonium ions should be highest. The difference in behaviour of the tetraethylammonium ion towards the enolate anion and the pentan-2-one di-anion may be due to their differing stability and the possibility that reaction of the enolate anion takes place away from the electrode. The failure of the other supporting electrolytes to promote a similar alkylation reaction may be attributed to their rapid decomposition or amalgamation in the vicinity of the electrode.

Until recently, the only reported¹²⁸ related reaction involved the cathodic alkylation of anthracene to 9-butylantracene in molten tetrabutylammonium nitrate. This is believed¹²⁹ to result from alkylation of an anthracene anion by the tetrabutylammonium cation. However similar products have since been obtained by Shono and co-workers¹³⁰ from the reduction of aliphatic ketones at a carbon cathode in DMF in the presence of tetraethylammonium tosylate (Scheme 33).



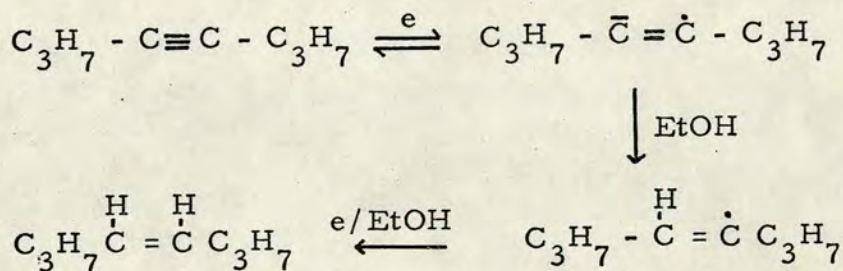
The low yields of alkylated products formed from phenyl-substituted ketones may result from the higher stability of their di-anions compared to the alkyl-substituted compounds. The di-anions may in this case survive long enough to diffuse away from the electrode without first being alkylated. These workers also carried out similar reductions in the

presence of other quaternary ammonium salts but, in accordance with our observations, ethylation predominated. For example reduction of heptan-2-one resulted in 55% ethyl-alkylation, 12% propyl-alkylation and negligible amounts of methyl- and butyl-alkylation. No mechanism for the formation of alkylated products was proposed. However, a recent report¹³¹ on the electrochemical behaviour of graphite cathodes in the presence of tetra-alkylammonium cations (Me_4N^+ , Et_4N^+ and Bu_4N^+) seems relevant. At potentials more negative than -1.8V vs. Ag/AgI (ca. -1.8V vs. SCE) the graphite was found to reversibly accept a large negative charge, whereby it acquires properties akin to those of an amalgam or an alkali metal graphite. The charging of the graphite is possible only in the presence of a counter-ion, a layer of cations being strongly bound to the electrode (or even inside the graphite crystal) and the charged graphite was found to have the ability to transfer its electrons to a more difficultly reducible substrate. It is possible that such a mechanism operated during Shono's experiments. A situation involving electron transfer from negatively charged graphite followed by alkylation by strongly bound counterions is akin to that postulated for the reduction in liquid ammonia, although the possibility of tetraalkylammonium radicals stabilized at the graphite must also be considered.

3. The Electrochemical Reduction of Oct-4-yne by Solvated Electrons.

During the course of the electro-reduction of other substrates e.g. benzophenone, acetophenone, diphenylacetylene etc. (see following Section III) in the presence of tetraethylammonium fluoroborate, alkylation products were not observed. It was thought that this might be due to the higher stability of the aryl-substituted intermediates compared to those obtained from reduction of the dialkyl ketones previously discussed. It was therefore hoped to promote a similar alkylation using oct-4-yne as substrate; this compound should give highly reactive intermediates on reduction.

Disubstituted acetylenes, such as oct-4-yne, are readily reduced¹³² by solutions of alkali metals in liquid ammonia to afford trans-olefins. The reaction is believed to proceed by an ECE type mechanism, ammonia acting as a proton source. It is also possible to reduce acetylenes to trans-olefins electrochemically or with a solution of lithium generated electrochemically.¹³³ In this case it is necessary to use an undivided cell so that the strongly basic lithium methylamide, formed by protonation of the radical anion, is neutralized by the anodic products before this base can catalyse isomerization of the starting acetylene.¹³⁴ It was therefore surprising to find that oct-4-yne (dissolved in THF as co-solvent) was not reduced by electrochemically produced solvated electrons in a solution of tetraethylammonium fluoroborate. Unreacted starting material was also recovered following reduction under more extreme conditions (higher current density) in a 1-compartment cell. In the latter case it was hoped that ammonium ions produced at the anode would act as a proton source. Reduction in the presence of ethanol however afforded a 5:1 mixture of two isomers of octene, as indicated by mass spectrum/g.l.c., although the products were not separated. It therefore appears that only very small concentrations of the radical anion of oct-4-yne are produced by electrochemically generated solvated electrons. Only in the presence of ethanol, when protonation of the radical anion occurs, is the equilibrium displaced sufficiently to allow reduction to proceed. (Scheme 34).



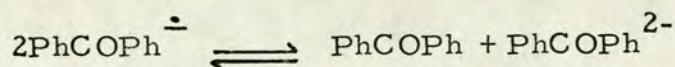
Scheme (34)

A similar situation is observed in the sodium/ammonia reduction of benzene. 1,4-Dihydrobenzene is only produced in the presence of ethanol.¹³⁵

III. Electrode Reductions of Organic Compounds in Liquid Ammonia.

1. Introduction

Polarography in liquid ammonia was pioneered by Laitinen and Nyman^{87, 94, 95, 112, 136} but probably the first organic electrode reaction in liquid ammonia was performed, appropriately, by Birch,¹³⁷ who reduced m-methoxytoluene to 2, 5-dihydro-3-methoxy-toluene. Subsequent reports on electro-reductions in liquid ammonia have been far and few between. Among the more recent studies are those by Wrobel^{126, 138} and his co-workers who carried out the reductive cleavage of several quaternary ammonium salts containing unsaturated groups. The reduction of nitro-compounds has also been conducted¹³⁹ and the e. s. r. spectra of the corresponding radical anions has been examined. Alkyl-¹⁴⁰ and quaternary ammonium¹²⁰ amalgams have been prepared in liquid ammonia, the latter being used to reduce acrylonitrile. The effective hydrodimerisation of acrylonitrile has also been achieved¹⁴¹ by direct electro-reduction in liquid ammonia. However by far the largest contribution to organic electro-chemistry in liquid ammonia has been made by Bard and his co-workers^{88, 142, 143} 171, 172 who, by the use of modern electrochemical methods, demonstrated the unusual ability of this solvent to stabilise reactive intermediates, such as radical anions and di-anions. This stability can be attributed to the low acidity of the solvent, the possibility of preparing highly pure solutions and the fact that these studies are carried out at low temperatures, thus decreasing the rate of homogeneous chemical reactions following the electron transfer steps. For example reduction of benzophenone in liquid ammonia⁸⁸ gives a stable radical anion and di-anion, and this allows the equilibrium constant for the disproportionation reaction



to be determined. In the presence of alcohol protonation of the di-anion occurs thereby confirming the mechanism of the reduction by alkali metal/ammonia/alcohol systems as involving reduction of benzophenone by solvated electrons to give the di-anion which is rapidly protonated by the

alcohol. A study¹⁴² of the reduction of nitro- and nitrosobenzene in the absence of proton donors, and also in the presence of propan-2-ol and ammonium ions, similarly enabled the reduction mechanism to be understood. Further papers considered the reductive alkylation of quinoline¹⁴³ and the CV behaviour of diethylfumarate, cinnamionitrile and acrylonitrile¹⁷¹ and cyclooctatetraene¹⁷² in liquid ammonia.

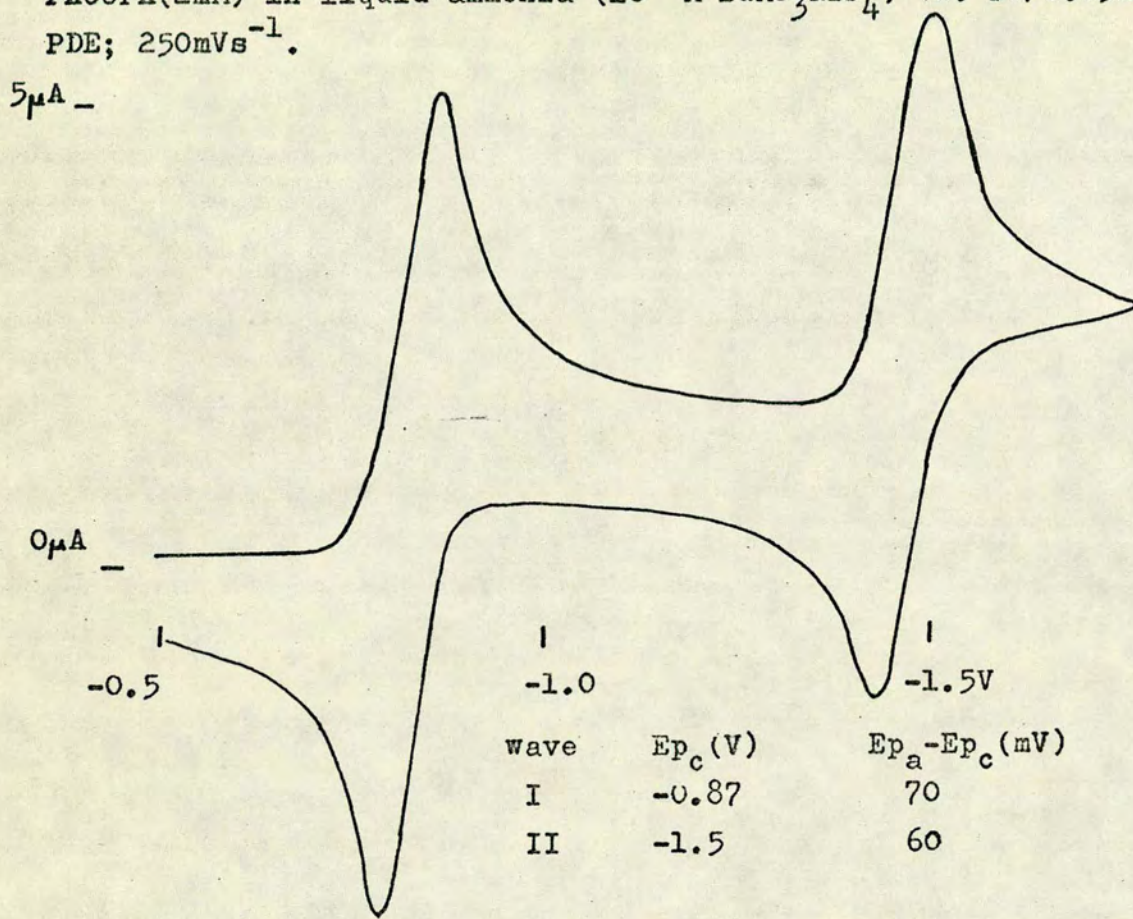
As a result of the proved usefulness of liquid ammonia as a solvent for electro-reductions discussed above, some preliminary investigations involving analytical and preparative studies were carried out on the following organic compounds: benzophenone, benzoylcyclopropane, acetophenone, azobenzene, stilbene and diphenylacetylene. A summary of the CV data for these compounds, recorded under similar conditions, is given in Table X.

2. The Reduction of Benzophenone in Liquid Ammonia.

As previously described in detail for the reduction of acetophenone in acetonitrile, the reduction of benzophenone in aprotic solvents involves two successive 1e transfers to afford the radical anion and di-anion. Investigations have been carried out in DMF,^{28, 144, 80} acetonitrile,¹⁴⁵ pyridine,¹⁴⁶ and liquid ammonia⁸⁸ by polarography and cyclic voltammetry. In the majority of cases^{28, 144, 145, 146} formation of the benzophenone radical anion was found to be chemically and electrochemically reversible, whereas the second electron transfer was slower and afforded a di-anion which was believed to undergo chemical reaction, presumably with the solvent or supporting electrolyte. In liquid ammonia, however, a reversible second wave and stable di-anion was obtained. This, as mentioned above, was attributed to the unusual ability of the solvent to stabilise the di-anion and its failure to act as a proton source. This was in agreement with the earlier work of Wooster¹⁴⁷ (using sodium in liquid ammonia) who demonstrated that stable mono- and di-sodium derivatives of benzophenone could be prepared by adding the correct proportion of sodium. More recently, Jensen and Parker⁸⁰ reduced benzophenone in DMF containing tetramethylammonium fluoroborate and suspended neutral alumina and showed that under these conditions both charge transfers were reversible at the sweep

FIGURE 15.1

PhCOPh(2mM) in liquid ammonia (10^{-1} M BuMe₃NBF₄) vs. Pb/0.05M Pb²⁺;
 PDE; 250mVs⁻¹.



No change on addition of Et₄NBF₄ (10^{-1} M).

Measurement of Peak Heights.

Sweep time 0.4scm⁻¹

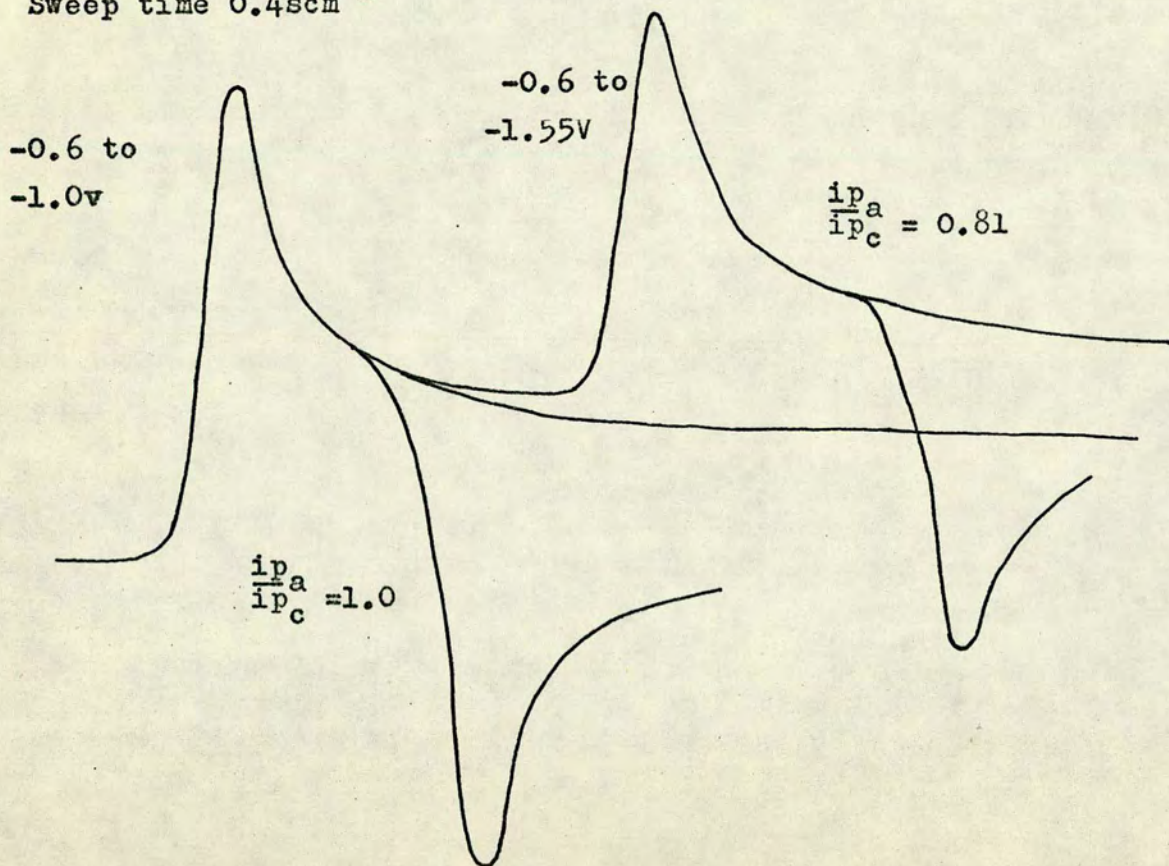


FIGURE 15.2

PhCOPh(2mM) in liquid ammonia (10^{-1} M KI) vs. Ag/satd. AgCl/satd. KCl);
PDE; 200mVs^{-1} .

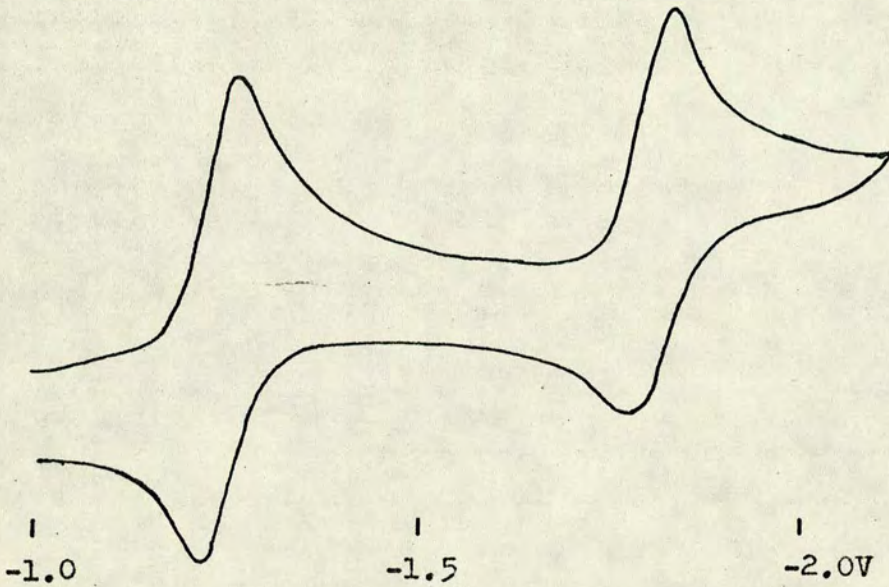
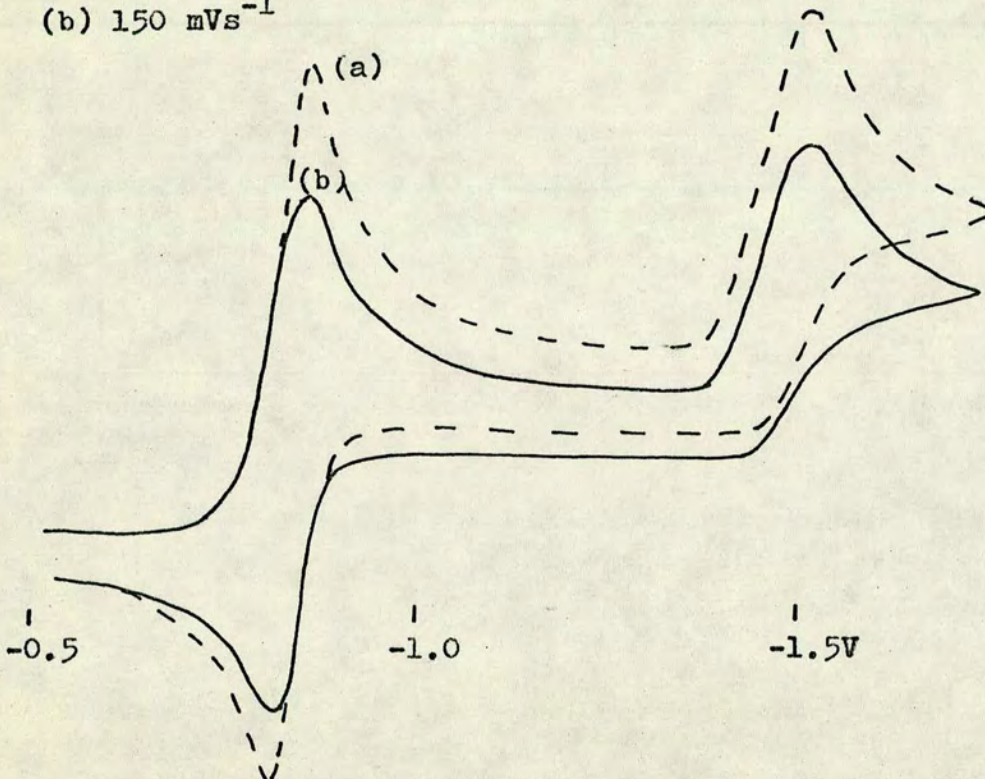


FIGURE 15.3

PhCOPh(2mM) in liquid ammonia (10^{-1} M Et_4NBF_4) vs. Pb/0.05MPb²⁺;
PDE.

- (a) 250mVs^{-1}
- (b) 150mVs^{-1}



speed employed (306 mV s^{-1}). The result indicated that the spontaneous reaction of the di-anion of benzophenone with the solvent or supporting electrolyte previously postulated was incorrect and rationalised the behaviour in terms of scavenging of all traces of proton donors and other electrophilic impurities by the alumina.

Following the reported observation by Bard et al⁸⁸ that two, reversible, 1e waves were obtained on reduction of benzophenone in liquid ammonia, this compound was initially selected for study in order to ascertain the degree of reversibility attainable using the equipment described. Cyclic voltammetry and polarography was conducted in the presence of lithium, potassium and quaternary ammonium salts. A summary of the data obtained from these experiments is given (Table XI).

In the presence of butyltrimethylammonium and potassium cations, the first and second electron transfers showed almost reversible behaviour (Figs. 15.1 and 15.2), although the peak separations ($E_{p_a} - E_{p_c}$) were somewhat greater (60-70mV) than the theoretical peak separation for a Nernstian reaction at -36°C . The peak potential varies with the standard electrode potential and the diffusion coefficients of the oxidized and reduced species, which are temperature dependent.¹⁴⁸ Thus for a reversible charge transfer, the peak potential shifts towards more positive potentials and the peak potential separation decreases as the temperature is lowered. Using the relationships:¹⁴⁹

$$E_p = E_{\frac{1}{2}} + 1.109 \frac{RT}{nF}$$

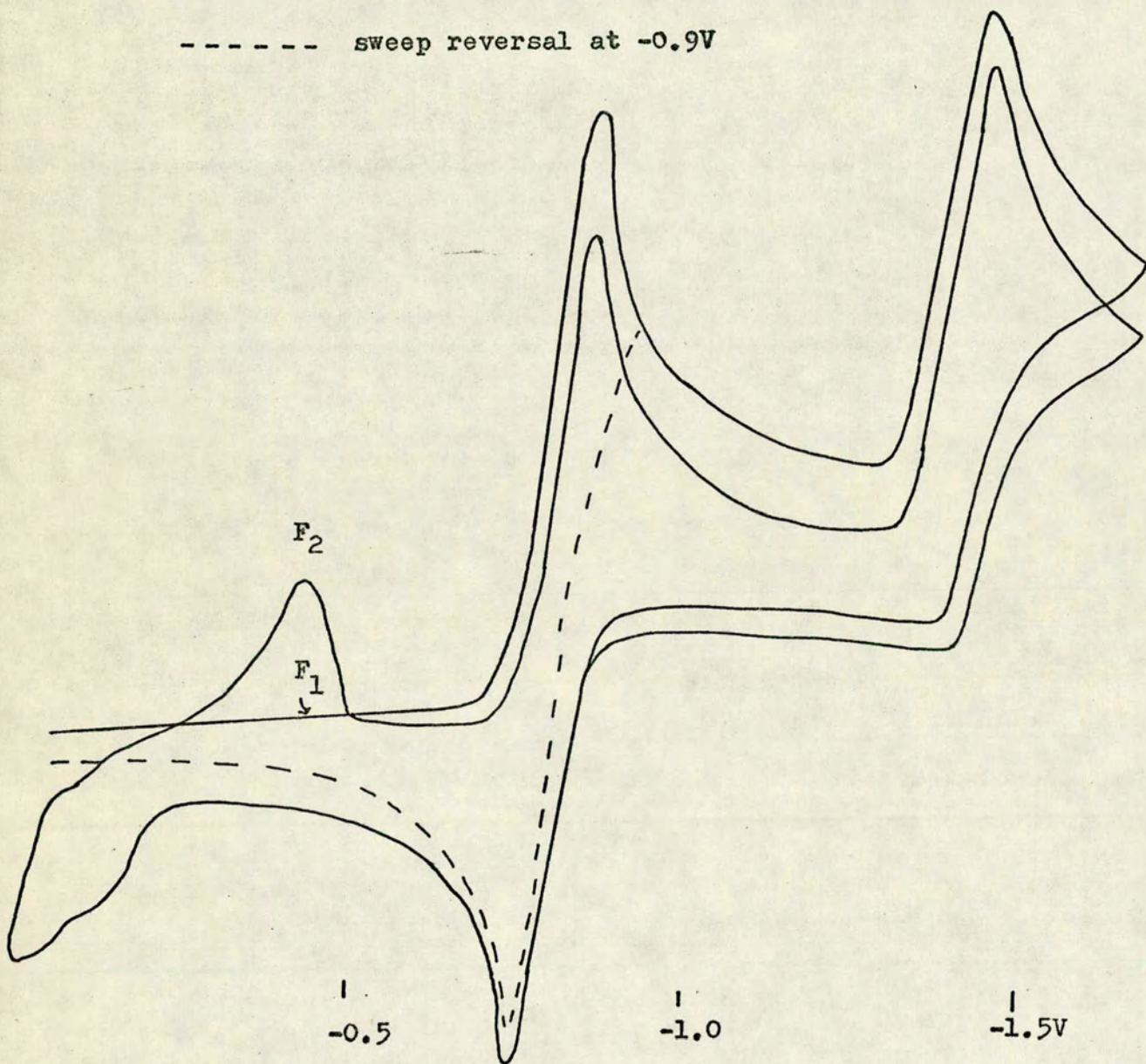
$$E_{p_{\frac{1}{2}}} = E_{\frac{1}{2}} - 1.09 \frac{RT}{nF}$$

we can estimate that the theoretical peak separation at -36°C ($E_p - E_{p_{\frac{1}{2}}}$) i. e. ($E_{p_a} - E_{p_c}$) = 45 mV. However a study¹⁴⁸ of the CV behaviour of model reversible systems in various solvents at varying temperatures indicated that extensive peak broadening and increases in peak separation ($E_{p_a} - E_{p_c}$) occur at low temperatures. The effects were attributed to some heterogeneous charge transfer control and an iR drop contribution and were found to be very sensitive to the surface history of the platinum

FIGURE 15.4

PhCOPh in liquid ammonia ($10^{-1}M Et_4NBF_4$) vs. Pb/0.05M Pb^{2+} ;
HMDE; $250mVs^{-1}$.

----- sweep reversal at -0.9V



electrode used.

The ratio of $\frac{i_{p_a}}{i_{p_c}}$ in the presence of butyltrimethylammonium and potassium salts was found to be almost unity for the first wave but was somewhat less (0.65-0.9) for the second wave, the latter being very sensitive to protic impurities. A similar observation was made by Demortier and Bard⁸⁸ even at the lower temperature employed (-50°C cf. -36°C). The second wave was also slightly smaller than the first ($\frac{i_{p(I)}}{i_{p(II)}} = \frac{1.0}{0.8}$). A similar CV response was observed at a HMDE in the presence of butyltrimethylammonium fluoroborate (the range at mercury is too small to observe a second wave for benzophenone in the presence of potassium ions), although in some instances an anomalous anodic wave (E_p 0 to 0.15V) was observed on the reverse sweep. This appeared to be present only at mercury and only when the second wave was less reversible than expected, suggesting that it was due to oxidation of a species formed by reaction of the benzophenone di-anion with an electrophilic or protic impurity. This was supported by the observation that the wave did not occur when sweep reversal was carried out prior to the second wave for benzophenone. On the second cycle the wave had a cathodic counterpart (E_{p_c} ca. -0.4V), the symmetric shape of which suggested adsorption was occurring. A similar phenomenon was observed at mercury in the presence of tetraethylammonium fluoroborate (Fig. 15.4).

Contrary to the reversible behaviour observed in the presence of butyltrimethylammonium fluoroborate, a cyclic voltammogram recorded in the presence of tetraethylammonium fluoroborate (Fig. 15.3) showed no anodic peak for the second wave on scan reversal, using both a HMDE and a PDE. The addition of the tetraethylammonium salt had no effect on the voltammogram obtained in the presence of the butyltrimethylammonium cation i. e. the anodic peak current for wave II was not diminished. This suggests that, under these conditions, the di-anion of benzophenone does not react with the tetraethylammonium cation (for example by proton abstraction). This is supported by the observation of a reversible second wave for benzophenone in DMF reported by Jensen and Parker,⁸⁰ although the specific case of reduction of benzophenone in the presence of a tetraethylammonium salt was

not mentioned; the more reactive di-anions such as those from anthracene, but not perylene or benzanthracene, were reported to be protonated by tetraethylammonium but not by tetrabutylammonium salts. The peak potential for the second wave was, in all but one case, identical in the presence of both tetraethyl- and butyltrimethylammonium salts. This, together with the similar shape of the second wave observed in the presence of both cations, indicates that the behaviour is not due to a slower charge transfer in the presence of the tetraethylammonium salt (a cathodic shift of the wave would then be expected). Thus, possible effects of the size of the supporting electrolyte on the rate of charge transfer, such as those discussed previously for the reduction of benzoylcyclopropane in acetonitrile, can in this case be dismissed. When CV was conducted in a medium containing equal amounts of tetraethyl- and butyltrimethylammonium salts (0.05M in each) the curve resembled that of Fig. 15.3 i.e. a situation similar to that observed in the presence of tetraethylammonium fluoroborate alone.

Any attempt to rationalise the above observations is highly speculative. It is perhaps possible that specific adsorption of the quaternary ammonium cations occurs; in the presence of specifically adsorbed butyltrimethylammonium cations a reversible second charge transfer affords the stable di-anion of benzophenone, whereas in the presence of specifically adsorbed tetraethylammonium cations chemical reaction of the di-anion with the supporting electrolyte cation (or an associated adsorbed impurity) takes place. The observation that a similar peak potential is obtained for the second wave in the presence of both cations indicates that any follow-up chemical reaction is slow in comparison with the charge transfer process (an anodic shift in the peak potential would otherwise be expected).³

Unfortunately, owing to wave distortion, it was not possible to establish whether a stable di-anion was observable at faster scan rates in the presence of tetraethylammonium fluoroborate, although no apparent change in the CV behaviour occurred when the sweep rate was increased from 150 to 250 mV s^{-1} (Fig. 15.3). Addition of the tetraethylammonium salt to a solution of butyltrimethylammonium cations might have no effect on the specifically adsorbed ions at the electrified interface, thereby explaining

FIGURE 15.5

PhCOPh(5mM) in liquid ammonia ($10^{-1}M LiClO_4$) vs. Ag/satd. AgCl/
PDE; $100mVs^{-1}$. satd. KCl.

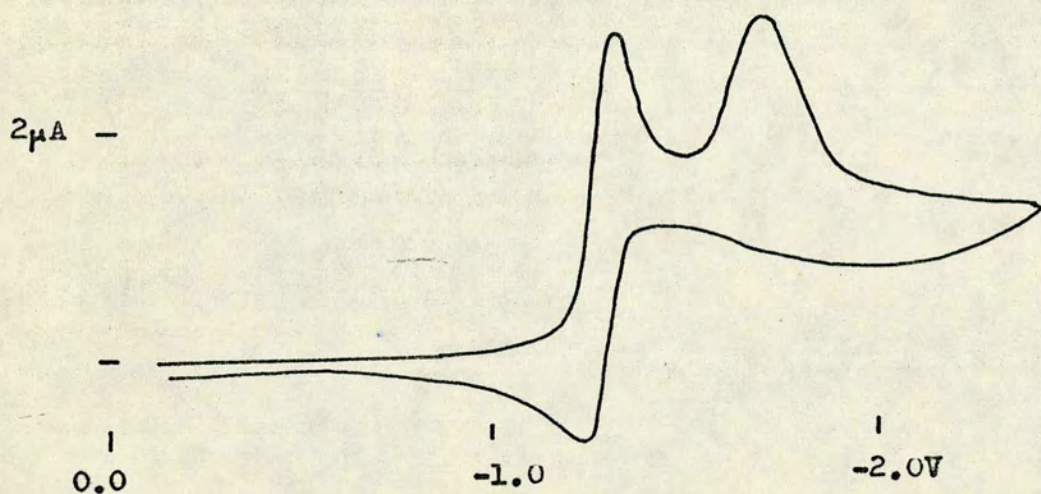
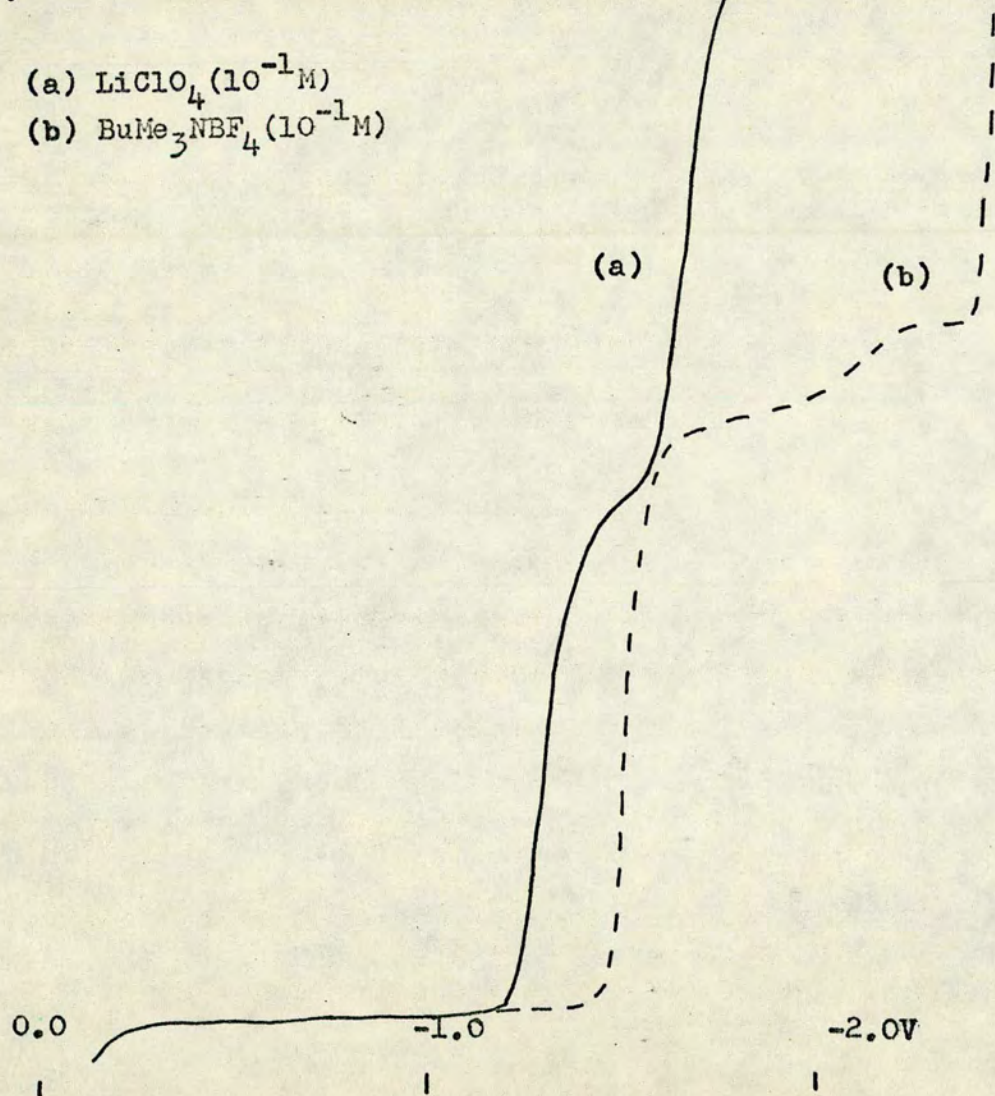


FIGURE 15.6

PhCOPh(5mM) in liquid ammonia vs. Ag/satd.
DME.

- (a) $LiClO_4 (10^{-1}M)$
- (b) $BuMe_3NBF_4 (10^{-1}M)$

AgCl in supporting
electrolyte soln.



why the originally observed CV behaviour is not altered. Addition of the butyltrimethylammonium salt to a solution of tetraethylammonium cations similarly has no effect on the original cyclic voltammogram. It would appear from the voltammogram recorded in an initially prepared mixture of supporting electrolytes that, in the light of this explanation, preferential adsorption of tetraethylammonium cations occurs on polarisation of a solution containing equal amounts of both salts, thereby giving rise to a trace resembling Fig. 15. 3.

CV and polarography was also conducted in the presence of a lithium salt (Figs. 15. 5 and 15. 6a). The cyclic voltammogram showed a reversible first electron transfer but the symmetric shape and anodic shift of the second wave indicated that considerable ion-pairing and an adsorption effect occurred in the presence of this cation. The behaviour is similar to that observed by Bewick and Brown³⁰ for the reduction of acetophenone in DMF in the presence of a lithium salt. A comparison of the polarograms obtained in the presence of lithium and butyltrimethylammonium cations (Figs. 15. 6a and 15. 6b) shows that in the presence of the lithium salt the wave separation is considerably less [$E_{\frac{1}{2}}(I) - E_{\frac{1}{2}}(II) = 38 \text{ mV}$ cf. 68 mV]. This can also be attributed to ion-pairing between the di-anion of benzophenone and lithium cations. Owing to the anhydrous conditions employed it is less likely that in the presence of lithium ions the concentration of water at the electrode is increased and the shift in the $E_{\frac{1}{2}}$ for the second wave is due to protonation of the benzophenone di-anion. The apparent anodic shift in the first wave (Fig. 15. 6a vs. Fig. 15. 6b) in the presence of lithium ions is probably due to a shift in the reference electrode potential since a similar effect was not observed when the voltammograms were recorded versus the same reference (Figs. 15. 2 and 15. 5). This is in agreement with the results of Demortier and Bard,⁸⁸ and suggests that ion-pairing of the radical anion with lithium ions does not take place, contrary to the behaviour reported by Kalinowski.¹⁵⁰

The small second polarographic wave observed for benzophenone in the presence of a butyltrimethylammonium salt (Fig. 15. 6b) is surprising in view of the observed stability of the radical anion. A deactivation of the substrate by solution electron transfer i. e.

FIGURE 15.7

PhCOPh(2mM) in liquid ammonia (10^{-1} M Et_4NBF_4) vs. Pb/0.05M Pb^{2+} ; HMDE; 250mVs^{-1} .

----- + EtOH (0.02M)

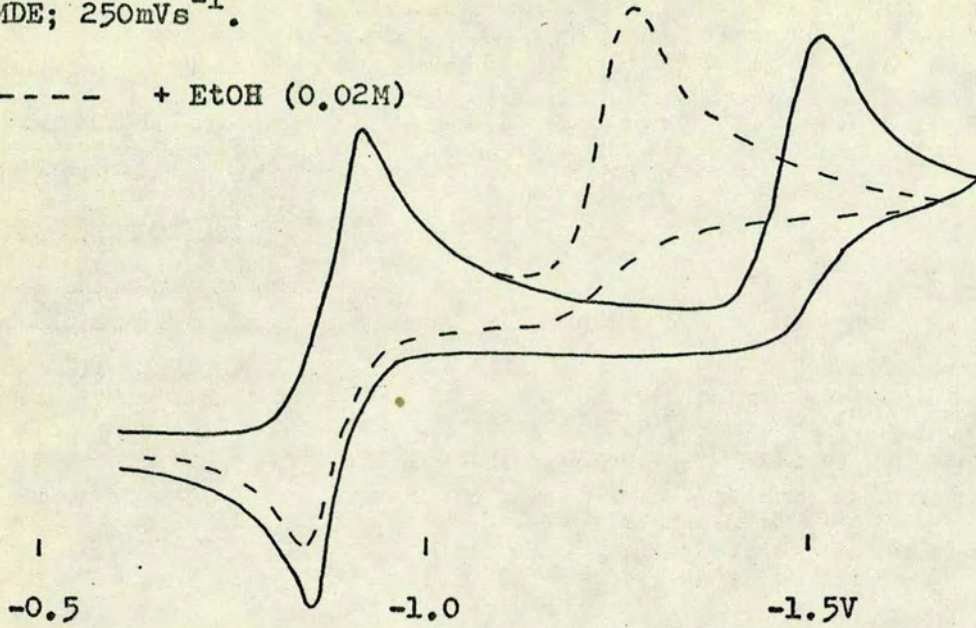
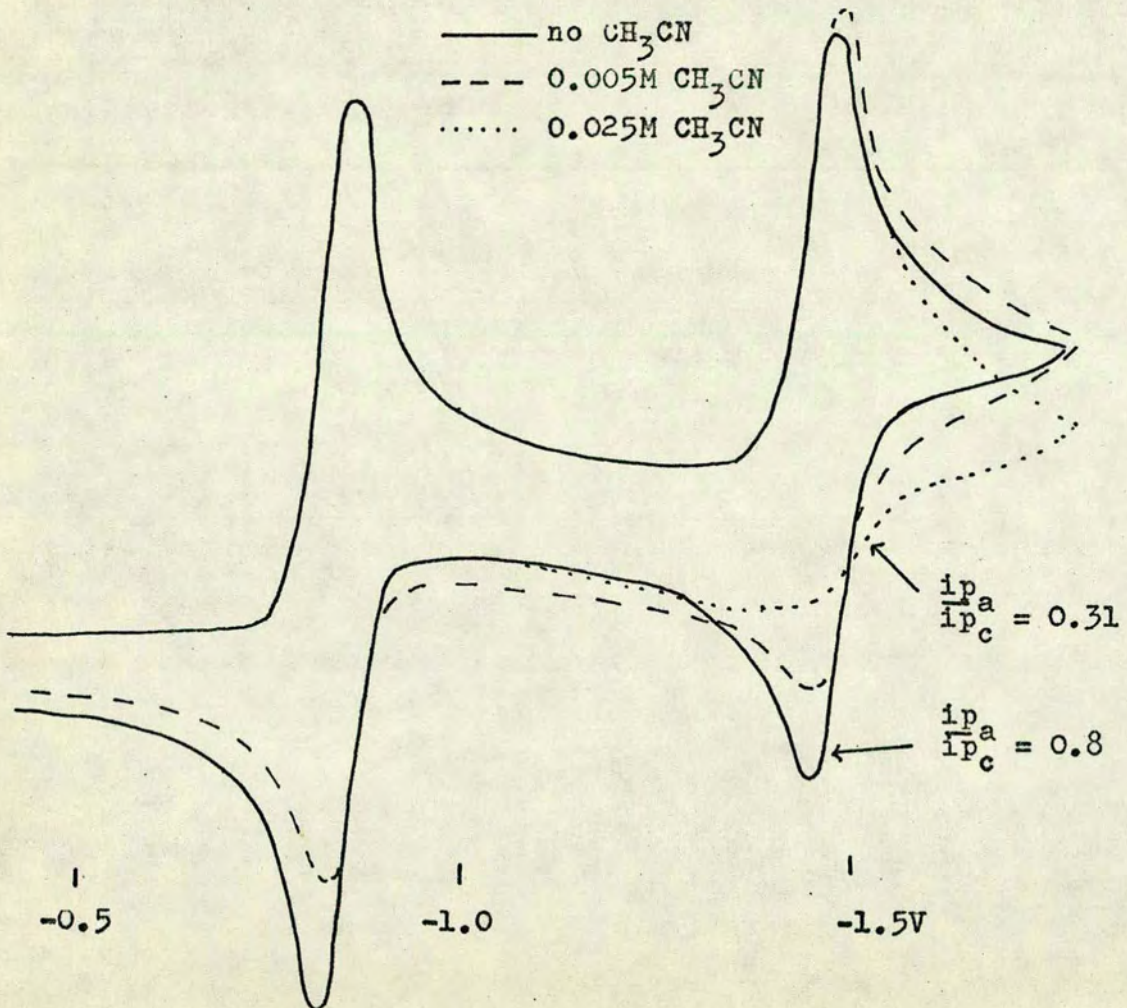
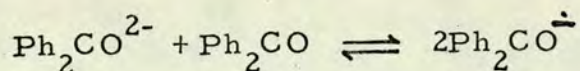


FIGURE 15.8

PhCOPh(2mM) in liquid ammonia (10^{-1} M $\text{BuMe}_3\text{NBF}_4$) vs. Pb/0.05M Pb^{2+} ; PDE; 250mVs^{-1} .

— no CH_3CN
 --- 0.005M CH_3CN
 0.025M CH_3CN





would only be significant if the radical anion underwent chemical deactivation on the polarographic time-scale. If the above reaction were applicable, one could explain the greater height of the second wave in the presence of lithium ions (Fig. 15.6a) in terms of ion-pairing, which would inhibit solution electron transfer. In conditions where two reversible CV waves are observed the above equilibrium is normally in favour of the radical anion as shown by the low K_d value. This can be estimated using the equation¹⁵¹

$$+ \log K_d = \frac{nF}{2.3RT} (E_{\text{II}}^{\circ} - E_{\text{I}}^{\circ})$$

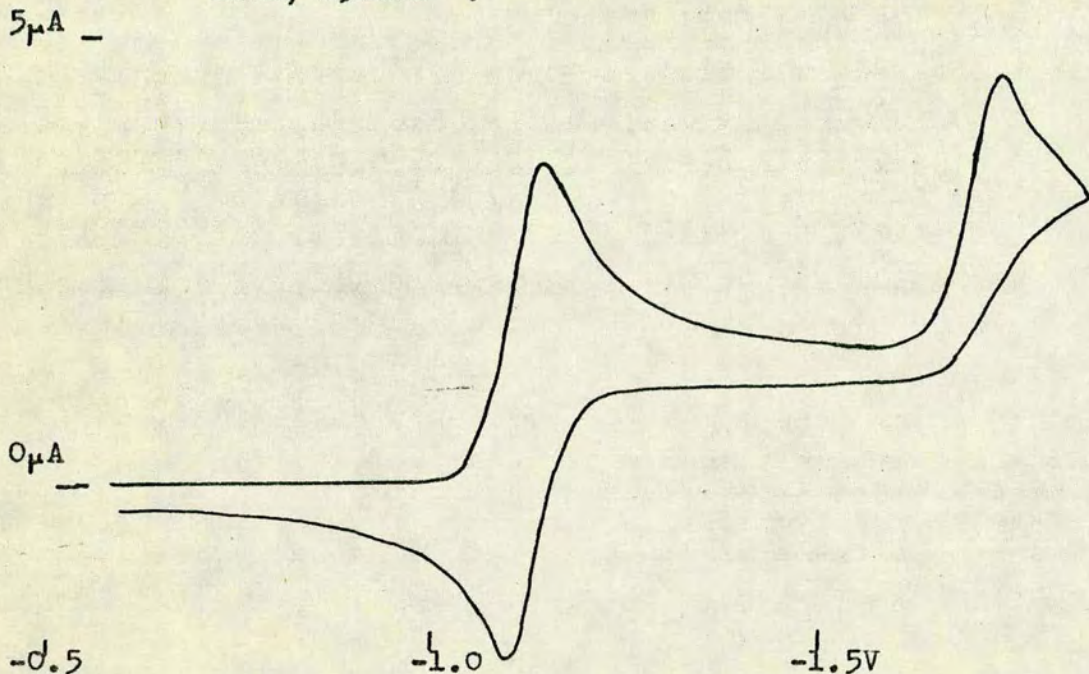
where E_{I}° and E_{II}° are the standard potentials of the first and second charge transfers. Substituting a peak separation of 0.6V, we obtain $K_d = 10^{-13} - 10^{-14}$ at -36°C indicating that the benzophenone radical anion only disproportionates to a minute degree.

Finally CV was conducted in the presence of a proton donor, ethanol (Fig. 15.7). In accordance with the reported behaviour⁸⁸ the peak potential of the second wave shifted anodically indicating that protonation of the di-anion was occurring. The first wave was unaffected. Addition of acetonitrile to a solution of benzophenone in ammonia containing butyltrimethylammonium salt also caused considerable diminishing of the anodic peak for the second wave observed on sweep reversal ($\frac{i_{\text{pa}}}{i_{\text{pc}}}$ decreased from 0.8 to 0.31 on addition of $2.5 \times 10^{-2} \text{ M CH}_3\text{CN}$) but the potential of the second wave was unaffected (Fig. 15.8). The resulting voltammogram thus resembled the trace observed in the presence of a tetraethylammonium salt. This suggests that a chemical reaction (presumably proton abstraction) by the benzophenone di-anion from acetonitrile takes place, but, owing to the failure to observe an anodic shift in the potential of the second wave, protonation must be slower than in the presence of ethanol i. e. the kinetic acidity of ethanol is higher than that of acetonitrile.

Controlled potential reduction of benzophenone at the potential of the second wave afforded the corresponding alcohol, diphenylcarbinol. There was no evidence for pinacol formation, in accordance with the observed

FIGURE 16.1

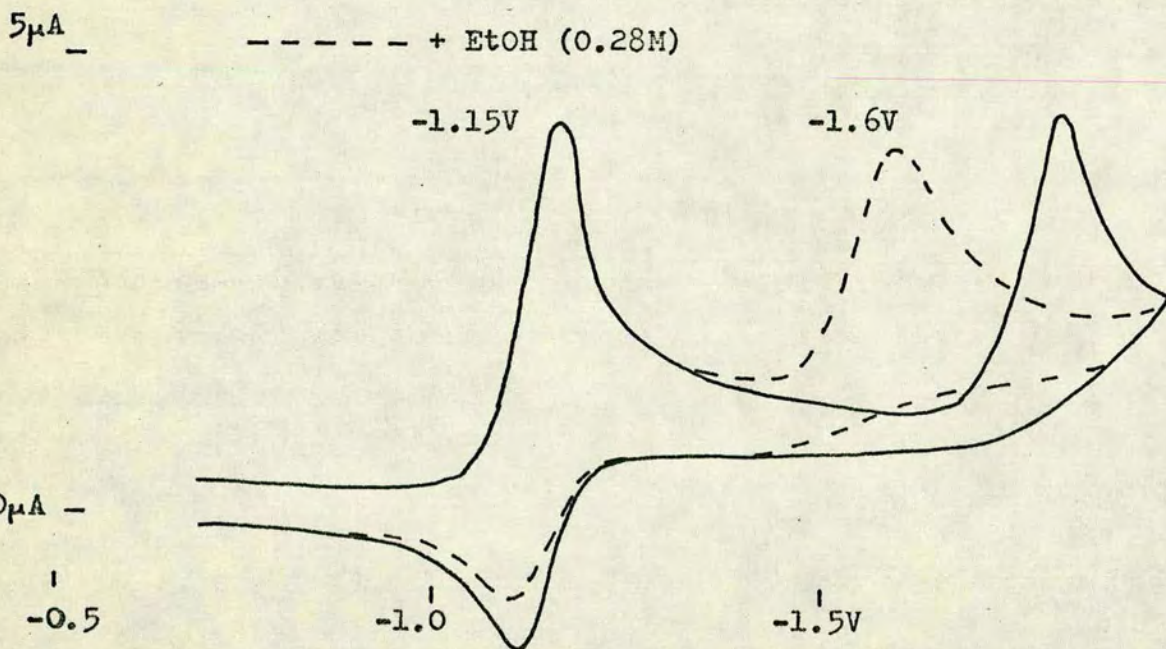
PhCO \triangleleft (2mM) in liquid ammonia (10^{-1} M Et $_4$ NBF $_4$) vs. Pb/0.05M Pb $^{2+}$;
HMDE; 250mVs $^{-1}$.



wave	E_{pc} (V)	$E_{pa} - E_{pc}$ (mV)	i_d (μ A)	$\frac{i_{pa}}{i_{pc}}$
I	-1.15	55	3.7	1.0
II	-1.75	-	3.3	0.55

FIGURE 16.2

PhCO \triangleleft in liquid ammonia (10^{-1} M BuMe $_3$ NBF $_4$) vs. Pb/0.05M Pb $^{2+}$;
PDE.



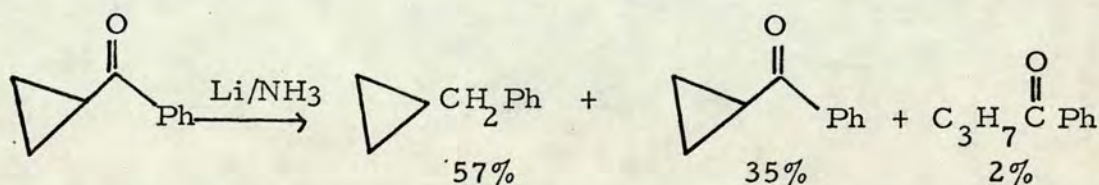
voltammetric behaviour. The solution initially turned blue-green in colour, presumably due to the formation of the di-anion, but the colour disappeared on continued electrolysis. The cell current was found to decrease prematurely ($1.44F \text{ mol}^{-1}$ passed) suggesting that side-reactions were also occurring. This was supported by unidentified peaks in the n. m. r. spectrum of the crude product. A cleaner reaction took place when leakage of the anode compartment into the catholyte occurred. Under these conditions the white crystalline alcohol precipitated from solution and the situation is analogous to conducting the electrolysis in the presence of a proton donor (ammonium ions), thereby quenching the benzophenone di-anion as it is produced. Under these conditions an 84% chemical yield of the alcohol was obtained.

3. The Reduction of Benzoylcyclopropane in Liquid Ammonia.

Cyclic voltammetry of benzoylcyclopropane in liquid ammonia indicated two 1e transfers to afford the radical anion and the di-anion (Fig. 16.1). The first wave was reversible ($E_{p_a} - E_{p_c} = 55 \text{ mV}$) and the radical anion is stable on the CV time scale ($\frac{i_{p_a}}{i_{p_c}} = 1.0$). The di-anion exhibited no anodic wave on sweep reversal, indicating the occurrence of a follow-up chemical reaction. A similar trace was obtained at both the HMDE and PDE and in the presence of butyltrimethyl- and tetraethylammonium salts. Addition of ethanol to the solution (Fig. 16.2) effected a slight decrease in the anodic wave for the oxidation of the radical anion. This may reflect a slow protonation of the latter or protonation of the di-anion formed by disproportionation of the radical anion. The second wave however exhibited an anodic shift typical of the behaviour expected for a rapid irreversible protonation of the di-anion. A comparison with the voltammogram obtained in acetonitrile as solvent (Fig. 8.3) suggested a more reversible first electron transfer in liquid ammonia [$E_{p_a} - E_{p_c} = 55 \text{ mV}$ (NH_3) vs. 85 mV (CH_3CN); $\frac{i_{p_a}}{i_{p_c}} = 1.0$ (NH_3) vs. 0.9 (CH_3CN)]. Also, in acetonitrile, the potential separation of the first and second electron transfers

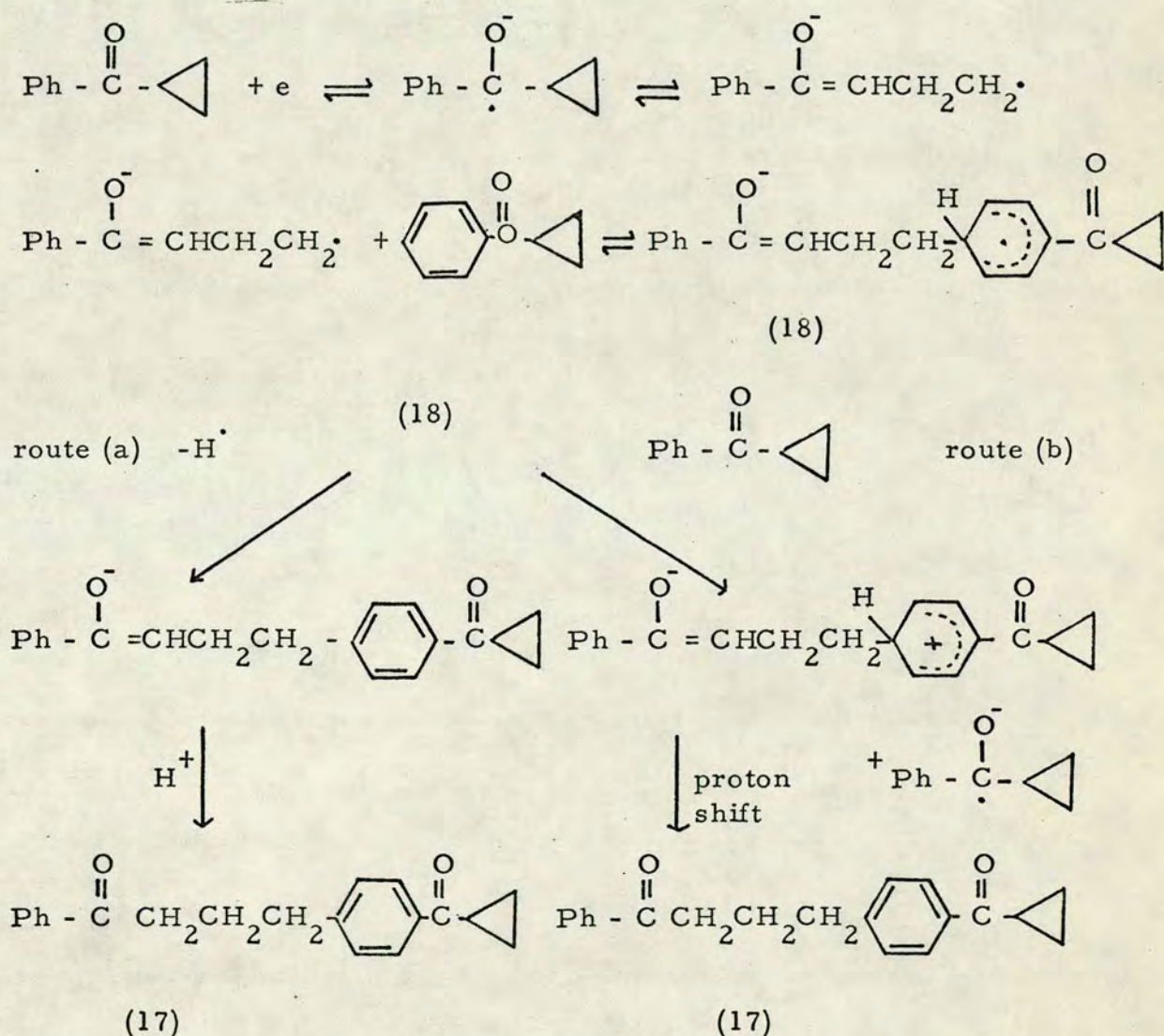
($E_{p_{II}} - E_{p_I} = 0.44$ V) was considerably less than in ammonia ($E_{p_{II}} - E_{p_I} = 0.6$ V). Owing to the higher dielectric constant of acetonitrile (36.2 at 25°C) compared to liquid ammonia (22 at -34°C), one might expect less ion-pairing of the di-anion in the former solvent, which would lead to a greater separation of the first and second waves. A similar effect might result from the greater stabilisation by solvation expected in liquid ammonia. This is opposite to the trend observed. However the standard potential of the second wave vs. that of the first may vary between solvents, so direct comparisons of E_p values are not altogether valid.

Despite the apparently straightforward CV behaviour exhibited by benzoylcyclopropane, CPE of this compound at the second wave in the presence of butyltrimethylammonium fluoroborate afforded a complex mixture of products, only about 30% of which were accounted for. A similar mixture was obtained on reduction at the first wave, and by electrochemically generated solvated electrons. A lithium-ammonia reduction of benzoylcyclopropane has been found¹¹⁵ to give mainly benzylcyclopropane. Considerable amounts of unreacted benzoylcyclopropane were also recovered, together with a trace of the ring cleaved product, butyrophenone:



The electro-reduction, however, afforded only a trace of benzylcyclopropane as indicated by g.l.c. Separation of the products by column chromatography afforded a trace (<1%) of butyrophenone, phenylcyclopropylcarbinol (9%), unreacted benzoylcyclopropane (ca. 14%), and a compound identified as *p*-(3-benzoylpropyl)-benzoylcyclopropane (17) (ca. 9%) by n.m.r. spectrometry, mass spectroscopy and elemental analysis. The low product recovery from the column (even on elution with chloroform), the tarry material formed on the electrode surface during the electrolysis, and the highly retentive nature of the products on a non-polar g.l.c. column (1% SE30, 210°C) suggest that considerable amounts of polymeric material are also produced. The formation of product (17) indicates that, contrary to the lithium/ammonia situation, rapid cleavage of the cyclopropyl ring takes place on electro-

reduction, followed by radical or nucleophilic attack on a molecule of the starting material at the p-position. Since the latter would require loss of a hydride ion, radical attack is perhaps the more likely mechanism. This would afford an intermediate radical (18), which could either lose an H atom, followed by protonation of the enolate anion to give (17) (Scheme 35, route a), or undergo solution electron transfer to a molecule of starting ketone. A proton shift in the resulting cation would then afford (17) (Scheme 35, route b).



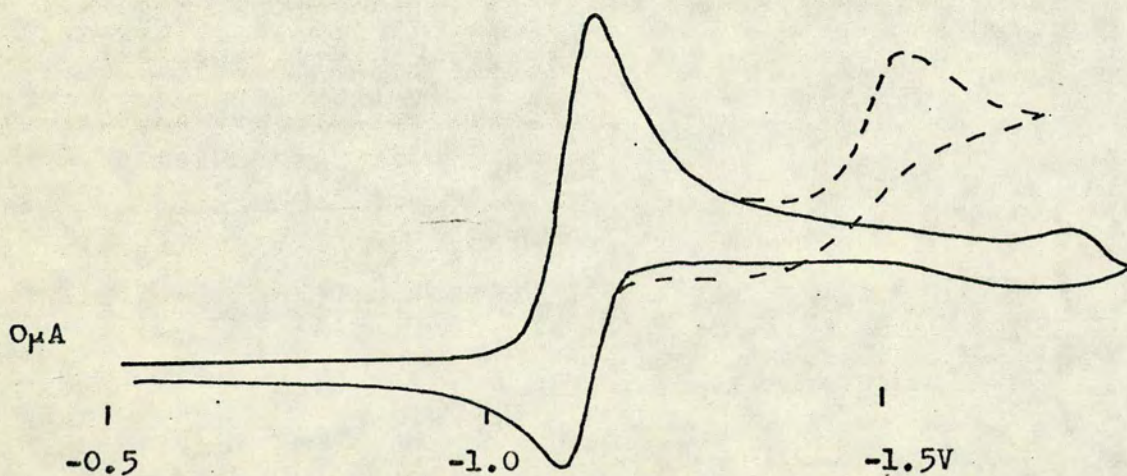
Scheme (35)

The possibility of a radical-radical coupling can not be eliminated but is thought to be less likely, since subsequent loss of a hydride ion would be necessary. Compound (17), which incidentally is not a reduction product, could itself undergo ring cleavage and further attack on substrate. Radical attack in other positions would also be possible. It is not therefore surprising that a complex reaction mixture is formed.

FIGURE 17.1

PhCOCH₃ (2mM) in liquid ammonia (10⁻¹M Et₄NBF₄) vs. Pb/0.05M Pb²⁺;
HMDE; 250mVs⁻¹.

5μA — — — — + EtOH (ca. 0.1M)

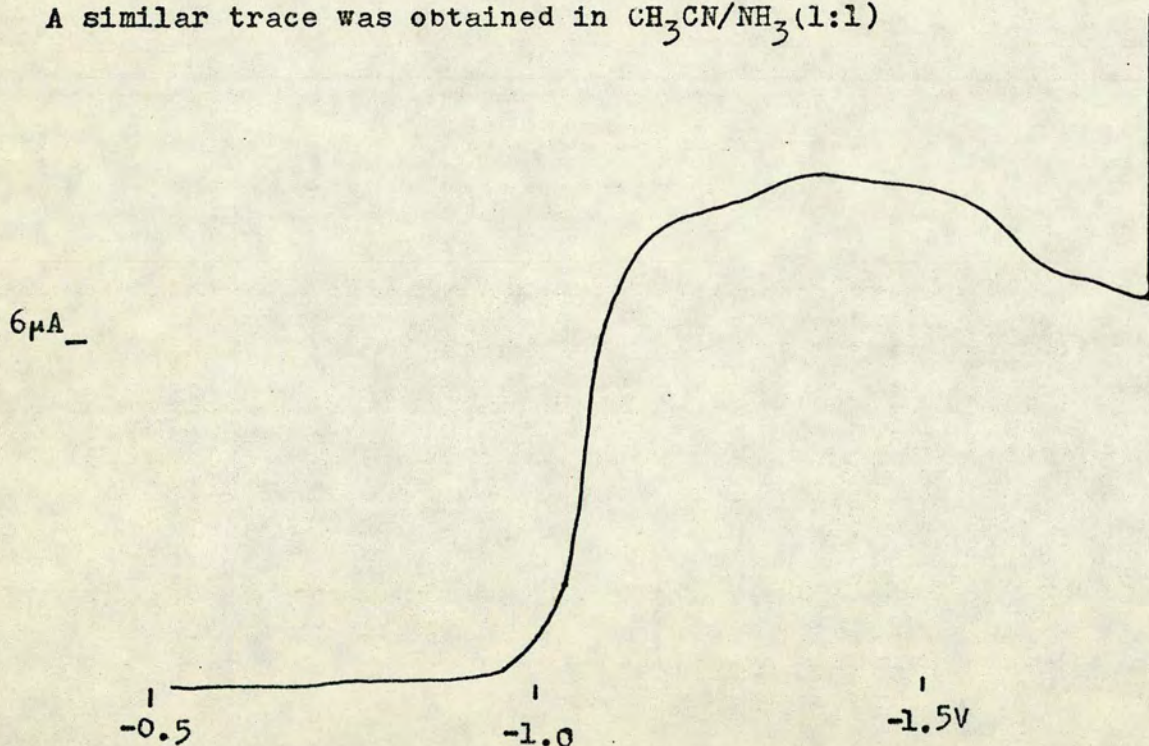


wave	Ep _c (V)	Ep _a - Ep _c (mV)	i _d (μA)	i _{p_a} / i _{p_c}
I	-1.14	60	3.7	0.8
II	-1.76	-	-	-

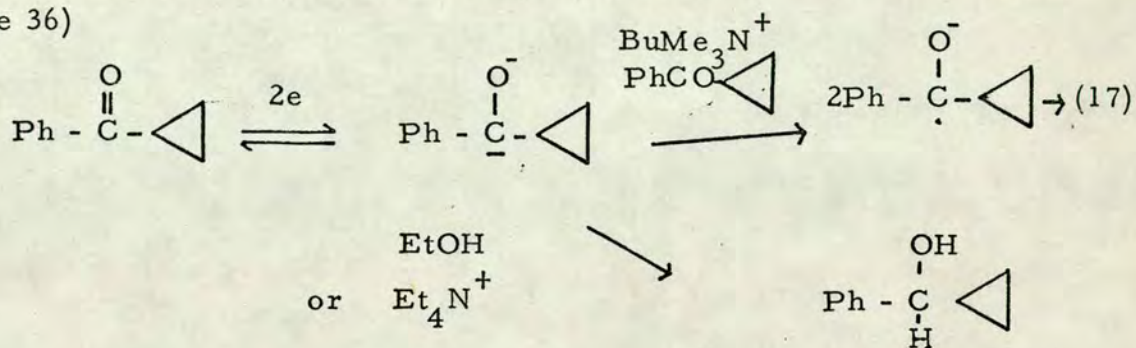
FIGURE 17.2

PhCOCH₃ (2mM) in liquid ammonia (10⁻¹M BuMe₃NBF₄) vs. Pb/0.05M Pb²⁺;
DME.

A similar trace was obtained in CH₃CN/NH₃ (1:1)



Since reduction was carried out at the potential of the second wave, and, assuming ring cleavage involves a radical-anion species as indicated above, it appears that solution electron transfer from the di-anion to the substrate occurs. When reduction was conducted in the presence of ethanol or tetraethylammonium fluoroborate, phenylcyclopropylcarbinol was formed to the exclusion of product (17), suggesting that under these conditions protonation of the di-anion is rapid enough to prevent solution electron transfer (Scheme 36)



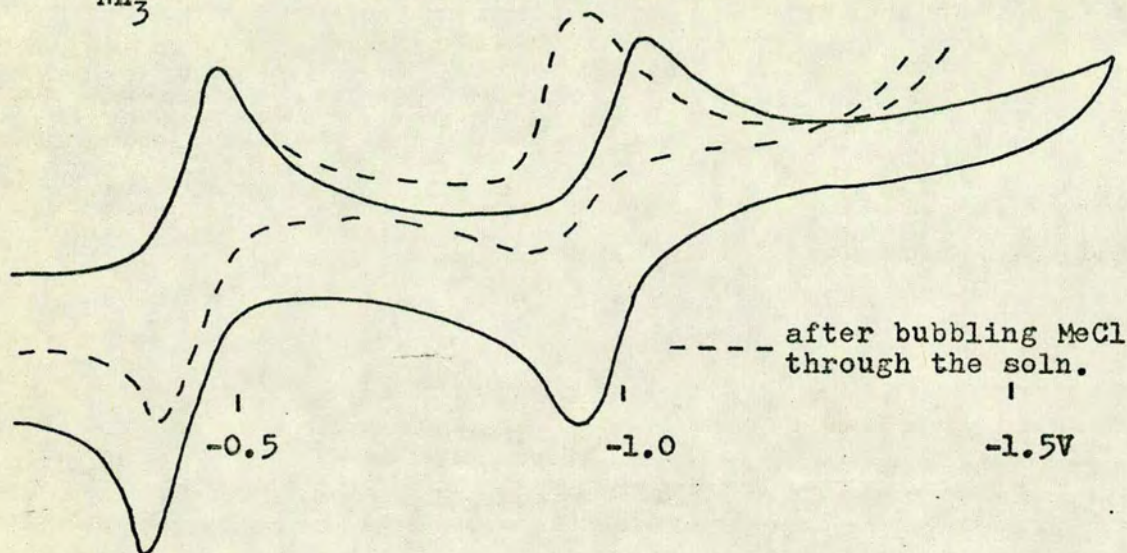
No evidence was obtained for alkylation of the di-anion by the tetraethylammonium cation.

4. The Reduction of Acetophenone in Liquid Ammonia

The CV and polarographic behaviour of acetophenone was similar when recorded in the presence of butyltrimethyl- and tetraethyl-ammonium salts. The cyclic voltammogram (Fig. 17.1) showed an almost reversible first wave, although the $\frac{i_{p_a}}{i_{p_c}}$ ratio was somewhat lower (0.8) than observed for benzophenone and benzoylcyclopropane under similar conditions. The first wave was however more reversible in ammonia than in acetonitrile (Fig. 5.2, $\frac{i_{p_a}}{i_{p_c}} = 0.67$), indicating a more stable radical anion in the former solvent. As in the case of benzoylcyclopropane, the potential separation of the first and second waves was considerably greater in ammonia ($E_{p_{II}} - E_{p_I} = 0.62$ V) than in acetonitrile ($E_{p_{II}} - E_{p_I} = 0.44$ V). Despite the reversibility of the first wave an abnormally small second wave was observed.

FIGURE 18.1

PhN=NPh(satd.) in liquid ammonia (10^{-1} M KI, after pre-treatment with e_{NH_3}) vs. Pb/0.05M Pb^{2+} ; PDE; $250mVs^{-1}$.

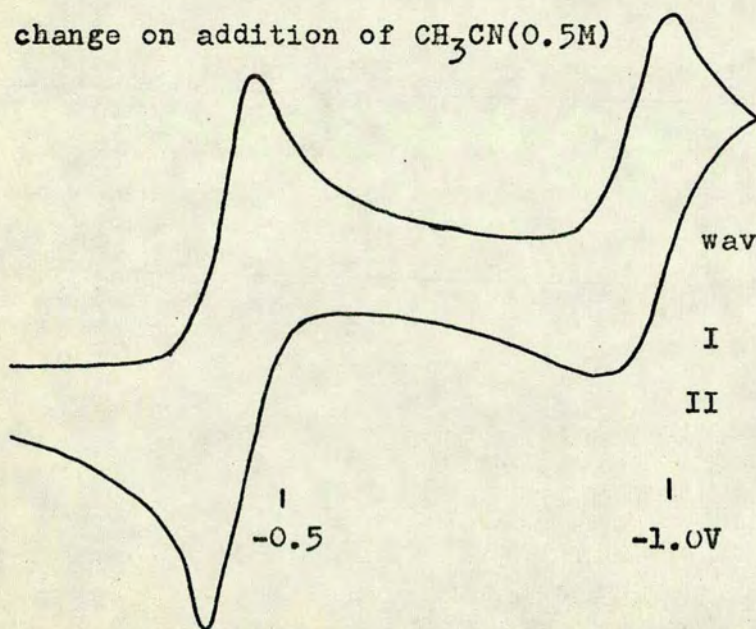


wave	E_{p_c} (V)	$E_{p_a} - E_{p_c}$ (mV)	$\frac{i_{p_a}}{i_{p_c}}$
I	-0.46	60	ca. 1.0
II	-1.0	70	ca. 1.0

FIGURE 18.2

PhN=NPh(2mM, added in THF) in liquid ammonia (10^{-1} M $BuMe_3NBF_4$) vs. Pb/0.05M Pb^{2+} ; HMDE; $250mVs^{-1}$.

No change on addition of $CH_3CN(0.5M)$



wave	E_{p_c} (V)	$E_{p_a} - E_{p_c}$ (mV)	$\frac{i_{p_a}}{i_{p_c}}$
I	-0.47	80	ca.1.0
II	-1.02	100	ca.0.9

This phenomenon is even more marked in ammonia than in acetonitrile and a satisfactory explanation is hard to find. Owing to the reversible nature of the first wave the usual explanations of removal of the radical anion from solution by following chemical reactions are not applicable here. The polarographic second wave (Fig. 17. 2) was similarly small.

Addition of ethanol to the solution caused the second CV wave to increase in height and shift anodically, suggesting rapid protonation of the di-anion occurs. The first wave was unaffected by ethanol indicating that the follow-up chemical reaction of the radical anion is dimerisation rather than protonation.

The major product from the CPE of acetophenone at the potential of the second wave in the presence of butyltrimethylammonium fluoroborate was the pinacol (23%, ca. 30% current yield). Traces of 1-phenylethanol and unreacted acetophenone were also indicated by g. l. c. The formation of pinacol suggests that solution electron transfer between the acetophenone di-anion and the substrate occurs, followed by dimerisation of the radical anion. This is analogous to the situation observed in acetonitrile. A similar product mixture was obtained on electro-reduction at the first wave. However reduction by electrochemically generated solvated electrons in the presence of tetraethylammonium fluoroborate afforded a relatively higher proportion of 1-phenylethanol, suggesting that protonation (but not alkylation) of the di-anion by this supporting electrolyte may take place.

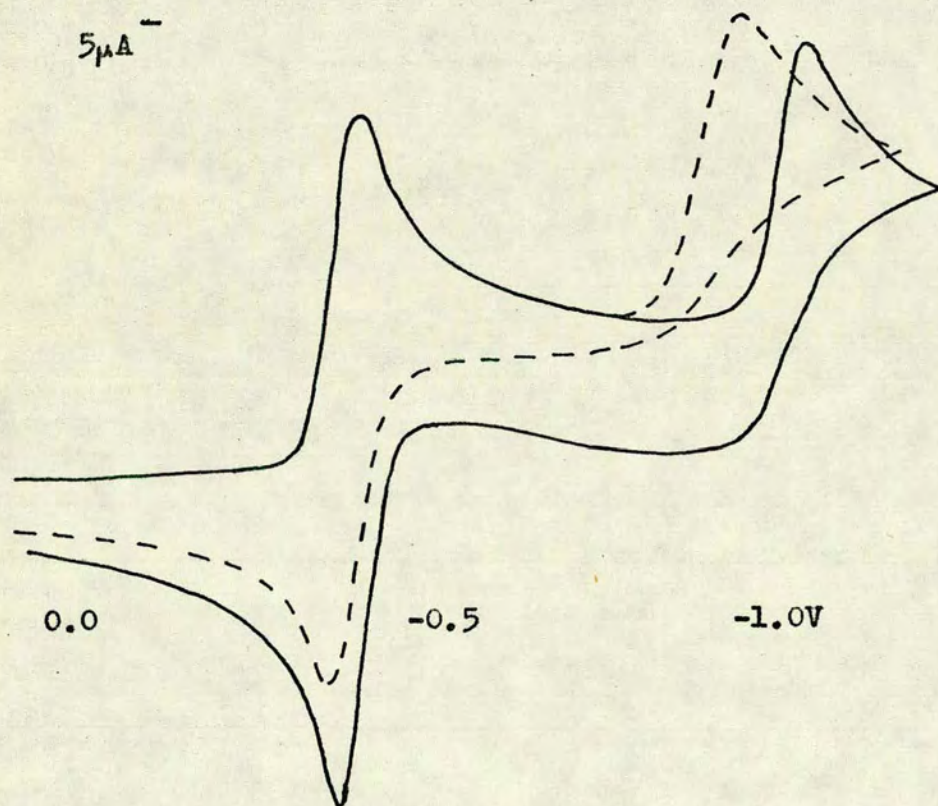
5. The Reduction of Azobenzene in Liquid Ammonia.

Azobenzene is only slightly soluble (<2mM) in liquid ammonia. A 2mM solution was obtained by dissolving the solid in a small amount of THF (ca. 0.1 ml) before adding it to the cell. Cyclic voltammograms were recorded in the presence of potassium, butyltrimethyl- and tetraethylammonium salts at a HMDE and PDE. An almost reversible first electron transfer was obtained in each case (Figs. 18. 1, 18. 2 and 18. 3) [$E_{p_a} - E_{p_c} = 60\text{mV}$; $\frac{ip_a}{ip_c} = \text{ca. } 1.0$]. The second wave exhibited quasi reversible behaviour, the most reversible situation (Fig. 18. 1, $E_{p_a} - E_{p_c} = 70\text{mV}$ $\frac{ip_a}{ip_c} = \text{ca. } 1.0$)

FIGURE 18.3

PhN=NPh(2mM) in liquid ammonia ($10^{-1}M Et_4NBF_4$) vs. Pb/0.05M Pb^{2+} ; HMDE; $250mVs^{-1}$.

----- + EtOH (ca. 0.003M)



wave	E_{p_c} (V)	$E_{p_a} - E_{p_c}$ (mV)	i_d (μA)	$\frac{i_{p_a}}{i_{p_c}}$
I	-0.46	60	3.9	1.15
II	-1.05	-	3.4	0.7

being observed when voltammetry was conducted in the presence of potassium iodide after first pre-treating the solution with solvated electrons. This was achieved by maintaining a potential of -2.7V ($i \approx \text{ca. } 100 \text{ mA}$) for 10 minutes at a Pt strip electrode and stirring the solution on open circuit until the blue colour was discharged (ca. 30 minutes). The di-anion was slightly more stable in the presence of butyltrimethylammonium cations (Fig. 18.2) than in the presence of tetraethylammonium cations (Fig. 18.3), as indicated by the more pronounced peak observed on sweep reversal in the former case. This suggests that protonation of the di-anion, by the quaternary ammonium salts (particularly the tetraethylammonium cation) may occur. This is similar to the situation observed for the reduction of benzophenone to its di-anion. A ratio of $\frac{i_{p_a}}{i_{p_c}} > 1$ was observed for the first wave in the presence of the tetraethylammonium salt, which may be due to the adsorption of the radical anion onto the electrode or the insolubility of the ion-pair formed between the radical anion and the quaternary ammonium cation, although these processes might also be expected to make the second wave greater in height than the first.

The CV behaviour described above is not unlike that observed by Sadler and Bard¹⁵² on reduction of azobenzene in DMF. These workers observed a reversible first wave and quasi reversible second wave. The second wave was considerably more reversible at mercury than at platinum. However the second electron transfer step in liquid ammonia gives a more pronounced reversal peak (Figs. 18.1 and 18.2) than observed in DMF at similar sweep rates in the presence of a tetrabutylammonium salt, suggesting a more stable di-anion is formed in the former solvent.

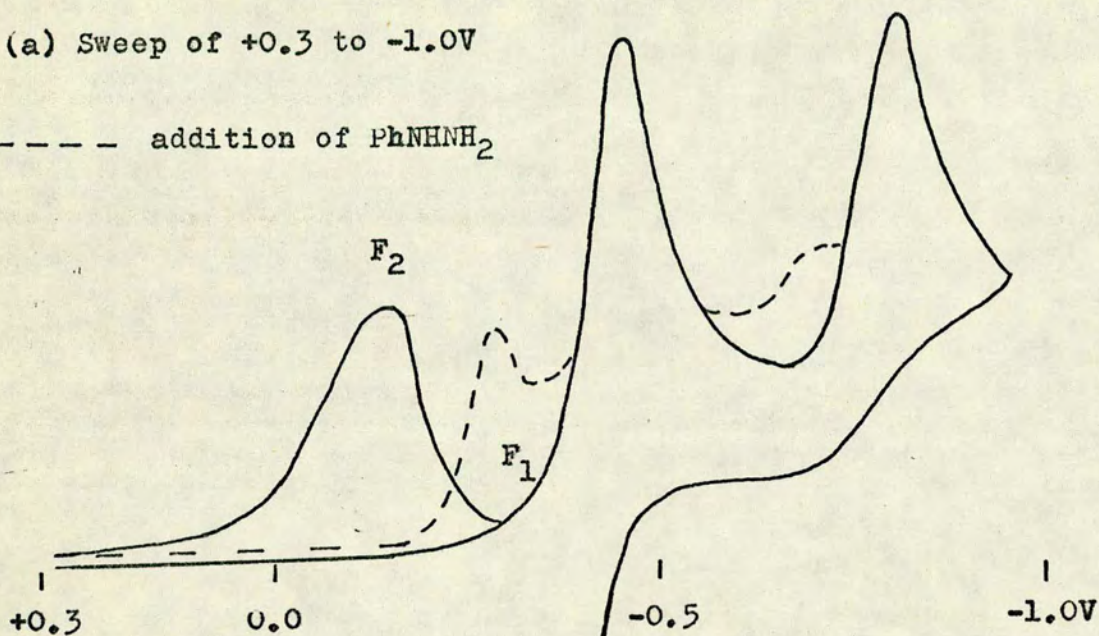
Other workers^{38, 54, 97} have similarly observed a reversible first wave and irreversible second wave for the reduction of azobenzene in DMF and acetonitrile, although more recently¹⁵³ reduction in DMF containing alumina was reported to afford two completely reversible waves. This suggests that protonation of the di-anion is due to impurities rather than the solvent or supporting electrolyte (tetrabutylammonium fluoroborate in this case).

FIGURE 18.4

PhN=NPh(satd.) in liquid ammonia ($10^{-1}M$ BuMe₃NBF₄) vs. Pb/0.05M HMDE; $250mVs^{-1}$. Pb²⁺.

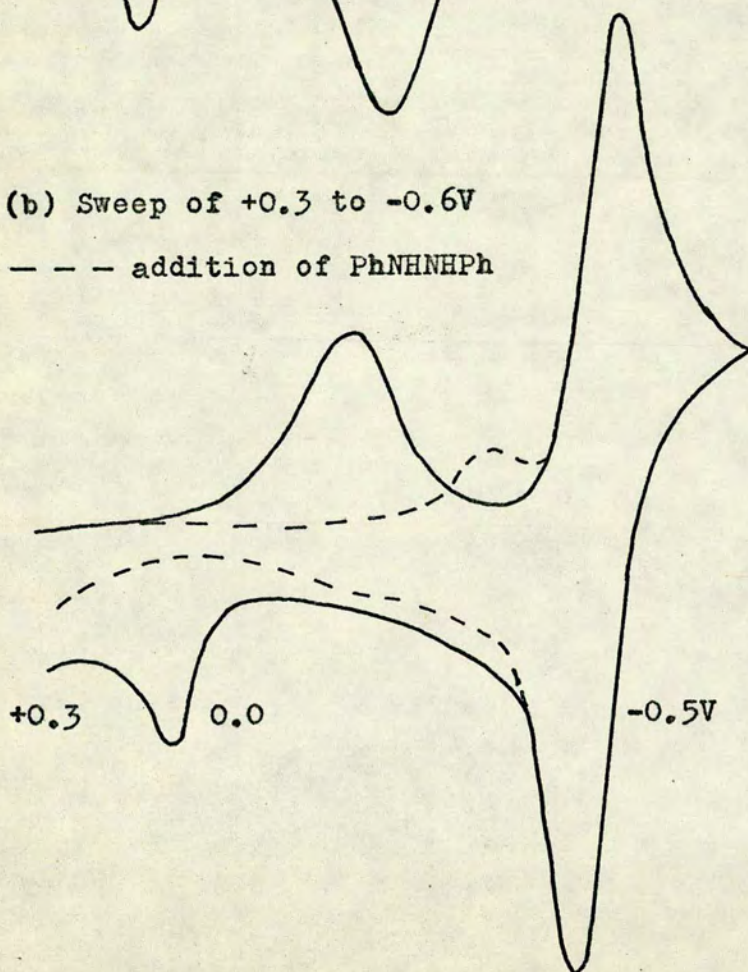
(a) Sweep of +0.3 to -1.0V

----- addition of PhNHNH₂



(b) Sweep of +0.3 to -0.6V

----- addition of PhNHNHPh



The addition of ethanol to the liquid ammonia solution (Fig. 18.3) caused the second wave of azobenzene to shift anodically, indicating that a rapid irreversible protonation of the di-anion occurs. The first wave was virtually unaffected. This is similar to the situation observed for benzophenone. The addition of acetonitrile, however, had no effect on the second wave, suggesting that proton abstraction does not occur. Baizer and Hallcher¹⁵³ similarly failed to observe deprotonation of acetonitrile by the azobenzene di-anion in DMF. This is contrary to previous observations on the reduction of azobenzene in acetonitrile⁵⁴ and to the observed^{56, 57} decrease in the i_p for the reduction of carbonyl compounds in acetonitrile in the presence of azo compounds, which was attributed to the addition of the electro-generated cyanomethyl anion to the carbonyl group. However the proton donating ability of a compound depends not only on its kinetic and thermodynamic acidity but also on its availability at the electrode and the failure of acetonitrile to act as a proton donor for the azobenzene di-anion in liquid ammonia and DMF may be due to its exclusion from the electrified interface and does not necessarily imply that proton abstraction fails to occur when acetonitrile is used as the solvent. In the case of liquid ammonia, the lower temperature employed (-36°C vs. 25°C) may also have a marked effect on the rate of protonation.

Anomalous oxidation waves (E_{p_a} ca. -0.2V and $+0.1\text{V}$) frequently appeared following the addition of ethanol to the solution when voltammetry was carried out at a HMDE. A reduction wave (E_{p_c} ca. -0.13V) was also observed during the second cycle (Fig. 18.4a). The oxidation wave at -0.2V appeared to be associated with the formation of the azobenzene di-anion as it was not present when sweep reversal was carried out before the second wave (Fig. 18.4b). A similar wave (E_p -0.6V vs. SCE) has been observed¹⁵³ by CV following the addition of weak proton donors to azobenzene in DMF; this was attributed to oxidation of the monoprotonated di-anion, $\text{PhNH}^-\text{N}^-\text{Ph}$. A wave corresponding to oxidation of this species was also noted by Sadler and Bard¹⁵² following controlled potential reduction at the second wave of azobenzene. An oxidation wave at more positive potential was attributed to phenylhydrazine, believed to be formed by slow decomposition of the product of the complete reduction. These workers also carried out reduction in the presence of a proton donor (hydroquinone) and obtained oxidation waves for the mono-protonated di-anion and

hydrazobenzene on reversal coulometry. Addition of hydrazobenzene and phenylhydrazine to the liquid ammonia solution, however, caused the anomalous oxidation wave at $E_p +0.1V$ and reduction wave at $E_p -0.13V$ to disappear. Pre-waves for azobenzene reduction, suggestive of adsorption were then also observed. Clearly neither of the anomalous oxidation waves are due to formation of hydrazobenzene or phenylhydrazine. The wave at $-0.2V$ may be due to oxidation of the monoprotated di-anion but, since the waves seemed to be highly dependent upon the electrode surface and surface effects, the results are open to question.

Controlled potential reduction at the second wave of azobenzene was conducted in the presence of methyl chloride in a solution of potassium fluoroborate which had been pre-treated with solvated electrons. Methyl chloride, which is sparingly soluble in liquid ammonia, caused a reduction in the cathodic limit to $-1.5V$. An anodic shift in the potential of the second wave for azobenzene and a decrease in the height of the anodic wave on sweep reversal (Fig. 18.1) suggested that alkylation of the di-anion might be occurring. However a product analysis of the reduced solution by n. m. r. spectroscopy indicated only unreacted azobenzene and hydrazobenzene (ca. 40% current yield). The latter was presumably formed by protonation of the di-anion during work-up and the result suggests that the C-Cl bond is too strong to permit alkylation by methyl chloride. This is supported by the fact that the red-brown colour formed on reduction of azobenzene is not quenched on bubbling methyl chloride through the solution. Rapid addition of methyl iodide, however, effected immediate quenching of the red-brown colour to afford a pale yellow solution, which, on work-up, was shown by n. m. r. spectroscopy to contain azobenzene, hydrazobenzene, N-methylhydrazobenzene and N, N'-dimethylhydrazobenzene in the approximate ratio of 1:0:0.04 : 0.12 : 0.24. The formation of hydrazobenzene and the mono-alkylated product suggests that protonation successfully competes with alkylation. This may be by protic impurities in the solution or by methylammonium iodide formed by reaction of methyl iodide with the solvent. Since the solution was pre-treated with solvated electrons and since a similar³⁹ reduction of azobenzene in a solution of HMPA/LiCl in the presence of methyl iodide afforded exclusively N, N'-dimethylhydrazobenzene when

FIGURE 19.1

trans-PhCH=CHPh(satd.) in liquid ammonia (10^{-1} M Et₄NBF₄) vs. Pb/0.05M Pb²⁺; PDE; 250mVs⁻¹. E_p -1.63V

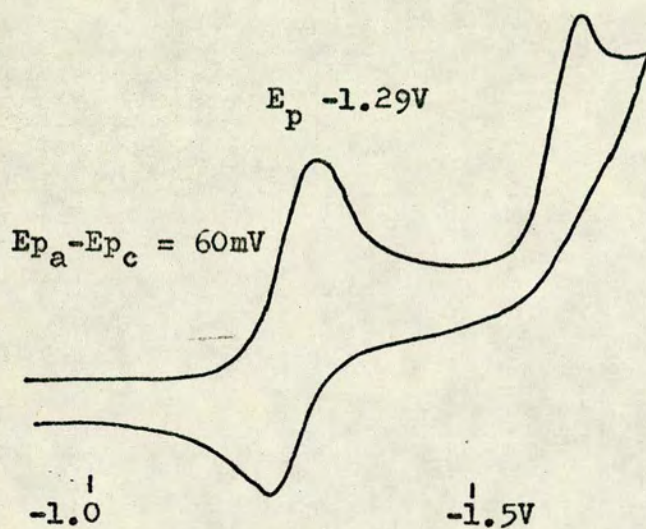
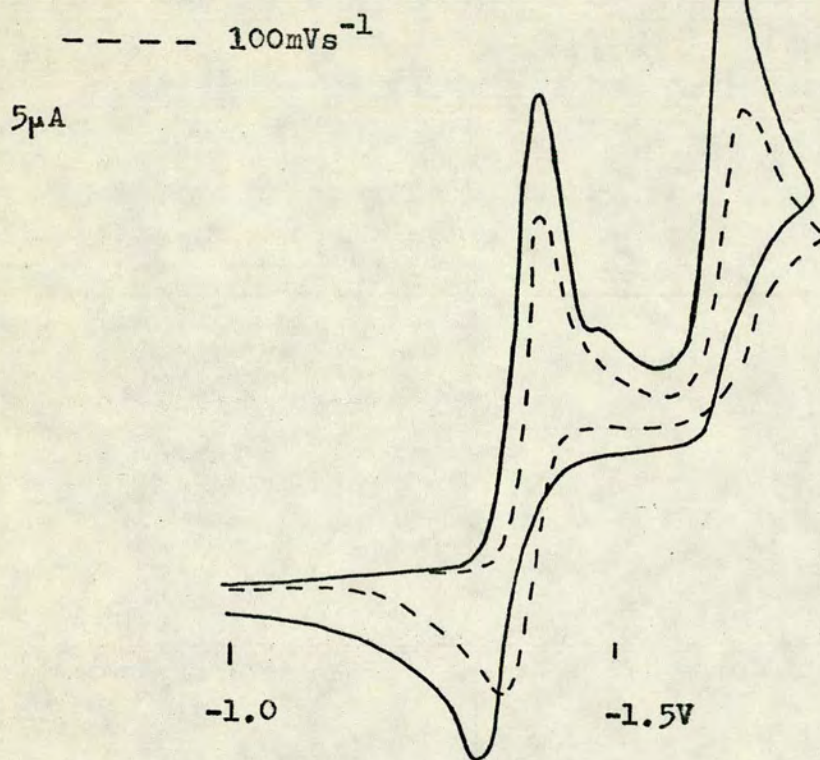


FIGURE 19.2

cis-PhCH=CHPh(2mM) in liquid ammonia vs. Pb/0.05M Pb²⁺; HMDE; 250mVs⁻¹. (10^{-1} M BuMe₃NBF₄)



wave	E _{p_c} (V)	E _{p_a} - E _{p_c} (mV)	i _d (µA)	$\frac{i_{p_a}}{i_{p_c}}$
I	-1.43	100 (75 at 100mVs ⁻¹)	5.28	0.92
II	-1.69	-	5.3	ca.0.35

the solution was pre-electrolysed by the formation of solvated electrons, protonation by methylammonium iodide is perhaps more likely.

6. The Reduction of cis- and trans-Stilbene in Liquid Ammonia

One of the earlier investigations into the electro-reduction of trans-stilbene was carried out by Wawzonek et al,¹⁵⁴ who studied the stereochemistry of the addition of carbon dioxide to the stilbene radical anion. The reduction was conducted in DMF at an uncontrolled potential so that reduction may have involved stilbene radical anions or di-anions and products of the reduction of carbon dioxide. A similar reduction by Dietz and Peover¹⁵⁵ was carried out at the potential of the first wave. Under these conditions a mixture of d, l- and meso-diphenylsuccinic acids was obtained indicating that isomerisation takes place prior to product formation. A $t_{\frac{1}{2}} > 15$ seconds was estimated for the radical anion of the cis-isomer. A more recent study¹⁵⁶ indicated that trans-stilbene exhibits two reduction waves in DMF and HMPA and the voltammetric data suggested an eec mechanism, rapid protonation of the di-anion occurring. The peak separation of the two wave ($E_{p_{II}} - E_{p_I}$) was 0.43V under these conditions. Parker and co-workers,¹⁵⁷ however, observed two completely reversible waves for the reduction of trans-stilbene when voltammetry was conducted in DMF containing neutral alumina and tetrabutylammonium fluoroborate. The peak separation ($E_{p_{II}} - E_{p_I}$) was 0.51V in this case.

trans-Stilbene is only sparingly soluble in liquid ammonia (<2mM) and voltammetry was conducted in a saturated solution or in the presence of THF as co-solvent. A reversible first wave was observed and a stable radical anion was obtained (Fig. 19.1). The second wave, however, showed no anodic peak on sweep reversal and the peak separation between the two waves ($E_{p_{II}} - E_{p_I}$) was only 0.34V. This might indicate that protonation of the di-anion by solvent or supporting electrolyte (tetraethylammonium fluoroborate) is occurring, although the standard potential of the second charge transfer E_{II}° may be less cathodic with respect to E_I° in the liquid ammonia system.

cis-Stilbene is more soluble than the solid trans-isomer. Cyclic

FIGURE 19.3

cis- PhCH=CHPh(2mM) in liquid ammonia (10^{-1} M Et_4NBF_4) vs. Pb/
PDE; 100mVs^{-1} . 0.05M Pb^{2+} .

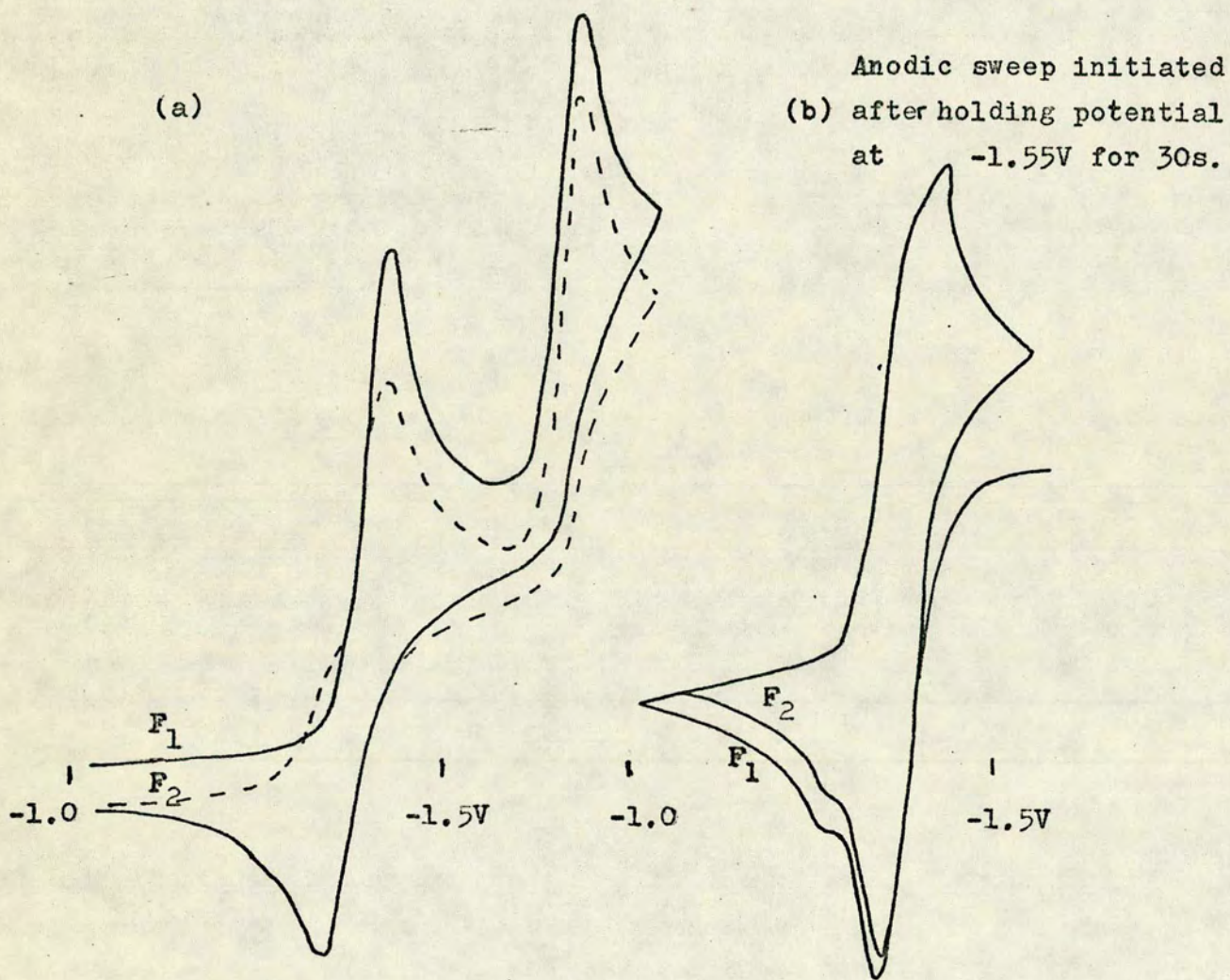


FIGURE 19.4

cis - PhCH=CHPh in liquid ammonia ($10^{-1}M$ Et₄NBF₄) vs. Pb/0.05M Pb²⁺; HMDE.

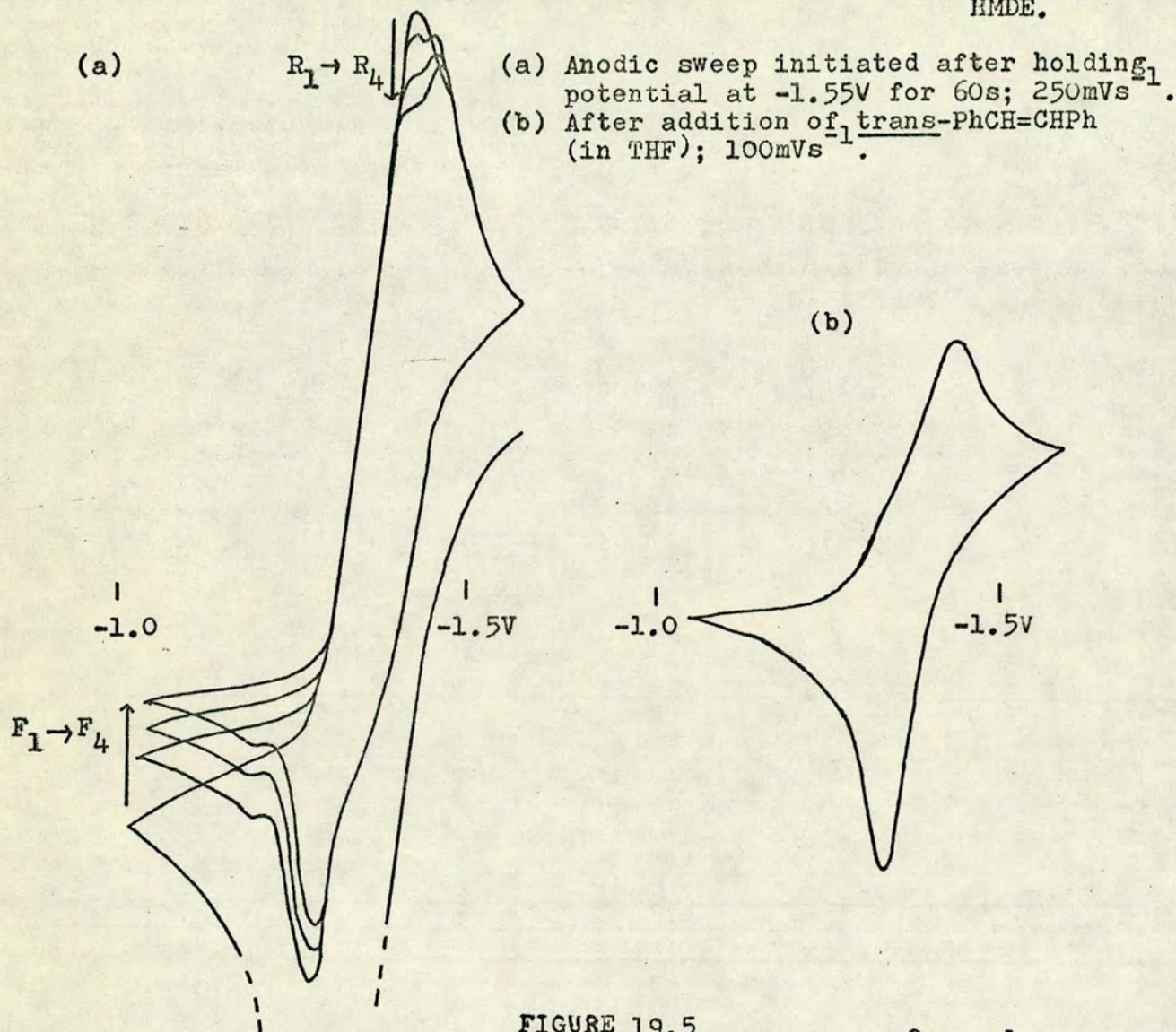
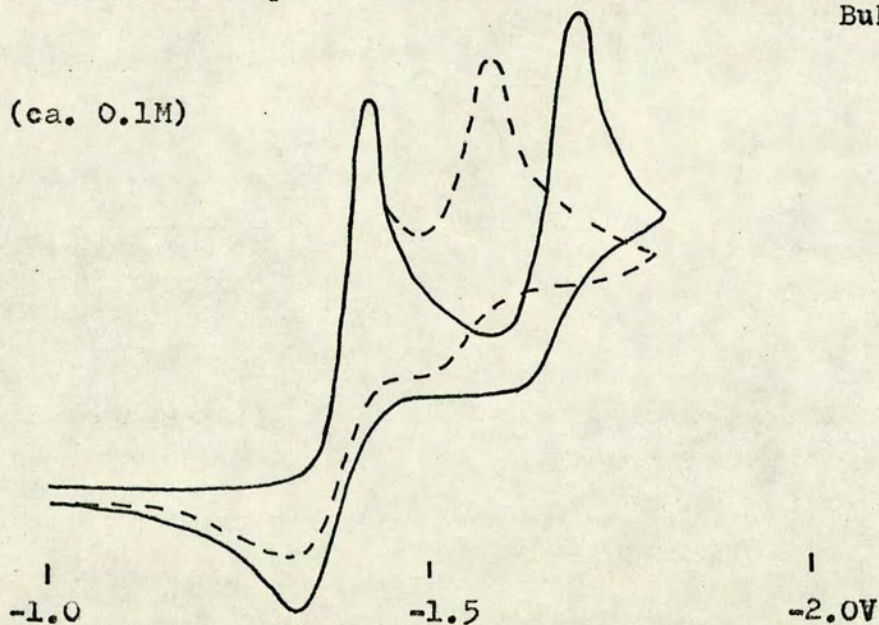


FIGURE 19.5

cis-PhCH=CHPh (2mM) in liquid ammonia vs. Pb/0.05M Pb²⁺ ($10^{-1}M$ BuMe₃NBF₄). HMDE.

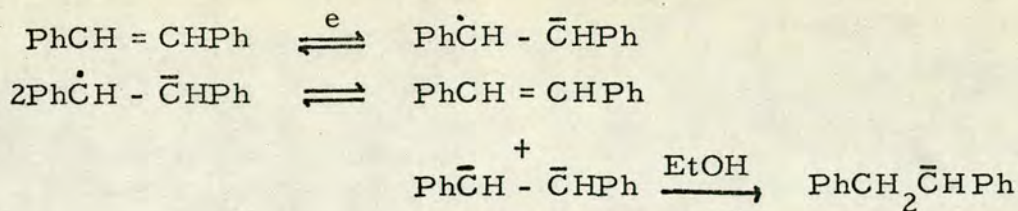
--- + EtOH (ca. 0.1M)



voltammetry in this case (Fig. 19.2) similarly indicated an eec mechanism, although a slower electron transfer to cis-stilbene is indicated by a comparison of the anodic and cathodic peak separations for the first wave (cis, 100mV vs. trans, 60mV). A cathodic shift of 0.14V in the potential of the first wave was observed on comparison with the trans-isomer. This may be in part due to the decreased reversibility of the wave, although at slower sweep speeds, when the wave approached the reversible situation, the peak potential did not approach the value of -1.29V shown by the first wave of trans-stilbene. The results suggest that trans-stilbene is more easily reduced than cis-stilbene. A similar observation was made by Parker and co-workers¹⁵⁷ in DMF; in this case the trans-isomer was found to be reduced about 0.05V more readily than the cis-isomer.

An indication of the isomerisation of cis-stilbene radical anion was given by CV studies in liquid ammonia. On the second cycle at a PDE (Fig. 19.3a) a shoulder on the first cathodic wave was observed. This was more pronounced on holding the potential between the first and second waves prior to initiating an anodic sweep and in this case a second anodic wave was also observed (Fig. 19.3b). The latter may be attributable to oxidation of the trans-stilbene radical anion, formed by isomerisation of the cis-intermediate produced at -1.55V. A similar effect, although more marked, was observed at mercury (Fig. 19.4a). Addition of trans-stilbene to a solution of the cis-isomer, however, failed to show two clearly defined sets of peaks, although considerable broadening of the anodic and cathodic waves occurred (Fig. 19.4b). Parker and co-workers¹⁵⁷ have also used CV techniques in DMF to illustrate the isomerisation described above and associated esr studies indicated that the cis-stilbene radical anion has a lifetime greater than 1 second.

Finally the effect of addition of ethanol on the voltammogram was studied (Fig. 19.5). The second wave shifted anodically indicating an increase in the rate of protonation of the di-anion; it was also diminished in height. The first wave was unaffected in position and height but a decrease in the anodic wave was observed on sweep reversal. This can perhaps be attributed to an increase in the extent of disproportionation of the stilbene radical anion to the di-anion, due to more rapid protonation of the latter:

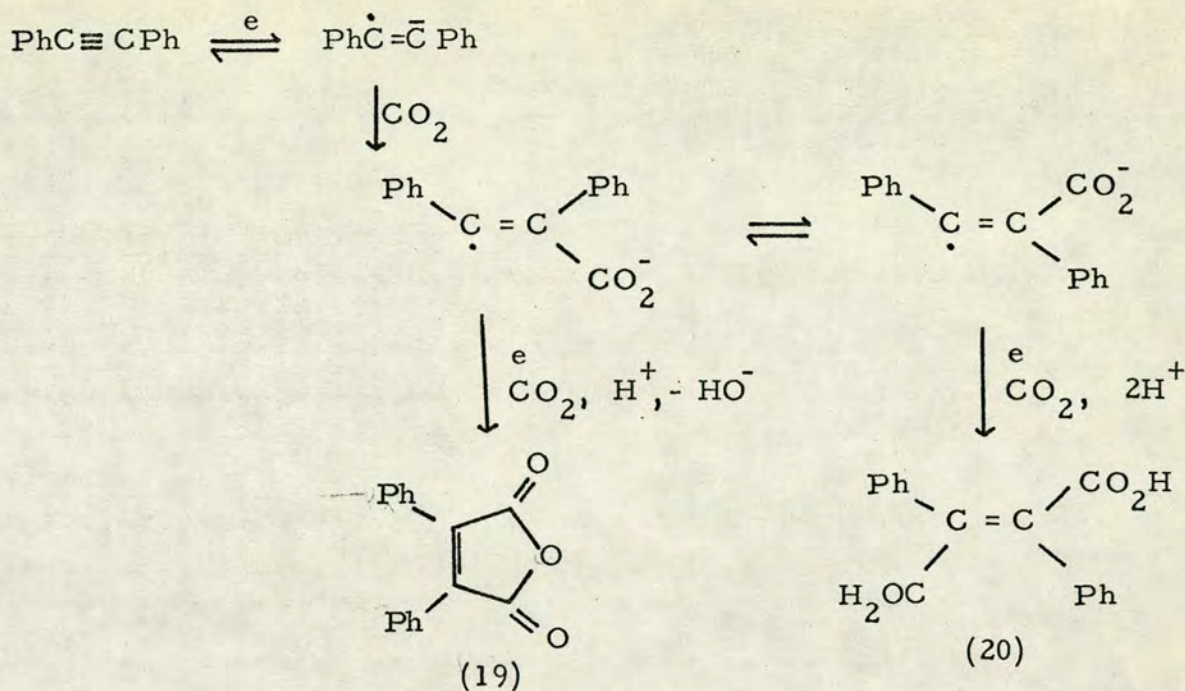


Further additions of ethanol had no effect, indicating that protonation of the radical anion by ethanol does not take place.

Additional evidence for isomerisation of the cis-stilbene radical anion was obtained by controlled potential reduction at the first wave. The transformation of cis- to trans-stilbene was achieved by either pulsing the potential between -1.5 and -1.0V at 1 second intervals or by maintaining a constant potential of -1.5V until reduction was completed, followed by re-oxidation of the radical anion at -1.0V. In both experiments the trans-isomer was precipitated from solution in good yields (60-80% based on cis-stilbene) during electrolysis. In the latter case 1, 2-diphenylethane (ca. 15%) was also formed. This presumably results from disproportionation of the stilbene radical anions under these conditions, whereas in the pulsed experiment there is less time for this to occur.

7. The Reduction of Diphenylacetylene in Liquid Ammonia

There are relatively few literature reports on the electro-reduction of diphenylacetylene. Wawzonek and Wearing¹⁵⁸ reported that diphenylacetylene exhibited two 1e waves in DMF at the DME. Large scale electrolysis at constant current afforded 1, 2-diphenylethane and 1, 2, 3, 4-tetraphenylbutane. In the presence of carbon dioxide diphenylmaleic anhydride (19), diphenylfumaric acid (20), and meso-diphenylsuccinic acid (21) were obtained. The formation of these compounds does not necessarily indicate a di-anionic intermediate; a more likely mechanism might involve carboxylation of the anion radical followed by further electron transfer and chemical reaction (Scheme 37).



Scheme (37)

Product (21) could then be formed by further reduction of the two unsaturated acids.

Studies by Sioda and co-workers,¹⁵⁹ however, indicated that polarography in DMF exhibits two 2e charge transfer, the number of electrons transferred being inferred by measurement of the diffusion constant, I_d . The authors were unable to observe an esr spectrum for the radical anion of diphenylacetylene at room temperature, although a stronger, better resolved spectrum was obtained at -40°C . Two mechanisms for the reduction at room temperature were postulated, involving a first wave corresponding to the transfer of either 2 electrons [Scheme 38, steps (a) - (d)] or 3 electrons [Scheme 38, steps (a) - (e)]. It was suggested that intervening chemical steps may have the effect of reducing the current expected for a 3e process, thus bringing the latter mechanism into line with the polarographic data. Kinetic effects were also inferred by the irreversibility of the first wave (slope of the plot of $\log \frac{i}{i_d - i}$ vs. $E = 82\text{mV}$). The mechanisms involve the formation of either stilbene or its radical anion at the first wave. (Scheme 38).

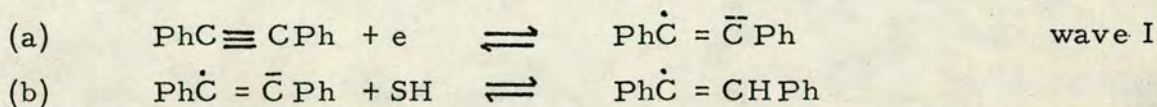


FIGURE 20.1

PhC≡CPh(2mM) in liquid ammonia ($10^{-1}M Et_4NBF_4$) vs. Pb/0.05M Pb²⁺; DME.

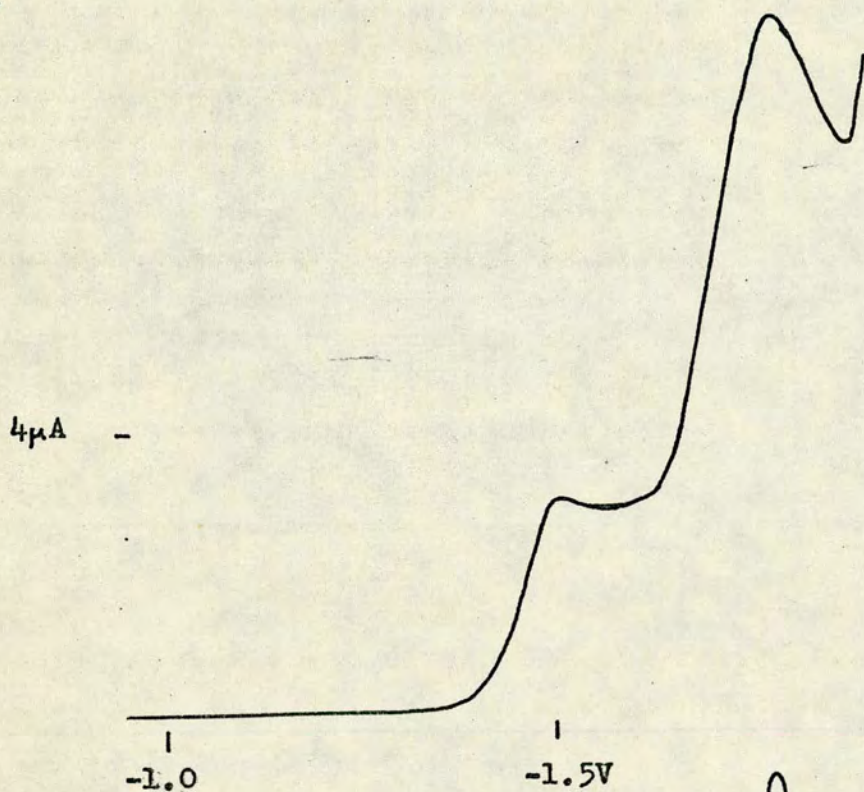
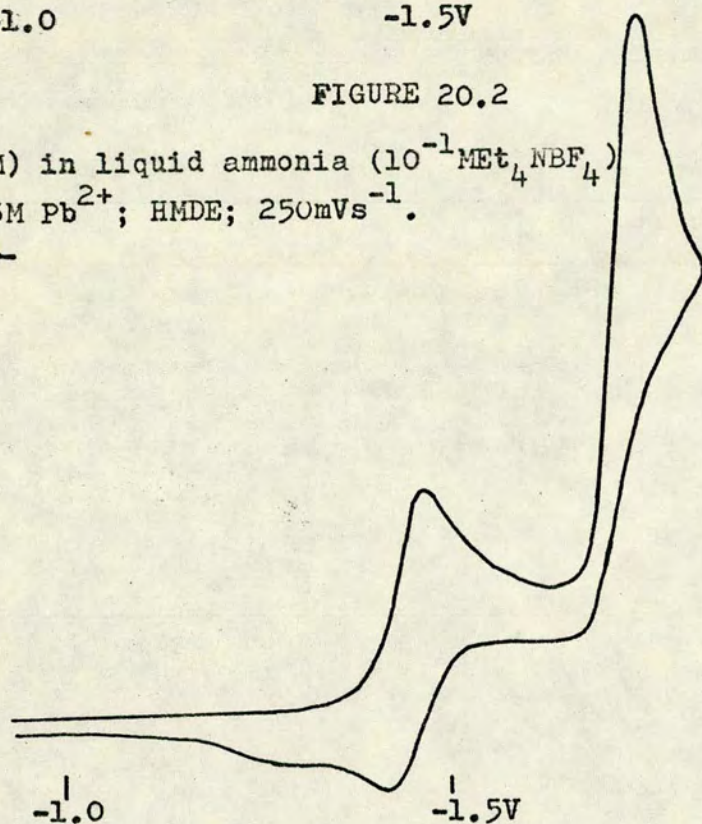


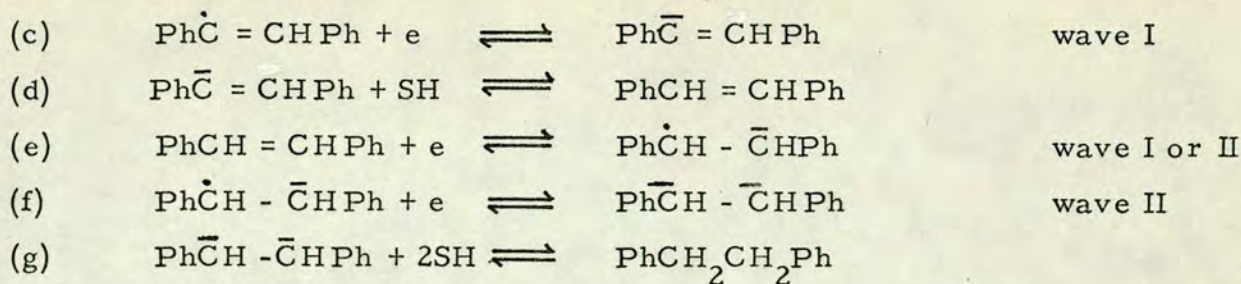
FIGURE 20.2

PhC≡CPh(2mM) in liquid ammonia ($10^{-1}M Et_4NBF_4$) vs. Pb/0.05M Pb²⁺; HMDE; $250mVs^{-1}$.

5 μA -

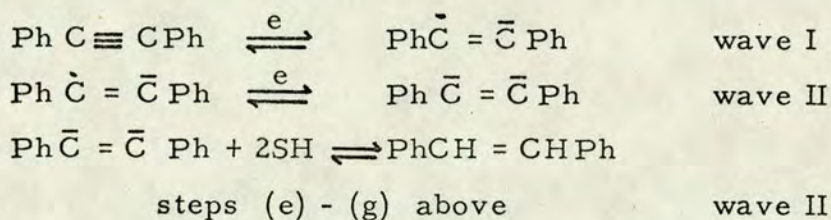


wave	E_{p_c} (V)	$E_{p_a} - E_{p_c}$ (mV)	i_d (μA)	$\frac{i_{p_a}}{i_{p_c}}$
I	-1.48	50	2.38	1.05
II	-1.67	-	5.98	-



Scheme (38)

An additional mechanism, involving an initial 1e transfer at the first wave followed by a second electron transfer at a more negative potential, was thought to be more significant at lower temperatures. Protonation of the diphenylacetylene di-anion and steps (e) - (g) of Scheme (38) completed the process [Scheme (39)].



Scheme (39)

It was suggested that at lower temperatures formation of the diphenylacetylene radical anion was possible due to a decrease in the homogeneous reaction rates, and explained why observation of an esr spectrum of the radical anion was possible under these conditions .

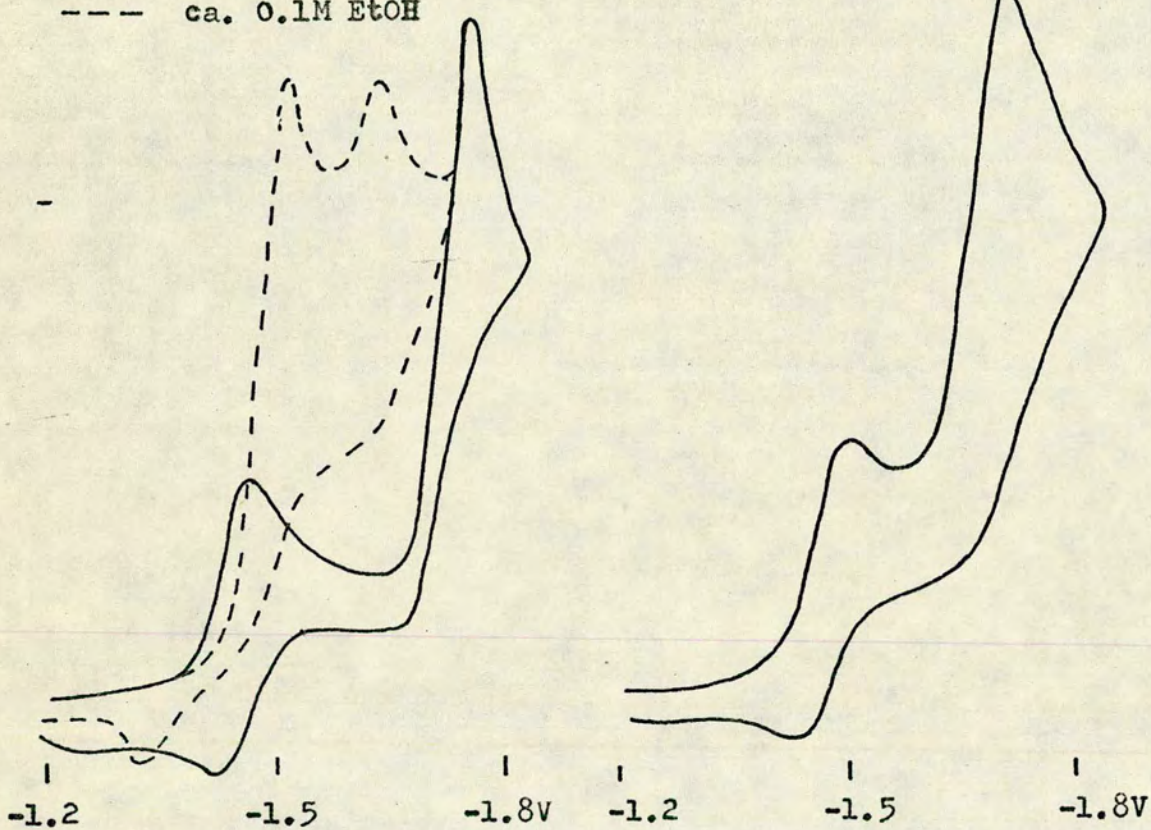
Diphenylacetylene is sparingly soluble in liquid ammonia. Polarography and cyclic voltammetry showed two waves (Figs. 20.1 and 20.2). The first wave was smaller than that previously observed for a 2mM solution of depolariser (see Table X). It is possible that undissolved solid was present but not visible. Assuming that the first wave represents a 1e transfer, the height of the second wave corresponds to the transfer of 2-3 electrons. The first wave showed reversible behaviour, indicating that a stable radical anion of diphenylacetylene is formed in liquid ammonia. The second wave exhibited no anodic peak on sweep reversal. The mechanism of reduction in liquid ammonia thus appears to be analogous to that described in Scheme (39).

FIGURE 20.3

$\text{PhC}\equiv\text{CPh}$ (2mM) in liquid ammonia ($10^{-1}\text{M Et}_4\text{NBF}_4$) vs. $\text{Pb}/0.05\text{M Pb}^{2+}$;
HMDE; 250mVs^{-1} .

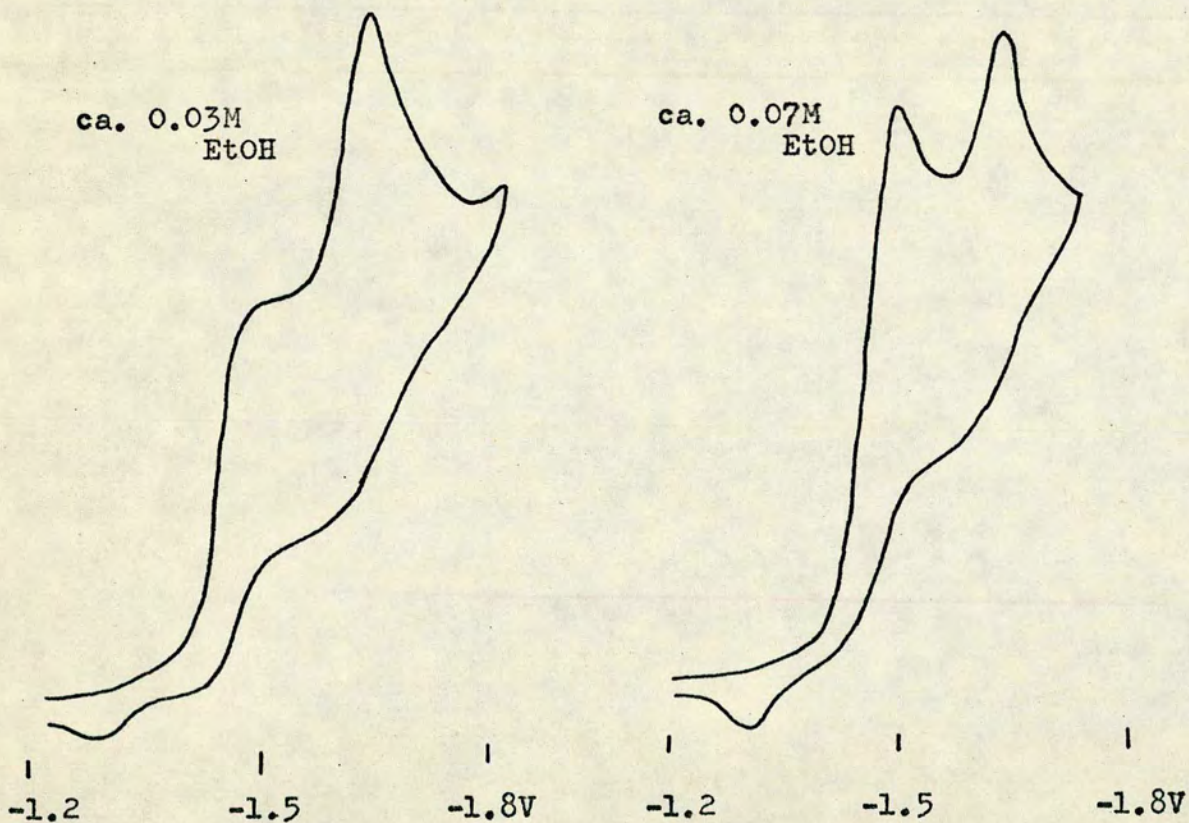
— no EtOH
--- ca. 0.1M EtOH

ca. 0.005M EtOH

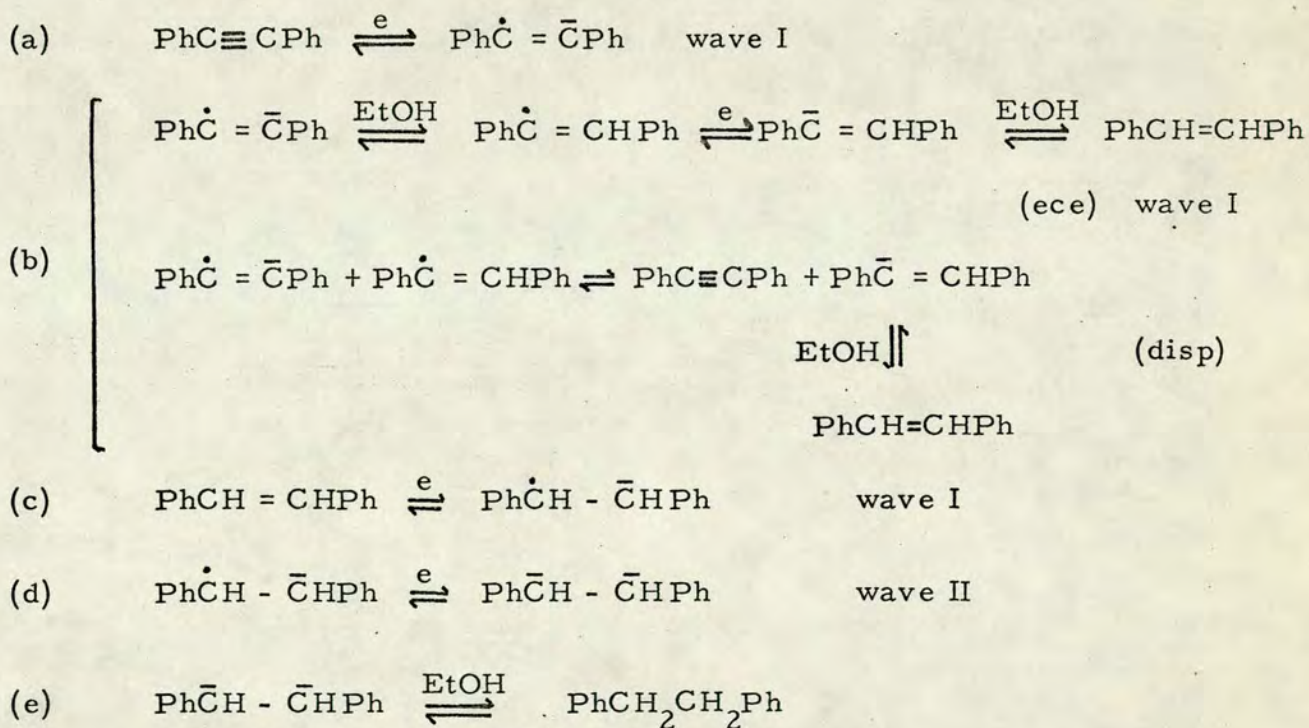


ca. 0.03M EtOH

ca. 0.07M EtOH



The addition of ethanol to the solution had a marked effect upon the cyclic voltammogram (Fig. 20.3). The first wave became irreversible and increased in height until it became considerably larger than the second wave at ca. 0.1M ethanol. The latter shifted anodically. The results suggest that the diphenylacetylene radical anion is rapidly protonated in ethanol to form the corresponding radical. This may then accept a second electron (ece mechanism) or disproportionate with the radical anion produced by the first electron transfer. These processes are thermodynamically equivalent⁹ as has been discussed previously for the reduction of acetophenone (Section A). At the potential of the first wave, the stilbene, formed by the above processes would itself be reduced to the radical anion. In the presence of ethanol, the first wave would thus correspond to a 3e transfer [Scheme (40), steps (a)-(c)].

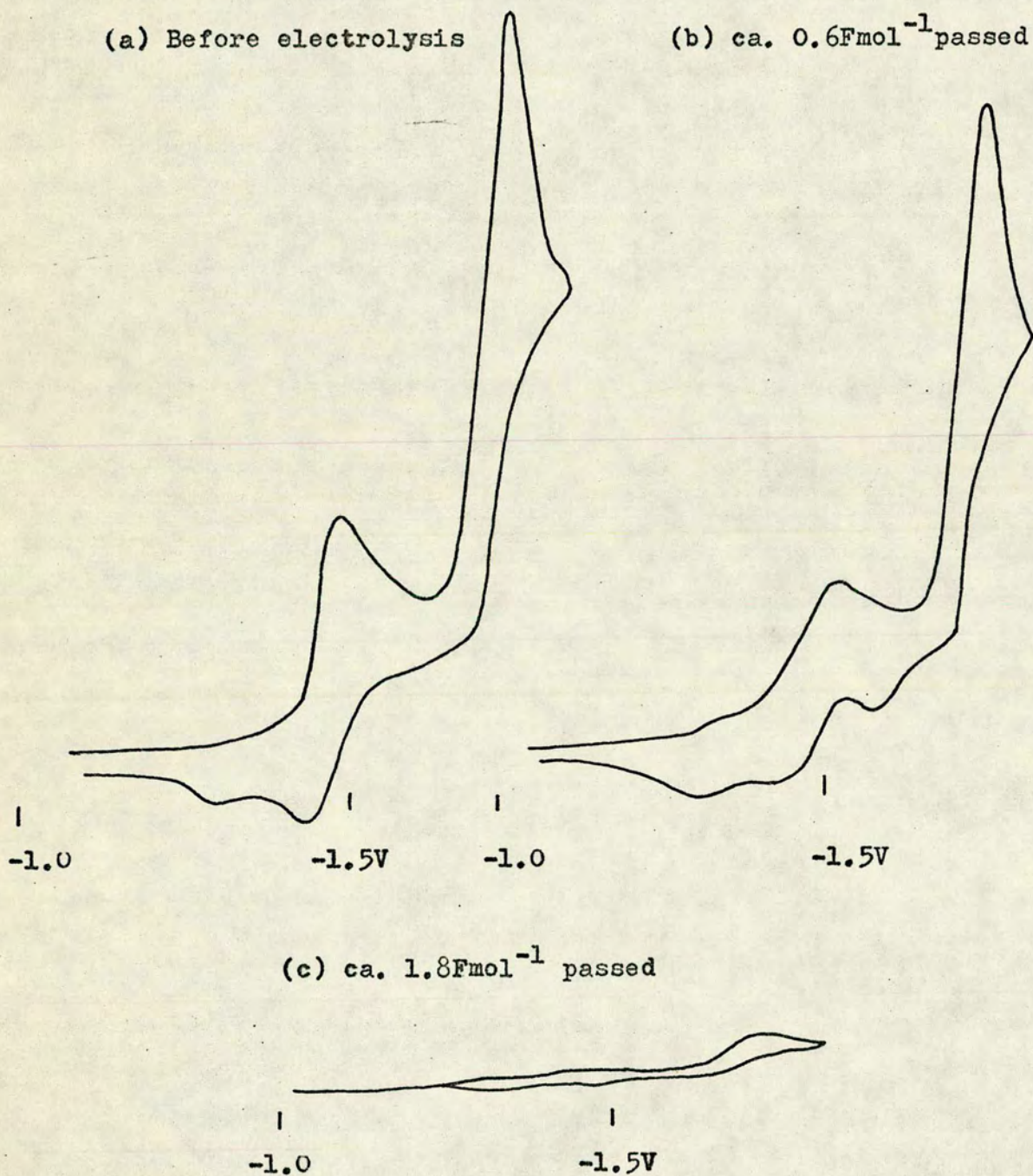


Scheme (40)

Previous studies on the reduction of stilbene in the presence of ethanol (see back) indicated that protonation of the stilbene radical anion does not take place. The second wave for reduction of diphenylacetylene in the presence of ethanol thus corresponds to steps (d) and (e) (Scheme 40) to afford 1, 2-

FIGURE 20.4

$\text{PhC}\equiv\text{CPh}$ (10^{-4} mole) in liquid ammonia (10^{-1} M Et_4NBF_4) vs. $\text{Pb}/0.05\text{M}$ HMDE for CV; Hg pool for electrolysis; 250mVs^{-1} . Pb^{2+}



diphenylethane, the potential corresponding closely to that observed for E_2 for the reduction of stilbene in the presence of 0.1M ethanol (Fig. 19.5).

Controlled potential reduction of diphenylacetylene was conducted (a) at mercury in the presence of tetraethylammonium fluoroborate, (b) at platinum in the presence of potassium iodide (after first pre-treating the solution with solvated electrons), and (c) in a 25% of THF in ammonia. In each case a mixture of unreacted acetylene (22), trans-stilbene (23), and 1,2-diphenylethane (24) was obtained. The relative yields from these experiments is summarised below:

	(22)	(23) relative %	(24)
(a) wave II (3.1F mol ⁻¹ passed)	28	24	48
wave I (2.5F mol ⁻¹ passed)	28	40	31
(b) wave II	unestimated		
(c) wave I (3.5F mol ⁻¹ passed)	19.7	7.8	72.5

The observation that reduction at the second wave affords 1,2-diphenylethane is in accordance with the CV results. Protonation of the intermediates presumably involves ammonia, since reduction in the presence of potassium ions similarly afforded this product; reduction might otherwise have been expected to stop at the trans-stilbene stage. The lime-green colour initially formed during electrolysis at the first wave is possibly due to the radical anion of diphenylacetylene, although the disappearance of this colour and the production of 1,2-diphenylethane indicates that disproportionation occurs on the preparative time-scale. In a 25% solution of THF, the yield of 1,2-diphenylethane was considerably higher. This would partly be due to the more extensive electrolysis (3.5 F mol⁻¹ passed) but might also be due to the higher concentration of substrate (and hence trans-stilbene) in solution, which would favour disproportionation.

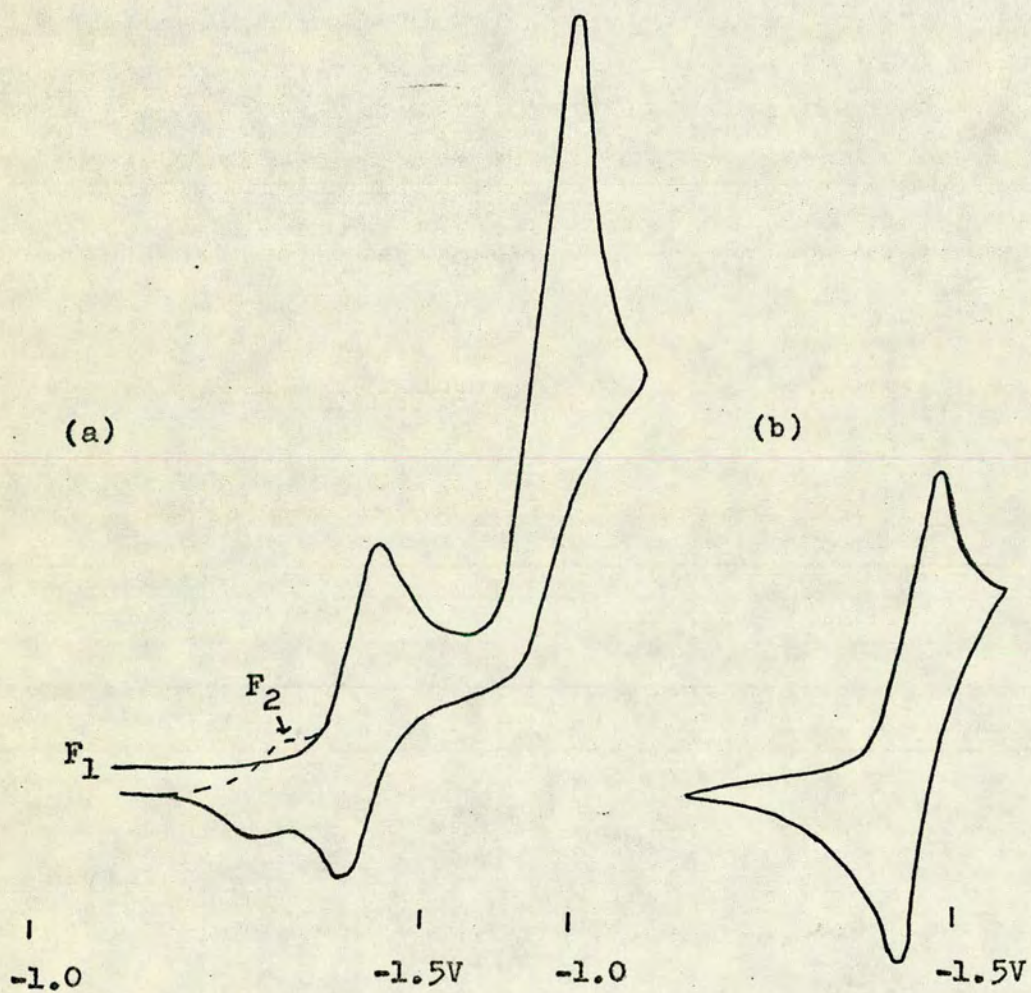
Some evidence for trans-stilbene as an intermediate in the reduction was afforded by CV. A voltammogram of a partially reduced solution (Fig. 20.4) exhibited oxidation-reduction waves anodic of the waves for diphenylacetylene. These may be attributable to reduction of trans-stilbene.

FIGURE 20.5

$\text{PhC}\equiv\text{CPh}$ (1mM) in liquid ammonia ($10^{-1}\text{M Et}_4\text{NBF}_4$) vs. $\text{Pb}/0.05\text{M Pb}^{2+}$;
PDE; 250mVs^{-1} .

(a) Sweep of -1.0 to -1.7V

(b) Sweep of -1.0 to -1.45V



The premature decrease in current during this experiment, from 18mA to 0.3mA after the passage of only $1.8F \text{ mol}^{-1}$, was probably due to undissolved substrate (and possibly trans-stilbene), which adhered to the sides of the cell above the solution level. Similar waves were observed on CV studies involving a second cycle (Fig. 20.5a); these waves were only present if the potential sweep extended beyond the second wave for diphenylacetylene.

EXPERIMENTAL SECTION

¹H Nuclear Magnetic Resonance Spectra were run on an E. M. 360 (60 MHz) or a Varian Associates H. A. 100 Spectrometer (100 MHz). Tetramethyl silane was used as the internal reference and all chemical shifts are quoted in p. p. m. (δ scale) with tetramethylsilane as 0 p. p. m. In the description of n. m. r. spectra the following abbreviations are used: singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). J is the coupling constant quoted in Hertz (Hz). ¹³C n. m. r. spectra were recorded on a Varian CFT-20 Spectrometer.

A Perkin Elmer 157G Spectrophotometer was used to record infra-red spectra and a Unicam S. P. 800A Spectrophotometer for ultra-violet spectra.

Mass spectra were run on an A. E. I. M. S. 902 double focussing instrument and mass spectra/g. l. c. on a V. G. Micromass 12, following analysis on a Perkin Elmer Model F. 11 gas chromatograph.

Gas chromatographs were otherwise recorded on a Pye 'Series 104' Model 24 instrument and peak areas integrated on a Kent Chromalog 3 Digital Integrator. Preparative g. l. c. separations were made on a Wilkins Instrument and Research Inc. Aerograph Autoprep Model A-700.

A Hermes Series 50 Potentiostat and a Chemical Electronics Transistorised Potentiostat Type TR70/2A were used for preparative electrolyses. Polarography, linear sweep voltammetry and cyclic voltammetry were carried out using a Chemical Electronics Linear Sweep Unit L. S. U. 1 and a Waveform Generator Type R. B. 1. The latter was also used for pulsed potential experiments. Current/potential (I/V) curves and current/time (I/t) curves were recorded on a Bryans X-Y/t Plotter Model 21005, or on a Tektronix 5103N storage oscilloscope. Polarographic cell currents were damped prior to recording by means of a 60 μ F capacitor. A counting resistor of 47,000 ohms was generally employed for use with a dropping mercury electrode, hanging mercury drop electrode and platinum disc electrode. A smaller counting resistor (about 4,700 ohms) was found suitable for use with the

platinum wire electrodes.

A N_2/H_2 coulometer (500 ml capacity) was used for current/time integrations during preparative electrolyses.

The alumina used in all chromatographic separations was of Activity III and contained Woelm Fluorescent Indicator Green.

Melting points were determined on a Reichert hot stage microscope.

The gaseous nitrogen used during electrochemical procedures was oxygen-free and was dried prior to use by passage over molecular sieve and self-indicating silica gel.

Supporting electrolytes were dried in vacuo at $100^\circ C$ for 24 h before use and solvents were purified as described.

Unless otherwise indicated all preparative electrolyses were carried out in a divided cell containing working, reference and secondary compartments. For analytical studies the working and secondary electrodes were usually assembled in the same compartment.

Electrode potentials were measured using either a Philips Digital Multimeter P4 2421 or a Keighley 616 Digital Electrometer.

A. Electrochemistry in Acetonitrile

I. General Techniques

Preparation of High Purity Acetonitrile

Acetonitrile was obtained from Fisons (Reagent grade) and was purified before use as an electrochemical solvent.

Initially¹⁸ purification involved distillation of commercial acetonitrile (800 ml) from anhydrous sodium carbonate (10 g) and potassium permanganate (15 g). The distillate was then made slightly acidic (concentrated sulphuric acid) and decanted from the precipitated ammonium sulphate. The purified solvent, b. p. 82.0°C, was distilled slowly through a Vigreux column, the first 40 ml being discarded.

A simpler method¹⁹ involved refluxing the solvent (1 l) over phosphorus pentoxide (2 g) for 10 minutes followed by rapid distillation. A similar treatment using calcium hydride was then carried out, the first and last 5% of the distillate from each distillation being discarded.

The solvent was stored over molecular sieve.

The water content of the purified acetonitrile, as prepared by the latter method, was estimated, by means of a Karl Fischer titration, at about 120 p. p. m., as compared to 1000 p. p. m. for the untreated solvent.

Cell Construction

(i) The Cell. A conventional H-type cell was used, the working and secondary compartments being separated by a glass frit. Each limb of the cell terminated in a large socket joint which accommodated the multi-joint cell heads. The latter held the electrodes and the inlet and the outlet tubes, which enabled the cell contents to be flushed with nitrogen.

(ii) Working Electrodes. For analytical studies either a DME or a platinum wire electrode was used. The latter was constructed by sealing a short length of platinum wire, soldered to a longer length of copper wire, into soda glass tubing, and fusing a small sphere of glass

onto the tip of the platinum wire. Electrical contact was made by means of the copper wire. The electrode was cleaned by immersion in hot aqua regia and washed with distilled water before use.

For preparative studies a mercury pool or platinum foil electrode was used.

(iii) Secondary electrode. A platinum foil electrode was used.

(iv) Reference electrode. The reference compartment was constructed by drawing out a length of pyrex tubing to make a narrow-bore tip, the end of which was plugged with glass wool. The plug was constructed so that leakage of the reference solution was minimal but sufficient to maintain electrical contact. The compartment was filled with a solution of silver nitrate (0.1M) in dry acetonitrile and a length of silver wire, fixed to glass tubing at its upper end, was fitted into the compartment.

The reference electrode was positioned via a screw-cap joint, at an angle to the horizontal, to a side-arm about half-way down the working compartment. The joint enabled the electrode to be moved along the axis of the side-arm, but the angle to the horizontal could not be varied. Thus, during potentiostatic reductions at a mercury pool electrode, the tip of the reference electrode could not be positioned very close to the cathode surface.

II Electrode Reductions of Organic Compounds

Supporting Electrolytes and Cathodic Limits in Acetonitrile

Tetrabutyl- and tetraethyl-ammonium fluoroborates were both readily soluble in acetonitrile ($>0.1M$) and gave similar polarographic ranges (Fig. 1). The range at a platinum wire electrode was considerably less than at mercury (Fig. 2). Tetramethylammonium iodide was less soluble in acetonitrile (ca. $0.1M$) and did not give an improved range. Lithium perchlorate however was readily soluble and gave an extended range at platinum compared to the quaternary ammonium salts but was less suitable for use with a mercury electrode (Fig. 3). The cathodic ranges available in acetonitrile in the presence of various supporting electrolytes have been summarised (Table I).

An impurity wave ($E_{\frac{1}{2}} -2.6V$), attributable to acrylonitrile, was always observed in the background current-voltage curves (Fig. 1a). This was reduced in height by pre-treating the electrolyte solution before use. A potential of $-3.0V$ at a mercury pool electrode was maintained until the background current decreased to zero, the pre-treatment being carried out both before analytical and preparative studies.

Reduction of 5, 10-Dihydro-5, 10-dimethylphenazine (DMPZ)

Estimation of Electrode Reversibility.

The polarographic and cyclovoltammetric oxidation of DMPZ in acetonitrile was studied in order to determine the degree of wave reversibility obtainable using the apparatus described previously.

A solution of the depolariser (2mM) in acetonitrile containing tetraethylammonium perchlorate (0.1M) showed two 1e oxidation waves at a platinum wire electrode (Fig. 4. 1). The second oxidation wave occurred at a positive potential and could not be studied by polarography. A polarogram of the first wave (Fig. 4. 1) enabled graphs of $\log \frac{i}{i_d - i}$ vs. $-E$ and h (uncorrected) vs. i_d to be plotted (Figs. 4. 3 and 4. 4).

Analytical Studies: Polarography and Cyclic Voltammetry

1. The Reduction of Acetophenone in Acetonitrile

Polarograms of acetophenone were recorded in solutions of tetraethyl- (Fig. 5.1) and tetrabutyl- (Fig. 5.4) ammonium salts in acetonitrile. The effect of addition of water to the former was investigated (Fig. 5.3). A cyclic voltammogram was also recorded in the presence of a tetraethylammonium salt (Fig. 5.2).

No reduction waves for acetophenone were observed when lithium iodide was used as the supporting electrolyte and addition of lithium ions also caused the disappearance of the reduction waves observed in the presence of a quaternary ammonium salt.

The controlled potential reduction of acetophenone in acetonitrile was also followed polarographically (Fig. 5.5).

2. The Reduction of 3-Methylcinnamionitrile in Acetonitrile

Polarography and CV of 3-methylcinnamionitrile was conducted in solutions of tetrabutyl- and tetraethyl-ammonium salts (Figs. 6.1, 6.2 and 6.3). A polarogram was also recorded in an 80% aqueous solution of acetonitrile (Fig. 6.4).

3. The Reduction of 3, 3-Dimethylacrylonitrile in Acetonitrile

Acetone was electro-inactive in acetonitrile. 3, 3-Dimethylacrylonitrile was however reducible just prior to the cathodic limit and polarography and CV were carried out in the presence of tetraethylammonium fluoroborate (Figs. 7.1 and 7.2). In association with these studies a polarogram of azobenzene was also recorded (Fig. 7.3).

4. The Reduction of Benzoylcyclopropane in Acetonitrile.

A comparison of the polarograms of benzoylcyclopropane, when conducted in the presence of tetramethyl-, tetraethyl- and tetrabutyl-ammonium salts, was made (Fig. 8.1). The slopes of the graphs, obtained by plotting $-E$ vs. $\log \frac{i}{i_d - i}$ for the first wave, were also compared in the latter two cases (Fig. 8.2). The effect of water on the polarogram (Fig. 8.4) and a cyclic voltammogram (Fig. 8.3) were also recorded.

Preparative Studies: Controlled Potential Reductions in Acetonitrile

Reductions were generally carried out at a mercury pool cathode in a 3-compartment cell. Prior to addition of substrate, the catholyte was pre-treated at -2.8V, the background current typically decreasing from 10mA to 0.5mA.

At the end of the electrolysis, the catholyte was quenched with ammonium chloride. Failure to do this resulted in the formation of 4-amino-2,6-dimethylpyrimidine, which was obtained as white crystals on distillation of the extracted product mixture. The crystals, m. p. 176°C (lit $182\text{-}183^{\circ}\text{C}$) were identified by their n. m. r. spectrum (60 MHz, CDCl_3) δ 2.3 (s, 3H, 6- CH_3) 2.44 (s, 3H, 2- CH_3) 5.0 (broad s, 2H, NH_2) 6.08 (s, 1H, CH) and synthesis of an authentic sample.⁶⁷

After addition of ammonium chloride, the usual work-up procedure involved concentration of the catholyte solution by distillation of acetonitrile on a rotary evaporator, addition of water (25 ml) to the residue, and extraction of the aqueous layer with ether (3 x 100 ml). The combined extracts were washed with brine, dried (anhydrous MgSO_4) and concentrated.

1. Reduction of Acetophenone in Acetonitrile

Acetophenone (1.2 g, 0.01 mole) was reduced potentiostatically (-3.0V) at a mercury cathode in a solution of tetraethylammonium fluoroborate (0.1M). An initial cell current of 90mA rose to 125mA during the first hour and then decreased to about 20mA after 4 hours. Continued electrolysis resulted in no further decrease in current (1090 C passed; 2e reduction requires 1930C). At the start of the electrolysis a brown colour streamed from the surface of the electrode until eventually a brown solution was obtained. The final pH of the cathodic and anodic solutions was 9.0 and 6.0 respectively.

The catholyte was worked-up in the usual manner to give a brown oil (1.66 g) whose n. m. r. spectrum (60MHz, CDCl_3) was complex δ 1.0-4.0, 7.1-7.6, the ratio of aliphatic to aromatic protons being

about 5:9. Absorption in the infra-red occurred at 3470, 3380, 2250 and 2180 cm^{-1} suggesting the presence of amino or hydroxyl and cyano groups. The major signals in the mass spectrum were observed at m/e 184, 145, 144, 106, 105, 103, 79, 77, 51. T.l.c. (alumina, eluent 50:50 petrol-ether) also indicated a complex mixture and g.l.c. (APL, 175°C) showed, in addition to unreacted acetophenone, one major peak and one minor peak. Separation of the minor component, following a larger scale preparation, was achieved by preparative g.l.c. (10% SE 30, 200°C). Examination of its n.m.r. spectrum and mixed injection on g.l.c. with an authentic sample confirmed its identity as 3-methylcinnamionitrile.

The crude reaction mixture was separated by wet column chromatography (alumina; eluent petrol/ether, ether and ether/ethanol). A colourless liquid, corresponding to the major peak observed by g.l.c., was readily eluted and identified as 3-phenylbutyronitrile (0.48 g, 34.5%) on spectral evidence. Characteristic nitrile absorption was observed in the i.r. spectrum (liquid film) at 2225 cm^{-1} and its n.m.r. spectrum (100 MHz, CCl_4) δ 1.39 (d, 3H, CH_3 ; $J = 7\text{Hz}$) 2.43 (d, 2H, CH_2 ; $J = 7\text{Hz}$) 3.07 (sextet, 1H, CH; $J = 7\text{Hz}$) 7.15 (m, 5H, aromatic); the assignment was confirmed by proton decoupling. ^{13}C n.m.r. spectroscopy showed signals at p.p.m. 20.593 (CH_3) 26.191 (CH_2) 36.415 (CH) 126.362 (Ph, C_2 and C_6) 127.099 (Ph, C_4) 128.644 (Ph, C_3 and C_5) 142.982 (Ph, C_1) and a parent ion m/e 145 was formed in the mass spectrum, with fragmentation giving rise to peaks at m/e 130 (P-CH_3), and 105 ($\text{P-CH}_2\text{CN}$).

A more polar liquid fraction was collected (0.828 g) whose major component corresponded to 3-methyl-3-phenylglutarodinitrile (ca 40%) as shown by n.m.r. spectroscopy. The presence of a minor component in the latter was indicated by mass spectral, n.m.r. and i.r. evidence. The mass spectrum of the mixture showed signals at m/e 288 and 184, the latter corresponding to the parent ion of 3-methyl-3-phenylglutarodinitrile. Unassigned signals in the n.m.r. spectrum of the mixture (60 MHz, CDCl_3) δ 0.8-3.7, 7.1-7.3 were weak and

complex. I. r. spectroscopy indicated, in addition to the dinitrile compound, the presence of a primary amine $3450, 3350$ and 3230 cm^{-1} , together with a low frequency nitrile absorption at 2180 cm^{-1} characteristic of unsaturated nitriles. This, together with a peak in the u. v. spectrum (EtOH) at $\lambda_{\text{max}} 260 \text{ m}\mu$ suggested the identity of the minor component as 1-amino-2-cyano-3,4-dimethyl-3,4-diphenylcyclopent-1-ene, the highest mass peak at 288 corresponding to the parent ion of $\text{C}_{20}\text{H}_{20}\text{N}_2$. Comparison of the u. v. spectrum with that of an authentic sample of this compound supported the assignment. Attempts to separate this product from 3-methyl-3-phenylglutaronitrile by distillation (boiling range $90\text{-}130^\circ\text{C}/0.2 \text{ mm}$) or by chromatography failed. After distillation, the residue contained the greatest proportion of the unsaturated compound as shown by i. r. spectroscopy.

In addition to the major reaction products described above, small amounts of the pinacol and 1-phenylethanol (ca 5%) were also indicated by peaks in the mass spectrum at m/e 242, 122 and 121.

Similar reduction products were obtained when electrolysis was carried out at the potential of the first wave (-2.5V) and at a platinum electrode. Addition of water (1%) to the solvent had little effect on the course of reaction as indicated by an n. m. r. spectrum of the crude product mixture.

Current-time Curves for Reduction of Acetophenone

The reduction of acetophenone (1.2 g, 0.01 mole) was carried out as described previously, the cell current being monitored during the electrolysis. A graph of current versus time was plotted (Fig. 5.6).

Analysis of the product mixture by column chromatography indicated 3-phenylbutyronitrile (34.5%), representing a current efficiency of 61% for formation of this compound (1093 C passed; 666 C required for 34.5% yield of 2e reduction product). Other reduction products, 1-phenylethanol, the pinacol, and 1-amino-2-cyano-3,4-dimethyl-3,4-diphenylcyclopent-1-ene could not be estimated with sufficient accuracy to determine the current efficiencies for their formation.

Attempt to Follow the Electrochemical Reduction of Acetophenone
by Polarography and Spectroscopy

Acetophenone (0.0005 mole) was reduced at a mercury pool cathode as described previously. Polarograms were recorded before reduction was commenced and after the passage of a known number of coulombs (Fig. 5.5) (96.5 C required for 2e reduction). An initial cell current of 30mA decreased to 10mA (48 C passed) and reduction was terminated when the cell current had dropped to 1.0mA (86 C).

During a similar reduction of acetophenone (0.01 mole) it was hoped to examine the catholyte solution by i. r. and n. m. r. spectroscopy. Preliminary observations on the spectroscopy of the possible products of reduction in a solution of tetraethylammonium fluoroborate in acetonitrile using the pre-treated cathode solution as a blank, established that in the i. r. spectrum peaks for acetophenone were visible at 1680, 1260, 955, 750 and 690 cm^{-1} . No absorption of 3-phenylbutyronitrile or 3-methyl-3-phenylglutaronitrile was visible in the available range but peaks for 3-methylcinnamonnitrile could be observed at 2210 and 830 cm^{-1} . In the n. m. r. spectrum a range downfield from δ 4.0 was visible. A sample of the catholyte was withdrawn after the passage of 150 C (2e reduction requires 1930 C), and examination by i. r. spectroscopy suggested that a small amount of 3-methylcinnamonnitrile had been formed in addition to peaks corresponding to unreacted acetophenone. In the n. m. r. spectrum (60MHz) a signal δ 7.03 (s) had appeared in addition to signals corresponding to the aromatic protons of acetophenone.

The catholyte was then stirred overnight without the passage of any more current and its components were separated by dry column chromatography after extraction into ether in the normal manner. The weight of crude product (0.28 g) was considerably lower than in previous reductions and this was thought to be due to evaporation from the catholyte during stirring. The electrolysis products, 3-methylcinnamonnitrile (0.13 g), 1-phenylethanol (0.07 g) and pinacol (0.07 g) were identified by n. m. r. spectroscopy of the column fractions.

Influence of Electrode Area, Potential and Cell Current on Product Distribution

During the course of several reductions of acetophenone, it was observed that the electrode area and the position of the reference electrode with respect to the cathode surface had an effect on the product distribution.

The initial experiments (expts 1-4, Table II), were carried out using a mercury pool of unspecified area (volume ca 3-5 ml; area ca 10-15 cm²). The reference electrode was positioned in the bulk solution about 2.0 cm above the cathode surface. Under these conditions an 'apparent' voltage of -3.0V as measured by a voltmeter, could be applied (although the true potential of the working electrode would be considerably lower) and the cell current was relatively large (60-100 mA). The effect of moving the reference electrode nearer to the cathode was to overload the potentiostat so that the set voltage of -3.0V could not be maintained. This could be remedied by reducing the area of the mercury pool and the subsequent electrolyses (expts 5-8, Table II) were carried out using a small electrode (volume ca 1.0 ml; area ca 3.0 cm²) and a reference electrode more closely positioned to the mercury surface. Under these latter conditions the initial cell current was lower (20-40mA).

The product yields obtained under these varying cell conditions are summarised (Table II).

Reduction of Acetophenone in 10% Aqueous Acetonitrile

A similar reduction of acetophenone (0.01 mole) was carried out in acetonitrile containing water (10% by volume). The potential was maintained at -2.8V, the initial cell current of 60mA increasing gradually to 83mA after about 3 hours and then decreasing rapidly to 12mA (1323 C passed; 2e reduction requires 1930 C). The catholyte was extracted into ether in the usual manner to afford, on evaporation of solvent, a white solid whose n. m. r. spectrum indicated mainly the pinacol (1.0 g, 82%) with a small amount of starting material.

Preparation of 1-Phenylethanol

Sodium borohydride (0.5 g) was added gradually with stirring to a cooled solution of acetophenone (1.2 g, 0.001 mole) in dry methanol (20 ml). The mixture was stirred for 30 minutes at room temperature, after which time water (40 ml) was added. The aqueous methanol was then extracted (x3) with ether and the extracts were washed, dried and concentrated. The crude product was distilled to afford 1-phenylethanol (0.8 g, 65%) b. p. $99^{\circ}\text{C}/3.0\text{ cm}$ N. m. r. (60MHz, CCl_4) δ 1.28 (d, 3H, CH_3 ; $J = 8\text{Hz}$) 3.75 (d, 1H, OH, $J = 4\text{Hz}$) 4.59 (d of q, 1H, CH) 7.12 (s, 5H, aromatic).

Preparation of 2,3-Diphenylbutan-2,3-diol (the Pinacol of Acetophenone)

The electrochemical reduction of acetophenone was carried out in a 3-compartment cell at a mercury pool cathode. The anode compartment contained a solution of lithium chloride (0.1M) in 80% aqueous ethanol and the catholyte consisted of a solution of potassium acetate (2.0M) in the same solvent. Polarography indicated a cathodic range of -1.7V (vs. SCE); addition of acetophenone reduced the range slightly. Controlled potential reduction of the ketone (1.2 g, 0.01 mole) was carried out at -1.7V (1000 C passed; 1e reduction requires 965 C). The catholyte was then concentrated and the residue extracted with benzene. After washing the extract with water and drying, evaporation of solvent afforded a brown oil which, on addition of ether/petrol partially solidified. The white crystals were filtered off and shown to be acetophenone pinacol (0.2 g, 16.5%), m. p. 110°C . N. m. r. (CDCl_3) δ 1.5 (s, 6H, 2CH_3) 2.7 (broad s, 2H, OH) 7.17 (s, 10H, PH).

A more efficient preparation of the pinacol involved reduction of the ketone in 10% aqueous acetonitrile as described previously.

Preparation of 3-Hydroxy-3-phenylbutyronitrile⁶³

A suspension of lithium amide in liquid ammonia was prepared.¹⁶⁰ A small piece of lithium was added to a 3-necked flask, equipped

with a mechanical stirrer, separating funnel and dry-ice condenser. Anhydrous liquid ammonia (500 ml) was added and the contents of the flask were stirred. After the appearance of a blue coloration, a few crystals of ferric nitrate were introduced, followed by small pieces of lithium (0.6 g, atom in total). The mixture was stirred for about 30 minutes until the blue colour had been discharged and a grey suspension of lithium amide remained.

Acetonitrile (16.4 g, 0.4 mole) dissolved in dry ether (60 ml) was added to the above suspension and stirring was continued for 10 minutes, before a solution of acetophenone (48 g, 0.4 mole) in dry ether (50 ml) was introduced. The mixture was stirred for 1 hour and then quenched with ammonium chloride (32 g, 0.6 mole). Evaporation of ammonia was aided by immersing the flask in a bath of ethanol, while ether (100 ml) and water (150 ml) were slowly run into the flask. The ether layer was separated and, after washing and drying, was concentrated to afford a crude product which was distilled, b. p. $148^{\circ}\text{C}/3.0\text{ mm}$, to afford 3-hydroxy-3-phenylbutyronitrile (49 g, 74%). N. m. r. (60MHz, CDCl_3) δ 1.74 (s, 3H, CH_3) 2.75 (s, 2H, CH_2) 2.8 (s, 1H, OH) 7.2-7.55 (m, 5H, Ph). Hydroxyl and nitrile absorptions were observed in the i. r. spectrum (nujol mull) at 3430 and 2250 cm^{-1} respectively.

Preparation of 3-Methylcinnamionitrile

1. Using Sodium in Acetonitrile⁶¹

Small pieces of sodium (0.3 g, 0.015 g, atom) were slowly added to purified acetonitrile (10 ml) at room temperature and the mixture was stirred until all of the sodium had dissolved; a white suspension formed in the solution. A solution of acetophenone (1.2 g, 0.01 mole) in acetonitrile (5 ml) was added dropwise and the mixture was refluxed for 1 hour. On cooling, the reddish-brown reaction mixture was poured into water (100 ml) and extracted with ether. The extracts were washed, dried and then concentrated to afford a product whose n. m. r. spectrum (60MHz, CDCl_3) suggested the presence of unreacted acetophenone, some 3-methylcinnamionitrile and 3-hydroxy-3-

phenylbutyronitrile. Dehydration of the latter was carried out by refluxing the crude reaction product for 4 minutes with a mixture (5 ml) of glacial acetic acid and concentrated sulphuric acid (25:1 by volume).⁶³ The cooled mixture was diluted with water and extracted with ether, the extracts being then washed with an aqueous solution of sodium bicarbonate followed by water. Distillation of the dried, concentrated extract, b. p. $74^{\circ}\text{C}/0.01\text{ mm}$, afforded a colourless liquid, <20%, whose n. m. r. spectrum (60 MHz, CCl_4) indicated a mixture of the cis- and the trans-isomers of 3-methylcinnamionitrile δ 2.39, 2.41 (s, 3H, CH_3) 5.48, 5.5 (s, 1H, CH) 7.3 (s, 5H, Ph). Absorption in the i. r. spectrum at 2175 cm^{-1} was characteristic of an unsaturated nitrile.

In an attempt to improve the yield of 3-methylcinnamionitrile a similar reaction was carried out using a greater excess of sodium (0.46 g, 0.2 g. atom) and the reaction mixture was refluxed overnight. The products were extracted into ether as described previously and distilled, b. p. $70-90^{\circ}\text{C}/0.15\text{ mm}$, to afford a colourless liquid from which a white solid (0.4 g) crystallised. The remaining liquid was decanted off and identified as 3-methylcinnamionitrile (0.12 g, 10%) by n. m. r. spectroscopy. The solid was shown to be 4-amino-2,6-dimethylpyrimidine by comparison of its n. m. r. spectrum (60 MHz, CDCl_3) δ 2.3 (s, 3H, 6- CH_3) 2.44 (s, 3H, 2- CH_3) 5.2 (broad s, 2H, NH_2) 6.07 (s, 1H, CH) with that of an authentic sample.⁶⁷

2. Using Lithium Amide

3-Hydroxy-3-phenylbutyronitrile was prepared as described previously. Dehydration to 3-methylcinnamionitrile was efficiently carried out using glacial acetic acid/sulphuric acid.

Attempted Preparation of 3-Methyl-3-phenylglutaronitrile

1. From 3-Hydroxy-3-phenylbutyronitrile

Sodium (0.0575 g, 0.0025 g. atom) was added in small pieces to

dry acetonitrile (37.5 ml) and the mixture was stirred under nitrogen until the sodium had dissolved. Tetraethylammonium chloride (0.46 g, 0.0025 mole) was introduced and stirring was continued for a further 30 m. After adding 3-hydroxy-3-phenylbutyronitrile (0.402 g, 0.0025 mole) the mixture was stirred overnight at room temperature. Ammonium chloride (0.25 g) was added, followed by water, and the aqueous layer was extracted with ether. Concentration of the dried extracts afforded only a small amount (ca. 10%) of the hydroxy nitrile with no evidence of 3-methyl-3-phenylglutaronitrile formation, as indicated by n. m. r. spectroscopy.

2. From 3-Methylcinnamonnitrile

A similar reaction was carried out using 3-methylcinnamonnitrile (0.357 g, 0.0025 mole) instead of hydroxy nitrile but only unreacted starting material was recovered.

Preparation of 3-Methyl-3-phenylglutaronitrile

The reaction was carried out using 3-methylcinnamonnitrile (0.357 g, 0.0025 mole) as described above but the mixture was heated under reflux overnight. In the absence of tetraethylammonium chloride a product mixture was obtained whose n. m. r. spectrum indicated a 65:35 mixture of 3-methyl-3-phenylglutaronitrile and unreacted 3-methylcinnamonnitrile. In the presence of tetraethylammonium ions, however, complete conversion to 3-methyl-3-phenylglutaronitrile (0.23 g, 50%) occurred, n. m. r. (60 MHz, CDCl_3) δ 1.63 (s, 3H, CH_3) 2.75 (s, 4H, CH_2) 7.3 (s, 5H, Ph).

Preparation of 1-Amino-2-cyano-3,4-dimethyl-3,4-diphenylcyclopent-1-ene.

The method was based on a preparation carried out by House et al⁷⁹ on α, β -unsaturated ketones.

A solution of 3-methylcinnamonnitrile (1.22 g, 0.00853 mole) in THF (10 ml) was stirred with sodium (0.3 g, 0.03 g atom) at 0°C for 4 hours. Methanol (5 ml) was added to the reaction mixture to destroy the

excess of sodium, followed by water. The mixture was extracted with ether and the extracts were washed, dried and concentrated to give an oily residue (1.2 g), which afforded a small amount of white solid on trituration with ether. The solid was identified as 1-amino-2-cyano-3,4-dimethyl-3,4-diphenylcyclopent-1-ene, m. p. 167-170°C by its spectroscopic properties; n. m. r. (100 MHz, CDCl_3) δ 1.0 (s, 3H, 3 or 4- CH_3) 1.06 (s, 3H, 3 or 4- CH_3) 2.36 (d, 1H, C(S)H; $J = 8$ Hz) 3.32 (d, 1H, C(S)H; $J = 8$ Hz) 4.74 (broad s, 2H, NH_2) 7.0-7.5 (m, 10H, Ph); a parent ion m/e 288 was observed in the mass spectrum and fragmentation gave rise to signals at m/e 273 (P- CH_3), 211 (P- C_6H_5) and 183 (P- $\text{C}_6\text{H}_5\text{CCH}_3$); absorption in the i. r. spectrum at 3420, 3340 and 2175 cm^{-1} suggested a primary amine and an unsaturated nitrile, the latter also giving rise to a peak in the u. v. spectrum at λ_{max} 264 m μ . Examination of the n. m. r. spectrum of the crude reaction mixture suggested that the above product was present in about 30% yield.

When the reaction was not quenched with methanol before addition of water (after decanting from excess sodium) the crude product had a very complex n. m. r. spectrum and was not further examined.

2. Reduction of 3-Methylcinnamionitrile in Acetonitrile

A typical reduction of 3-methylcinnamionitrile (1.43 g, 0.01 mole) was carried out at a mercury pool cathode (area ca 3.0 cm²) at -3.0V in a 0.1M solution of tetraethylammonium fluoroborate. A cell current of 24mA increased initially and then decreased to 7mA (1209 C passed; 2e reduction requires 1930 C). Extraction of the catholyte into ether in the usual manner afforded a crude product (1.56 g) which was separated by dry column chromatography (alumina; eluent ether). Two products were identified, the less polar one corresponding to 3-phenylbutyronitrile (0.174 g, 12%) as indicated by its n. m. r. spectrum. The major product fraction (0.797 g) was shown by n. m. r., i. r. and mass spectroscopy to consist of a mixture of 3-methyl-3-phenylglutaronitrile (ca 30%) and 1-amino-2-cyano-3,4-dimethyl-3,4-diphenylcyclopent-1-ene (ca 10%), the yields being estimated from the integration of the n. m. r. spectrum of the crude product mixture. The mass spectrum of the most polar fraction indicated a highest mass peak at m/e 329 which was not identified.

Reduction of 3-methylcinnamionitrile (5.0 g) was also carried out at -2.4V in a 0.4M solution of tetraethylammonium fluoroborate in 80% aqueous acetonitrile. The electrolysis was terminated when the cell current had decreased from 50mA to 20mA (3740 C passed). Examination of the reduction mixture by n. m. r. spectroscopy suggested that only 3-phenylbutyronitrile had been formed.

Reduction of 3-Methylcinnamionitrile in DMF³⁷

3-Methylcinnamionitrile (18.6 g, 0.133 mole) was reduced at a mercury pool cathode in a solution of tetraethylammonium tosylate (0.2M) in DMF (100 ml) containing water (3.3 ml). A cathodic range of -2.1V (vs. SCE) was observed and during electrolysis the potentiostat was maintained at its limit (70V). The initial cell current of 175 mA increased to 300mA and reduction was continued until almost no starting material remained, as indicated by n. m. r. spectroscopy of the catholyte. The reduction mixture was concentrated on a high vacuum rotary evaporator and extracted into ether. The concentrated extract was shown by its n. m. r. spectrum to contain only 3-phenylbutyronitrile.

3. Reduction of Acetone (in the Presence of Azobenzene) in Acetonitrile

Acetone was electroinactive in the available cathodic range in acetonitrile. The electrolysis was carried out in the presence of azobenzene (0.182 g, 0.001 mole), the reduction of which served as an initiator for the production of the acetonitrile anion. Azobenzene gave two 1e waves at a DME in acetonitrile containing 0.1M tetraethylammonium fluoroborate (Fig.7.3).

Controlled potential reduction of the azobenzene was carried out at -3.15V at a mercury pool cathode (area ca 3.0 cm²), during which period the cell current decreased from 70mA to 28mA. Acetone (2.32 g, 0.04 mole) was then added to the catholyte and the solution was stirred for 5 minutes before reduction at -3.15V was re-commenced. The cell current was now 40mA and decreased to 12mA, at which point the electrolysis was terminated. (1726 C passed, 2e reduction requires 7720 C). After addition of ammonium chloride and extraction of the reduction products into ether in the usual manner, a crude product (2.148 g) was obtained. Its i. r. spectrum (liquid film) showed broad absorption at 3350 cm⁻¹ and three peaks attributed to nitrile groups at 2250, 2210 and 2185 cm⁻¹. N. m. r. spectroscopy (60 MHz, CDCl₃) gave a complex spectrum in the region δ 0.9-2.7 and comparison with the spectra of authentic samples indicated the presence of 3-hydroxy-3-methylbutyronitrile [δ 1.43 (s, CH₃) 2.5 (s, CH₂) 3.6 (broad s, OH)], 3,3-dimethyl acrylonitrile [δ 1.91 (s, CH₃) 2.05 (s, CH₃) 5.1 (m, CH)], and 3,3-dimethylglutaronitrile [δ 1.2 (s, 2CH₃) 2.43 (s, CH₂)] in the approximate ratio of 2:1.6:1, together with unidentified signals at δ 1.4 (s) 1.44 (s) 2.13 (s) 2.6 (s) 2.97 (s). Only small signals were observed in the region δ 1.0, suggesting only a small amount of 3-methylbutyronitrile had been formed, although the presence of this compound was suggested by a peak in the mass spectrum of the crude product at m/e 83. Unidentified peaks in the mass spectrum occurred at m/e 188, 162, 140. The presence of the cyclised hydrodimer,

1-amino-2-cyano-3,3,4,4-tetramethylcyclopent-1-ene was suggested by the low frequency nitrile absorption in the i. r. spectrum at 2185 cm^{-1} , although an authentic sample of this compound was not prepared for comparison.

An attempt was made to observe the formation of 3,3-dimethylacrylonitrile from reduction of acetone in acetonitrile, reduction waves for the former compound being observable in acetonitrile. Voltammograms were recorded by sweeping to potentials beyond the cathodic limit but even in the absence of acetone an anodic shift of the cut off potential (ca 0.3V) was observed on the second sweep. This would mask any waves due to 3,3-dimethylacrylonitrile and indeed in the presence of acetone no change in the second sweep voltammogram was observed.

4. Reduction of 3,3-Dimethylacrylonitrile in Acetonitrile

A controlled potential reduction (-3.2V) of 3,3-dimethylacrylonitrile (1.62 g, 0.02 mole) was carried out at a mercury pool (ca 3.0 cm²) in a 0.1M solution of tetraethylammonium fluoroborate in acetonitrile. The background current of 6mA increased to 30mA on addition of substrate and reduction was terminated after 2158 C had been transferred (2e reduction requires 3860 C). The cell current was then 25mA. After work-up in the usual manner, a crude product (1.41 g) was obtained whose n. m. r. spectrum (60 MHz, CDCl₃) showed complex absorption in the region δ 0.9-3.0, with signals at δ 1.27 (s, 2CH₃) 2.47 (s, 2CH₂) suggesting the formation of 3,3-dimethylglutaronitrile. A small amount of starting material remained as shown by an olefinic proton signal. I. r. spectroscopy indicated three different nitrile groups giving absorptions at 2240, 2210, and 2190 cm⁻¹. A broad peak at 3300 cm⁻¹, attributable to an amino group, together with the lowest frequency nitrile absorption suggested the formation of cyclised hydrodimer. This was supported by signals in the mass spectrum at m/e 165 (P+1) and 163 (P-1).

Reduction of 3,3-Dimethylacrylonitrile in Aqueous Acetonitrile

A similar reduction of 3,3-dimethylacrylonitrile (1.215 g, 0.015 mole) was carried out in 10% aqueous acetonitrile (1870 C passed; 2e reduction requires 2895 C). Only a small yield (0.127 g) of crude product was obtained. Its n. m. r. spectrum (60 MHz, CDCl₃) indicated mainly unreduced starting material together with 3-methylbutyronitrile, the latter being indicated by the signal at δ 1.5 (d, 2CH₃, J = 6 Hz). There was no evidence for the formation of the cyclised hydrodimer from the i. r. and mass spectra of the crude product.

Preparation of 3-Hydroxy-3-methylbutyronitrile

A method similar to that described for 3-hydroxy-3-phenylbutyronitrile was used. Lithium amide (0.6 mole) in liquid ammonia (500 ml)

was reacted with acetonitrile (16.4 g, 0.4 mole) and acetone (23.2 g, 0.4 mole). The product (19.8 g, 50%) was obtained by distillation of the crude product (b. p. 113-115°C/20 mm); n. m. r. (60 MHz, CDCl_3) δ 1.46 (s, 6H, 2CH_3) 2.52 (s, 2H, CH_2) 3.34 (broad s, 1H, OH); i. r. (liquid film) 3350 (broad, OH) 2260 cm^{-1} (CN).

Preparation of 3, 3-Dimethylacrylonitrile.

1. By Dehydration of 3-Hydroxy-3-methylbutyronitrile

(a) Using Acetic Acid/Sulphuric Acid. A method analagous to that described for the 3-phenyl derivative was used. Reaction of 3-hydroxy-3-methylbutyronitrile (14.85 g, 0.15 mole) afforded a crude product (10.3 g) whose n. m. r. spectrum (60 MHz, CCl_4) showed a signal at δ 5.0 (broad s, CH) attributable to the olefinic proton of 3, 3-dimethylacrylonitrile. Other signals in the n. m. r. spectrum in the region δ 1.3-3.0 were possibly due to the formation of an α -acylated product [δ 1.5 (s, 6H, CH_3) 1.95 (s, 3H, COCH_3) 2.82 (s, 2H, CH_2)]. Distillation of the product mixture afforded 3, 3-dimethylacrylonitrile (3.8 g, 31%) b. p. 140-160°C; i. r. spectrum (liquid film) 2210 cm^{-1} (conjugated nitrile); n. m. r. spectrum (60 MHz, CCl_4) δ 1.92 (broad s, 3H, CH_3) 2.05 (broad s, 3H, CH_3) 5.07-5.13 (m, 1H, CH).

(b) Using Phosphorus Pentachloride. Phosphorus pentachloride (20.824 g, 0.1 mole) was gradually added to 3-hydroxy-3-methylbutyronitrile (9.9 g, 0.1 mole) with stirring. An exothermic reaction was accompanied by vigorous effervescence. When the reaction ceased, water was slowly added to the mixture. The oil which separated was extracted into ether and washed with aqueous sodium bicarbonate and then water. After drying, the concentrated extract yielded a crude product (4.7 g) whose n. m. r. spectrum (60 MHz, CCl_4) indicated 3, 3-dimethylacrylonitrile, with extra signals at δ 1.7 (s, 6H, 2CH_3) 2.77 (s, 2H, CH_2) possibly corresponding to 3-chloro-3-methylbutyronitrile. The pure unsaturated nitrile (2.72 g, 33%) was obtained by distillation

of the mixture (b. p. $42^{\circ}\text{C}/7.0\text{ cm}$).

(c) Using Phosphoric Acid.⁶² The hydroxynitrile (2.5 g, 0.025 mole) was refluxed for 15 minutes with phosphoric acid (85%, 160 ml). The cooled mixture was diluted with water (100 ml) and extracted into ether. The extracts were washed to remove acid, dried and concentrated to afford a product whose i. r. spectrum showed no nitrile absorption.

2. From 3, 3-Dimethylacrylic Acid

3, 3-Dimethylacrylic acid (30.0 g, 0.3 mole) was added gradually to cooled thionyl chloride (59.5 g, 0.5 mole). The mixture was then refluxed for 1 hour and distilled (b. p. $65\text{-}75^{\circ}\text{C}/3.0\text{ cm}$) to afford the acid chloride (22 g, 62%); n. m. r. (60 MHz, CCl_4) 1.96 (s, 3H, CH_3) 2.14 (s, 3H, CH_3) 5.9-6.1 (broad s, 1H, CH).

The acyl chloride was then added dropwise with stirring to cooled concentrated ammonia (100 ml) and water (100 ml). Stirring was continued for 2 hours and the reaction mixture was then concentrated and extracted with chloroform. The extract was washed, dried and concentrated to afford a white solid product which was identified as 2, 2-dimethylacrylamide (10.0 g, 53%); n. m. r. (60 MHz, CDCl_3) 1.84 (broad s, 3H, CH_3) 2.14 (broad s, 3H, CH_3) 5.5-5.7 (m, 1H, CH).

Dehydration of the amide was achieved by heating with phosphorus pentoxide (18.0 g) at $200\text{-}220^{\circ}\text{C}$ in a flask connected to a distillation apparatus. A colourless liquid, b. p. 142°C , was collected, distillation in the later stages being aided by lowering the pressure. The distillate (2.3 g, 28.4%) was identified as 3, 3-dimethylacrylonitrile (overall yield ca 10%) by its n. m. r. spectrum.

Preparation of 3, 3-Dimethylglutaronitrile

The method employed was similar to that described for the 3-phenyl derivative. 3, 3-Dimethylacrylonitrile (0.2025 g, 0.0025 mole) was refluxed overnight in a solution prepared from sodium, acetonitrile and tetraethylammonium chloride. The crude product (0.252 g) was distilled

(b. p. $120^{\circ}\text{C}/30\text{ mm}$) to afford a pale yellow viscous liquid, whose n. m. r. spectrum (60 MHz, CDCl_3) δ 1.3 (s, 6H, 2CH_3) 2.5 (s, 4H, 2CH_2) indicated 3, 3-dimethylglutaronitrile; an unidentified signal at δ 1.56 (s) was also observed. The mass spectrum showed a major peak at m/e 123, corresponding to (P+1) for 3, 3-dimethylglutaronitrile, together with higher mass peaks at m/e 215, 171, 149, 140.

Preparation of 3-Methylbutyronitrile

3, 3-Dimethylacrylonitrile (0.81 g, 0.01 mole) dissolved in a mixture of ethyl acetate (37.5 ml) and glacial acetic acid (2.5 ml) was hydrogenated in the presence of a Pd/C catalyst (0.1 g, 10%) at 1 atmosphere pressure. When the uptake of hydrogen had ceased (195 ml; theoretical 224 ml), the mixture was filtered and the ethyl acetate was carefully removed by distillation. The residue was diluted with water and extracted into ether. After washing to remove acid, and drying, the extract was concentrated and distilled to afford a colourless liquid, b. p. 130°C , whose n. m. r. spectrum (60 MHz, CCl_4) δ 1.03 (d, 6H, 2CH_3 ; $J = 6\text{ Hz}$) 1.7-2.25 (m, 3H, CH and CH_2) suggested that the compound was 3-methylbutyronitrile (0.1 g, 22%).

B Electrochemistry in Liquid Ammonia

I. General Techniques.

Solvent Purification (Diagram I)

Cylinders of liquid ammonia were obtained from I. C. I. and B. O. C. Special Gases. Purification involved vacuum distillation from sodium to remove residual water and oxygen. A clean piece of sodium (1 cm^3) was placed in Vessel A and liquid ammonia (200 ml) was added from the cylinder. Vessel A was then immersed in a Dewar flask containing liquid nitrogen in order to freeze the ammonia, and the vessel was attached to the vacuum line by means of a cone and socket joint.

Vessel B served as a collection flask for the purified ammonia, which entered as a gas by taps (d) and (e). Prior to distillation the apparatus was evacuated through tap (b) with taps (a), (c), (d) and (e) open, and the absence of any leaks was verified by means of the manometers M^1 and M^2 . Taps (a) and (b) were then closed and the Dewar flask round A was removed. Melting of the ammonia was aided by alternately washing the flask with acetone to melt ice which formed on the surface, and blowing it with hot air. During this process the sodium dissolved, giving an intensely blue solution of solvated electrons and the mercury level in manometer M^1 fell, due to an increased pressure of ammonia. After leaving the solution for about 10 min distillation was commenced by opening tap (a) and adding liquid nitrogen to the Dewar flask surrounding vessel B. By continued heating and washing of vessel A and increasing the volume of liquid nitrogen in the Dewar flask surrounding vessel B, distillation of 200 ml of ammonia was completed in about 30 min. The purified ammonia was stored frozen under dry gaseous nitrogen until required.

Cell Construction

(i) The Cell (see Photograph)

The cell was constructed from a flange flask (size FG 75) with a

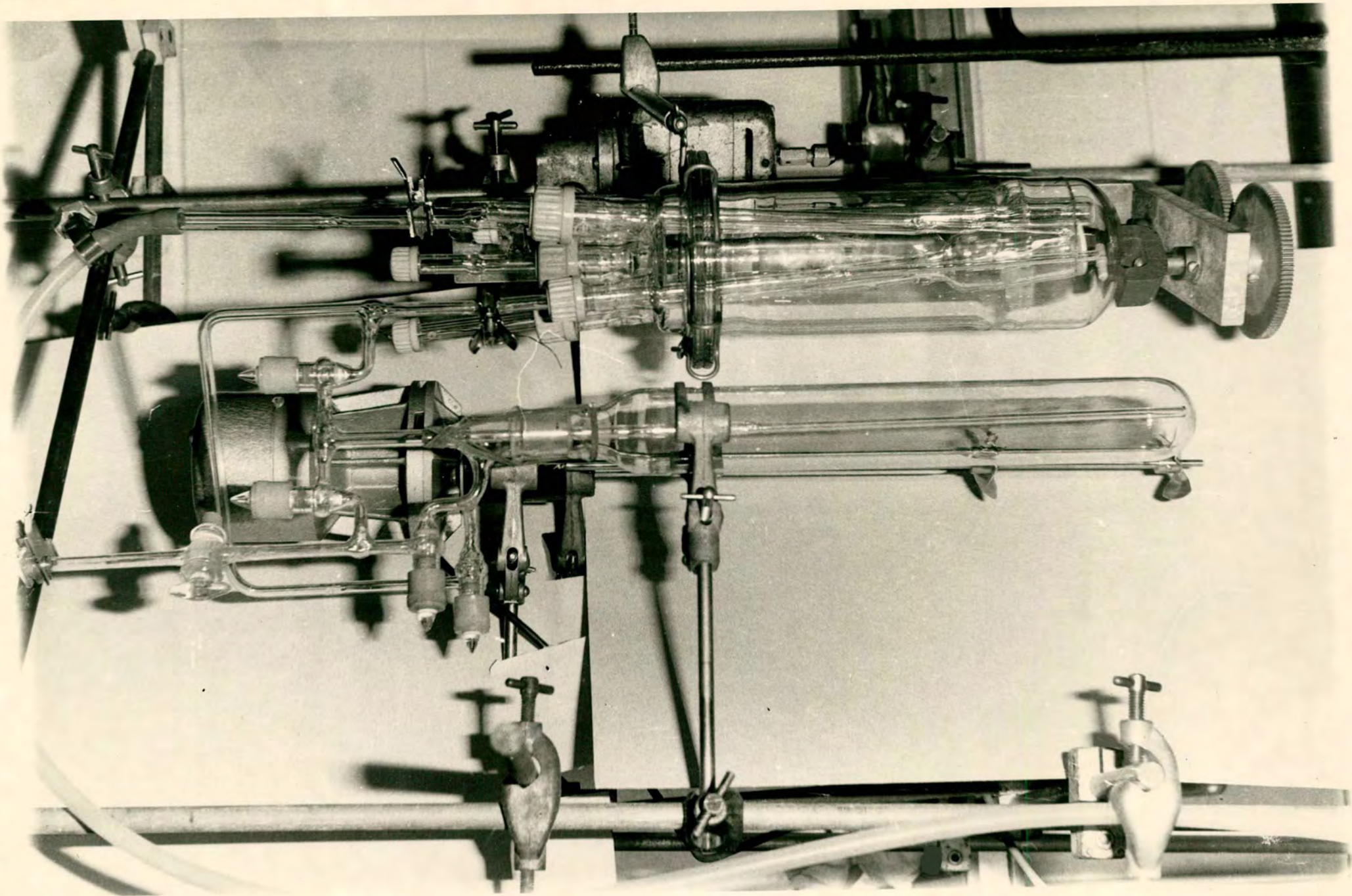
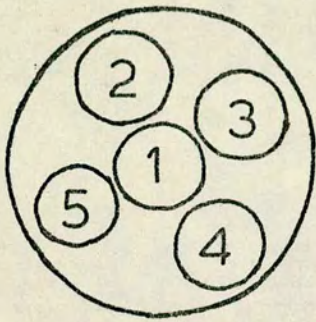
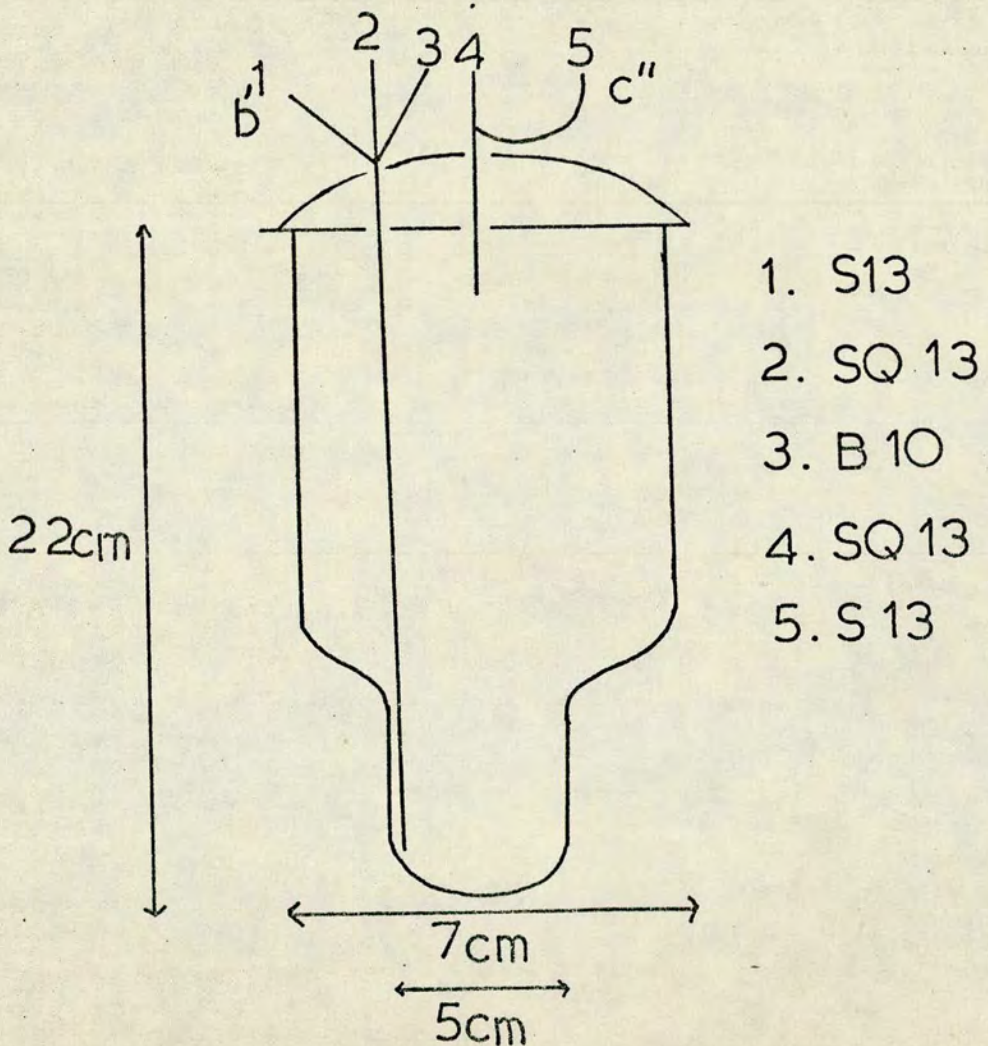


DIAGRAM 3.1
CELL HEAD - surface view



- 1. SQ 18 outlet tube
working electrode
- 2. SQ 18 secondary electrode
- 3. SQ 18 reference electrode
- 4. SQ 18 working electrode
- 5. SQ 13 inlet tube

DIAGRAM 3.2
ANALYTICAL CELL - inlet and outlet tube



head (Diagram 3.1) containing one SQ13 and four SQ18 Jobling joints. These joints accommodated the cell components described below. For analytical studies a smaller cell was constructed by reducing the diameter of the flask bottom and was suitable for use with volumes from 25-100 ml. The unmodified cell could be used for volumes up to 500 ml. The cells were graduated using furnace-fired transfers. The flange joint was retained by means of a spring wire clip attached to a steel rod, which was used to clamp the cell in position.

(ii) Inlet Tube (Diagram 3.2)

The inlet tube consisted of glass tubing (O. D. 6.5 mm) with a three-way top, terminating in an S13 cup joint, an SQ13 screw-thread joint and a B10 socket. These three tubes served to deliver liquid ammonia into the cell, as a nitrogen bubbler, and as a liquid and solid sample injection post, respectively. The inlet tube was assembled in the cell via the SQ13 joint (5) in the cell head.

(iii) Outlet Tube (Diagram 3.2)

The SQ18 joint (1) in the cell head accommodated a branched tube, one end of which terminated with an SQ13 screw-thread joint and the other with an S13 ball joint. The former held the working electrode and the latter served as an outlet to the vacuum line via an S13 cup joint and flexible polythene tubing. This isolated the cell from the atmosphere during cell operation.

(iv) Working Electrodes

The working electrodes were accommodated either via the SQ13 screw-thread joint in the outlet tube or via the SQ18 joint (4) in the cell head using an SQ13 screw-thread joint as an adapter.

a) Analytical Electrodes

Dropping mercury electrode (DME). Capillaries were obtained from Shandon Southern and were connected by means of glass and flexible polythene tubing to a mercury reservoir, whose height was adjusted to give a drop rate of about 1 drop every 3 seconds. Electrical contact was made via the mercury reservoir. The electrode tip was washed after use by immersion in distilled water and stored inverted with the tip protected by a cap.

Polished platinum disc electrode (PDE). A 1.0 cm length of platinum wire (O. D. 0.6 mm) was sealed into soft glass tubing (O. D. 6.5 mm). Electrical contact was made via a copper wire immersed in a small volume of mercury inside the tubing, which was stoppered at the upper end. The electrode tip was ground flat and polished. Pre-treatment involved immersion in hot aqua regia followed by washing with distilled water. A surface which was reproducible for many months was obtained but eventually the electrode gave high background currents associated with gas evolution and no satisfactory remedy was found.

Hanging mercury drop electrode (HMDE). A platinum disc electrode, constructed as described above, was coated with a hanging mercury drop using the method of Ramaley et al.¹⁶⁸ The platinum was first degreased with alcoholic potassium hydroxide and cleaned in boiling nitric acid. After immediately washing with distilled water, the electrode was made the cathode in a solution of 1M perchloric acid, a platinum foil electrode being used as the anode. The electrodes were connected to a 3V battery, evolution of hydrogen gas being observed at the cathode. After passing a current for about 10 min, and without breaking the circuit, the cathode was coated by lowering it into a pool of clean mercury in the base of the electrolysis cell. The electrode was tested by observing the potential range in 1M perchloric acid. At a completely coated electrode hydrogen evolution was observed to commence at -0.6V (vs SCE). Incomplete coating resulted in a reduced cathodic range. After use, the HMDE was washed with acetone and distilled water, and stored under clean,

DIAGRAM 3.3

C - PASTE
ELECTRODE

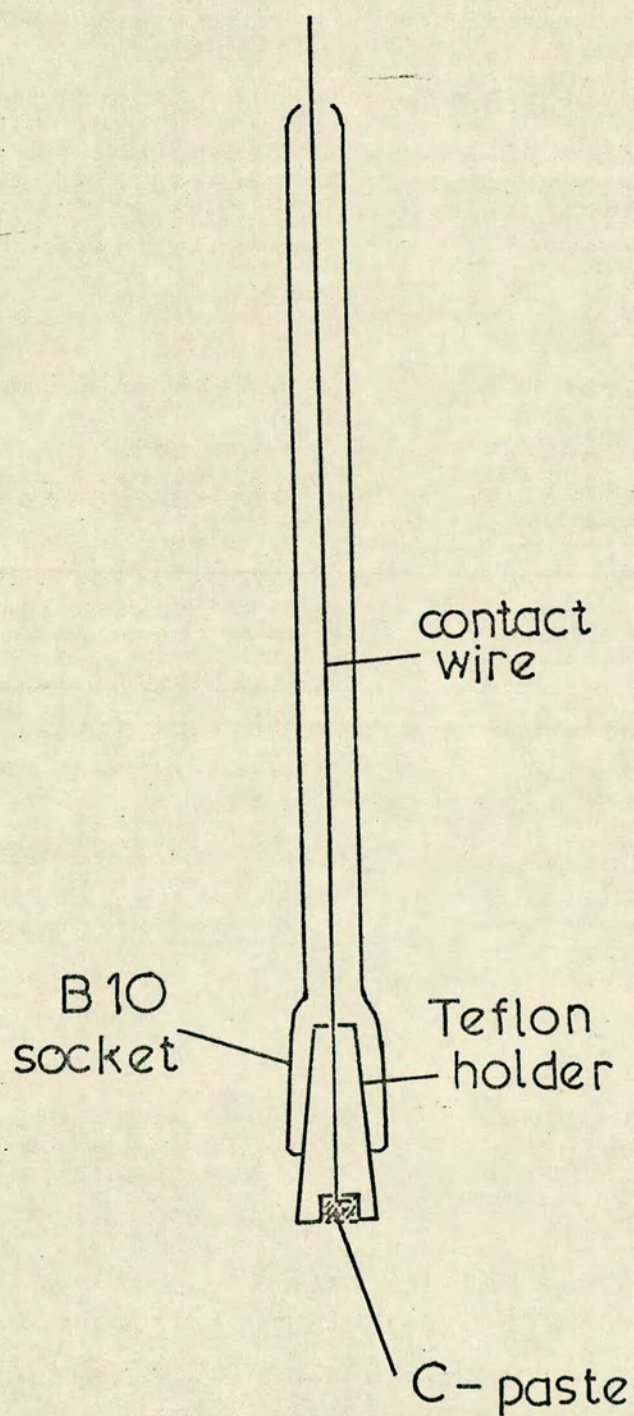
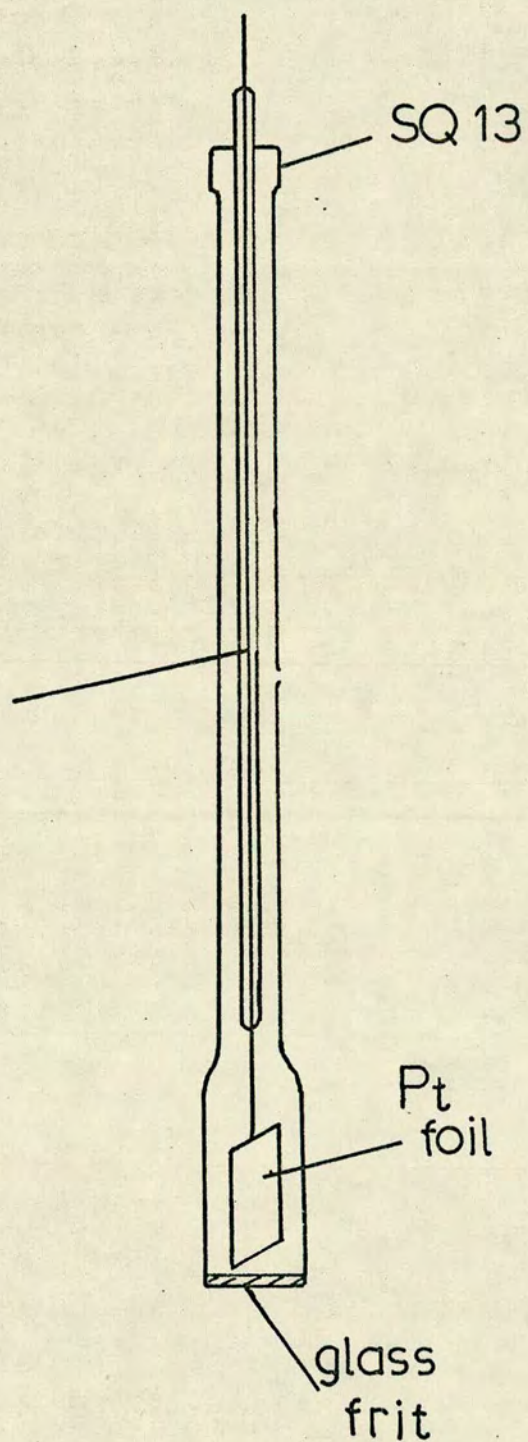


DIAGRAM 3.4

SECONDARY
ELECTRODE



dry mercury. A drop of fairly reproducible size could be formed by withdrawing the electrode from its storage test-tube along the plane of the mercury surface, thereby removing any excess mercury by surface tension.

Carbon-paste electrode (Diagram 3.3). Graphite powder Achieson Grade 38 was obtained from Fischer Scientific Co. and made up into a thick paste with Spectroscopic Grade Nujol. The paste was packed into a cylindrical well (diameter 7.0 mm) in a conical (B10) Teflon holder and the surface flattened by drawing it across a smooth surface. Any excess graphite paste adhering to the Teflon rim was removed. The cone was mated into a B10 socket attached to glass tubing (O.D. 6.5 cm). Electrical contact was made by a wire from the base of the well through a hole in the cone.

b) Preparative Electrodes

Mercury pool electrode. A mercury pool of volume 2.0 ml and surface area about 5.0 cm^2 was used unless otherwise indicated. Electrical connection was via a thin platinum wire sealed into soft glass.

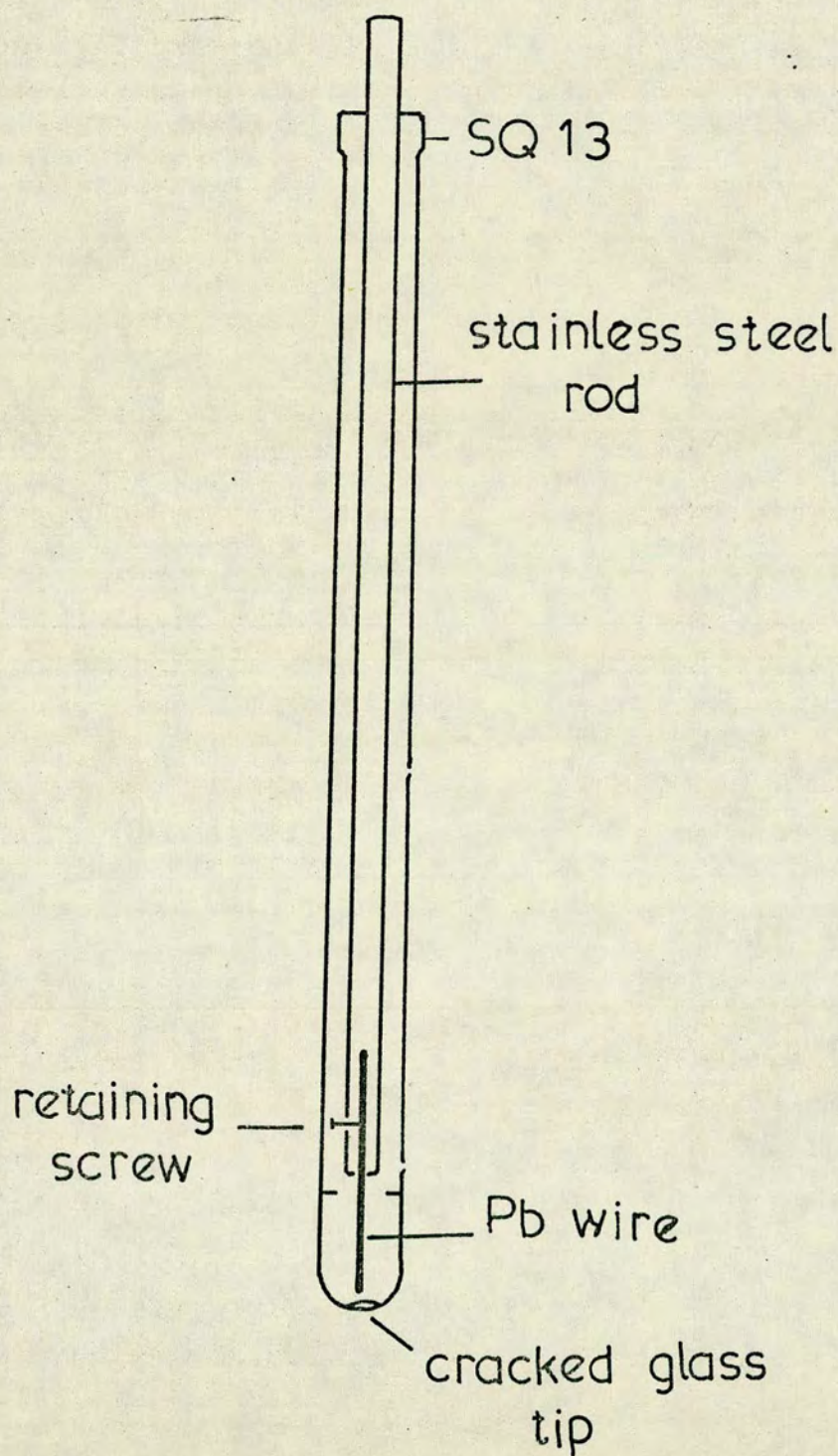
Platinum foil electrode. A platinum foil electrode, similar in design to the secondary electrode (see later) was used.

(v) Secondary Electrode (Diagram 3.4)

A platinum foil electrode (4.0 x 2.0 cm) was used as the electrode. Electrical contact was made by gold soldering the foil to a length of platinum wire (O.D. 2.0 mm) which was in turn soft soldered to copper wire. Soft glass tubing (O.D. 6.5 mm) was sealed onto the platinum wire by application of heat and a vacuum. The electrode was assembled in the cell via the SQ18 joint (2) in the cell head using an SQ13 screw-thread joint as adapter.

For preparative electrolyses, the secondary electrode was separated from the working electrode compartment by a glass frit (diameter 2.0 cm, porosity 4) sealed into pyrex tubing. The latter terminated in an SQ13 screw-thread joint at the upper end to accommodate

DIAGRAM 3.5
REFERENCE ELECTRODE



the glass tube of the platinum electrode. The maximum volume of the secondary compartment was about 25 ml. A small aperture was made at the upper end of the tube inside the cell to facilitate filling the secondary compartment through the frit.

(vi) Reference Electrode (Diagram 3.5)

Cell potentials were usually measured versus a lead electrode immersed in a 0.05M solution of lead nitrate in liquid ammonia (0.0165 g in 1.0 ml). The electrode was constructed by slotting a 10.0 cm length of lead wire [(diameter 2.0 mm), supplied by Alfa Chemicals] into a stainless steel rod (O. D. 6.5 cm), the lower portion of which was hollowed out, and retained by means of a grub screw. A fresh surface of lead was prepared by scraping the wire with a sharp blade before use. B. D. H. Analar lead nitrate was dried in vacuo at 100°C and the required amount was weighed into the glass reference electrode tube. The latter made electrical contact with the cell solution by means of a cracked glass tip. An SQ13 screw-thread joint at the top of the reference electrode tube held the lead electrode. Liquid ammonia entered the reference compartment by the lower of two small holes and its volume was measured by means of a graduation mark on the glass.

Thermostatting of the cell

Temperature control of the cell during operation was maintained by its immersion in a large unsilvered Dewar vessel (25 l, Camlab type no.45), containing ethylene glycol/water (60/40 by volume) at -36°C which was stirred mechanically. A refrigeration unit (MGW Lauda Type DLK 50) was attached to a peristaltic pump (Glen Creston Tube Pump Type L25), which circulated cooled ethanol from the refrigeration unit through a metal heat exchange coil in the base of the Dewar vessel. The pump operation was controlled by an electronic temperature sensor. Polyethylene spheres on the surface of the bath liquid helped to minimise heat gain from the atmosphere.

Stirring of the cell

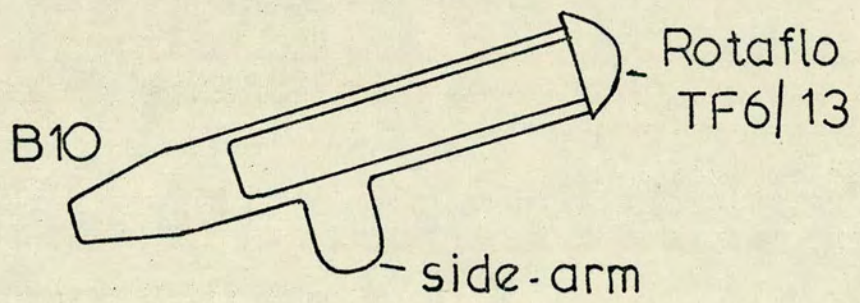
Stirring of the cell solution could be achieved in two ways. For most purposes it was found sufficiently effective to bubble cooled, dry, gaseous nitrogen through the cell. To reduce evaporation of the ammonia, the nitrogen was pre-saturated by bubbling through the transfer vessel B. For preparative electrolyses a more efficient method was by magnetic stirring. This was achieved by using a magnet driven by an air turbine (made in brass after the design of Townsen and Mercer 55A-220 Stirrer) which was immersed in the bath liquid. It was necessary to operate the turbine on a closed system in order to avoid ice collecting in the turbine rotor. The rate of stirring could be adjusted by regulating the flow of air through the turbine.

Cell Assembly (Diagram 1)

Vessel B, containing re-distilled liquid ammonia, was placed in the cooled thermostat bath whilst still attached to the vacuum line, all taps except (e) and (d) remaining closed. When all the ammonia had melted, taps (e) and (d) were closed and a' was attached to the assembled cell at c". Taps (b) and (c) were opened and the cell was evacuated (the inlet tube having been previously stoppered at b'). After closing tap (b), the cell was checked for leaks using manometer M². Dry gaseous nitrogen was admitted through M³ with tap (b) closed, after which the cell was evacuated and refilled with nitrogen three more times. With nitrogen still flowing into the cell via M, c and c", the stopper at b' in the cell outlet tube was removed. The cell was then immersed in the thermostat bath and attached to vessel B by connecting b' and b". The tap at M was closed and the nitrogen inlet tube was transferred from M to a". A flow of nitrogen was thereafter maintained through the cell in the direction a", b' and c" and escaped through a mercury bubbler attached to M.

DIAGRAM 3.6

Solid sample holder



Transfer of liquid ammonia to the cell

Transfer of liquid ammonia from vessel B into the cell was achieved by pressurising vessel B with nitrogen via taps (d) and (e) with (h) and (f) closed. Liquid ammonia entered the cell through tap (g) until the required volume had been transferred. Taps (e) and (g) were then closed and (f) and (h) opened to allow the passage of nitrogen saturated with ammonia through the cell. The reference electrode was lowered into the ammonia in the cell so that solvent entered through the bottom hole in the reference electrode compartment, which already contained lead nitrate. The influx of ammonia was facilitated by vigorously bubbling nitrogen through the ammonia in the cell and slightly releasing the cap of the SQ13 joint at the top of the reference electrode compartment.

Supporting electrolyte was added through the SQ18 joint (4) in the cell head, which had remained stoppered during cell assembly. After dissolution of the supporting electrolyte, the secondary compartment was lowered into the electrolyte solution and allowed to fill. Up to two working electrodes could be accommodated at one time, through the SQ13 screwthread joint in the outlet tube and the SQ18 joint (4) in the cell head. This enabled analytical studies to be carried out during the course of a preparative electrolysis without unnecessary exposure of the cell to the atmosphere.

Sample injection

Readily soluble liquid and solid samples were injected into the inlet tube and flushed into the cell with liquid ammonia from vessel B. Liquid injection was via a septum which sealed the SQ13 screw-thread joint in the inlet tube. Solids were weighed into the side-arm of the sample holder (Diagram 3.6), which was attached to the inlet tube via a B10 socket. By opening the tap of the sample holder and rotating about the B10 joint, the solid sample was ejected into the inlet tube.

Less soluble samples were added in a small glass capsule after

dissolution in a co-solvent (usually THF). The capsule was dropped into the cell through the SQ18 joint (4) in the cell head. In analytical studies the error in the concentration of the depolariser was estimated at $\pm 5\%$, the main error arising from inaccuracy in the measurement of solvent volume.

Preparation of Supporting Electrolytes

Tributylmethylammonium Iodide. - Tributylamine (18.5 g, 0.1 mole) and methyl iodide (20 g; excess) were stirred under reflux for 30 minutes in a flask equipped with a dry-ice condenser. The solid was filtered off and washed with ether. Traces of iodine were removed by dissolving the solid in chloroform and washing with an aqueous solution of sodium thiosulphate, followed by distilled water. Addition of ether to the dried chloroform solution (MgSO_4) precipitated white crystals of tributylmethylammonium iodide (89%), m. p. 184-185°C. Found: C, 47.59; H, 8.92; N, 4.54. $\text{C}_{13}\text{H}_{30}\text{NI}$ requires C, 47.69; H, 9.17; N, 4.28%.

Tributylethylammonium Iodide. - A solution of tributylamine (18.5 g, 0.1 mole) and ethyl iodide (20 g; excess) in THF (100 ml) was refluxed for 48 hours. Evaporation of solvent yielded the salt (86%) m. p. 209-210°C (from ethyl acetate/ethanol). Found: C, 49.02; H, 9.16; N, 4.29. $\text{C}_{14}\text{H}_{32}\text{NI}$ requires C, 49.25; H, 9.38; N, 4.10%.

Butyltrimethylammonium Iodide. - A solution of trimethylamine in ethanol (30.0 g of a 33% solution by weight) and butyl iodide (21.0 g; slight excess) was refluxed for 3 hours in a flask equipped with a dry-ice condenser. The iodide (87%) was precipitated by addition of ether. M. p. 235-236°C (from methylene chloride/chloroform). Found: C, 34.01; H, 7.31; N, 5.66. $\text{C}_7\text{H}_{18}\text{NI}$ requires C, 34.57; H, 7.41; N, 5.76%. The corresponding bromide was prepared using a similar method and was found to be more suitable than the iodide for conversion into the fluoroborate salt (see below).

Conversion of Quaternary Ammonium Halides into their
Fluoroborate Salts

Tributylmethylammonium iodide, tributylethylammonium iodide and butyltrimethylammonium bromide were all converted to the corresponding fluoroborate salts. A slight excess of 40% aqueous fluoroboric acid was added to a saturated solution of the halide in water. The precipitated fluoroborate was filtered off and the filtrate concentrated. Addition of ethanol/ether to the concentrate afforded more fluoroborate. Traces of halogen were removed by washing with sodium thiosulphate solution as described previously. Yields were quantitative.

Tributylmethylammonium Fluoroborate: M. p. 157-158°C (from water).

Found: C, 54.28; H, 10.21; N, 4.85. $C_{13}H_{30}NBF_4$ requires C, 54.39; H, 10.46; N, 4.88%.

Tributylethylammonium Fluoroborate: M. p. 188°C (from water).

Found: C, 55.89; H, 10.42; N, 4.66. $C_{14}H_{32}NBF_4$ requires C, 55.86; H, 10.64; N, 4.64%.

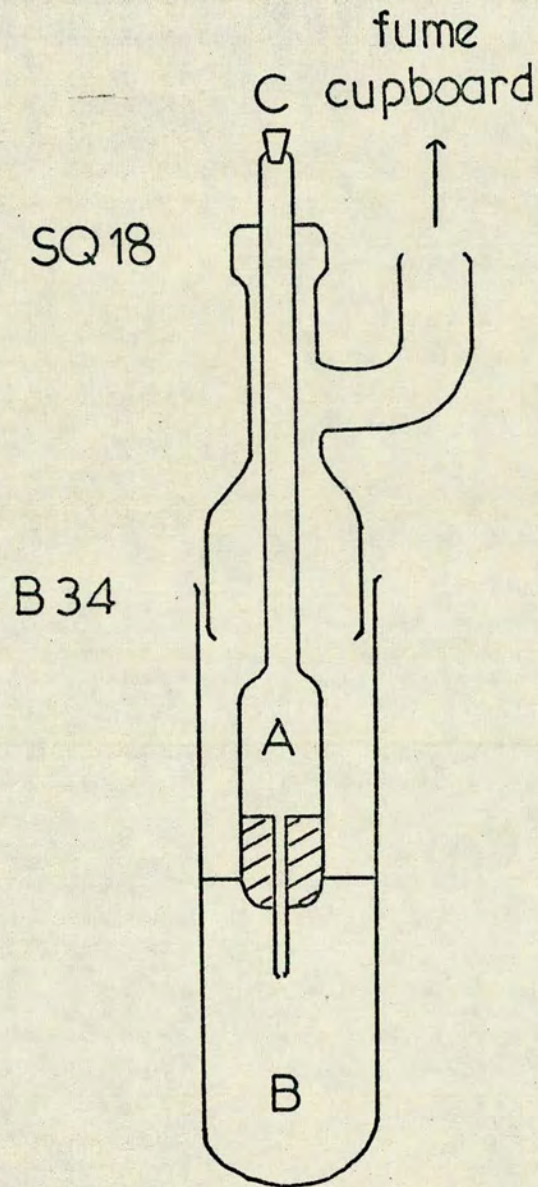
Butyltrimethylammonium Fluoroborate: M. p. 191-193°C (from ethanol).

Found: C, 41.66; H, 8.87; N, 6.81. $C_7H_{18}NBF_4$ requires C, 41.42; H, 8.87; N, 6.9%.

Tetraethylammonium Fluoroborate. - Fluoroboric acid (37.5 ml, 40%) was added to an aqueous solution of tetraethylammonium hydroxide (100 ml of a 25% solution). The precipitate was filtered off and more product was obtained by addition of ethanol/ether to the concentrated filtrate. The combined solids were recrystallised twice from aqueous ethanol to give white crystals of the fluoroborate (80%), m. p. > 300°C.

Tetrabutylammonium Fluoroborate. - An aqueous solution of tetrabutylammonium hydroxide (100 ml of a 40% solution) was reacted with aqueous fluoroboric acid (35 ml, 40%) and worked up as for the tetraethyl derivative above to yield the fluoroborate salt (85%), m. p. 162-162.5°C (from ethyl acetate/pentane).

DIAGRAM 4



Tetraethylammonium Tosylate. - Ethyl tosylate (200 g, 1.0 mole) was dissolved in absolute ethanol (100 ml) in a flask equipped with a mechanical stirrer, thermometer, condenser and addition funnel. Triethylamine (101 g, 1.0 mole) was added with stirring and the mixture was heated slowly until an exothermic reaction commenced. When the reaction had moderated, the mixture was refluxed for 6 hours. The alcohol was removed on a rotary evaporator and the residual white solid washed with ether. The product was recrystallised from ethanol to give white, hygroscopic crystals (85%), m. p. 104°C , δ (60 MHz, CDCl_3) 1.15 (t, 12H, CH_3 , $J = 7$ Hz) 2.34 (s, 3H, $\underline{\text{P}}\text{-CH}_3$), 3.22 (q, 8H, CH_2 , $J = 7$ Hz) 7.13 (d, 2H, aromatic, $J = 8$ Hz), 7.75 (d, 2H, aromatic, $J = 8$ Hz).

Butyltrimethylammonium Tosylate. - Butyltosylate (22.8 g, 0.1 mole) was added dropwise to a stirred solution of trimethylamine in ethanol (25 ml of a 33% solution) at room temperature. The flask was equipped with a dry-ice condenser and the mixture was stirred under reflux for 6 hours. On cooling, white crystals separated. These were filtered off, washed with ether and recrystallised from ethanol to yield the product (70%), m. p. 220°C , δ (60 MHz, CDCl_3) 0.7-2.0 (m, 7H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 2.34 (s, 3H, $\underline{\text{P}}\text{-CH}_3$), 3.2 (s, 9H, N-CH_3), 2.8-3.6 (m, 2H, N-CH_2 -), 7.2 (d, 2H, aromatic, $J = 8$ Hz), 7.72 (d, 2H, aromatic, $J = 8$ Hz).

Determination of the Solubility of Salts in Liquid Ammonia

Method I (Diagram 4). - The pipette A could be raised or lowered by means of a screw-thread joint. A saturated solution of the quaternary ammonium salt in liquid ammonia was prepared in B and the apparatus was thermostatted at -36°C . The pipette was gently lowered into B and when the cork at C was removed, the saturated solution entered A. The pipette was then raised above the surface of the solution in B, and the level of solution in A fell back to the top of the inlet tube (as shown).

The ammonia in A and B was then allowed to evaporate, and the pipette (after being oven dried) was weighed to determine the weight of salt which had been dissolved in the known volume of solution which the pipette held.

Method 2. The solubility of silver chloride in a 0.1M solution of butyltrimethylammonium fluoroborate was estimated by measuring the number of coulombs required to completely electrolyse a known volume of a saturated solution. The saturated solution was prepared and decanted into the working compartment of a two-compartment cell. Exhaustive electrolysis was carried out using a platinum electrode at -0.5v (vs. Hg pool) and the concentration of silver ions was calculated on the basis of 1 mole \equiv 96500 coulombs.

Results of the solubility measurements are given in Table IV.

Anodic and Cathodic Potential Limits in Liquid Ammonia

During the course of these studies a variety of supporting electrolytes were used and their anodic and cathodic limits were recorded at different electrodes. Representative examples of these background traces are shown to illustrate the available anodic and cathodic ranges available in liquid ammonia. Unless otherwise indicated potentials are measured versus the Pb/5 x 10⁻² M Pb(NO₃)₂ reference electrode.

Cathodic Limits. Tetraethyl- (Fig. 9), butyltrimethyl- (Fig. 10), and tetrabutyl-, tetrapropyl- and tetramethyl- (Fig. 11) ammonium fluoroborates were tested as supporting electrolytes, together with some lithium (Fig. 12) and potassium (Fig. 13) salts. In two examples (Figs. 9d and 10c) the effect of contamination of the platinum electrode surface on the background curve is shown and also the influence of pre-treating the system with solvated electrons in the presence of potassium ions is recorded (Fig. 13). Carbon paste electrodes were found to give poor cathodic ranges (ca. -1.0V) in the presence of quaternary ammonium cations and were not further studied. A summary of the cathodic limits attainable under various conditions is given in Table V.

Anodic Limits. Mercury is itself readily oxidised so anodic studies were carried out using platinum wire/glass tip and carbon paste electrodes.

1. Platinum anode. The anodic range was unchanged regardless of the nature of the supporting electrolyte anion, when fluoroborate, perchlorate and nitrate salts were used. A representative trace, and the effect of wave clipping, are illustrated using butyltrimethylammonium fluoroborate as supporting electrolyte (Fig. 14.1).

At the anodic limit bubbles of gas formed at the electrode surface. Controlled potential oxidation (+1.2V) at platinum was carried out and analytical scans using a platinum wire electrode were recorded at intervals (Fig. 14.2). The effect of ammonium ion addition on the voltammogram was also noted. Identification of the gas formed at the anode was achieved by g.l.c. analysis (molecular sieve X, room temperature, helium carrier gas). The anode compartment was flushed out with helium and the gas was collected by separating the area above the anode from the rest of the compartment with glass tubing terminating in a tap. As electrolysis proceeded the helium was displaced by the anode gas which, after 16 hours oxidation at +1.0V, was sampled by withdrawal into a syringe. Comparison of its g.l.c. behaviour with that of air suggested that the gas formed at the anode was nitrogen. A small oxygen peak was attributed to residual air in the syringe. After complete evaporation of ammonia from the cell, the residual solid from the anode compartment was treated with base (2M NaOH) and gave a strong smell of ammonia, thus suggesting the presence of ammonium ions.

2. Carbon paste anode. The carbon paste electrode was found to give an extended range compared to platinum (Figs. 14.3a and 14.3c). This enabled an oxidation wave to be observed for p-anisidine (Fig. 14.3b) and a controlled potential oxidation [+0.9V vs. Ag/satd. AgCl/satd. KCl] was carried out at a carbon rod electrode. In a typical electrolysis, p-anisidine (0.246 g, 0.002 mole) was oxidised in a solution of butyltrimethylammonium fluoroborate (0.1M). During the oxidation a red solution formed (125C passed; 1e reduction requires 193C). Evaporation of the ammonia and extraction of the anode solution into ether in the usual manner afforded a crude product

(0.2 g), which was separated by dry column chromatography (alumina III; eluent ether). The three least polar coloured bands afforded solid products. The major least polar product corresponded to 4,4'-dimethoxyazobenzene (0.074 g, 18%) m. p. 160-162°C (lit. 165°C), as shown by its n. m. r. spectrum (60 MHz, CDCl_3) δ 3.9 (s, 6H, OCH_3) 6.9-8.1 (q, 8H, aromatic). Its mass spectrum gave a parent ion m/e 242. The other two solids were not identified but appeared, on mass spectral evidence, to be polymers of azo- and hydrazo- derivatives which fragmented about the N-N bond.

III Reductions Using Solvated Electrons in Liquid Ammonia

1. Electrochemical Reduction of Acetylcyclopropanes and Pentan-2-one.

The liquid ammonia was dried before use as previously described.

Pentan-2-one, acetylcyclopropane and 1-acetyl-2,2-dimethylcyclopropane were all electro-inactive in the cathodic range available in liquid ammonia using a DME in the presence of butyltrimethylammonium fluoroborate. Their reduction was carried out at a potential beyond the cathodic limit, where solvated electrons were produced at the electrode. This was observed as a blue streaming of the mercury drop, associated with a cathodic current.

For preparative electrolyses, the cathode consisted of a mercury pool (volume 2.0 ml; area ca. 5.0 cm²) unless otherwise indicated and the catholyte was stirred by a stream of nitrogen. For potentiostatic reductions a three-compartment cell was used, but for some galvanostatic electrolyses a reference electrode was omitted. During electrolysis, gas evolution occurred at the platinum anode.

After completion of the electrolysis, an excess of ammonium chloride was added in one portion to the catholyte, ether was added and the ammonia was allowed to evaporate. The ether extract was washed with water, dried (MgSO₄), and concentrated to about 2.0 ml by distillation of the ether through a Vigreux column, using a water-bath at 50°C. The residue was analysed by g. l. c. (15% PEGA, 70°C) and the product identification was verified by mixed injections with authentic samples.

When necessary, further g. l. c. analysis was carried out after oxidation of product alcohols by chromic acid. A solution of the products (0.0025 mole) in ether (5.0 ml) was stirred with 3M chromic acid (0.83 ml) for 30 minutes at room temperature. The aqueous phase was extracted twice with ether (10.0 ml) and the combined extracts were washed with aqueous sodium bicarbonate solution and water, dried (MgSO₄), and concentrated as described above.

Relative product yields were calculated from g. l. c. peak integrations after sensitivity correction. The correction factors were obtained by integration of three weighed authentic sample mixtures. Actual yields based on starting material were calculated using nonane or mesitylene as an external standard, the former being less suitable as it was incompletely resolved from the ether peak. The standard was added in ether during extraction of the catholyte.

Reaction mixtures from the reduction of acetylcyclopropane and pentan-2-one were estimated before chromic acid oxidation, since a control experiment showed that up to 40% product loss could occur during the oxidation process.

Various silver/silver salt reference electrodes were used during these studies, but for conformity of results all potentials have been adjusted and are quoted versus the lead/lead nitrate (0.05M) reference electrode.

(i) Butyltrimethylammonium Fluoroborate as Supporting Electrolyte.

A solution of butyltrimethylammonium fluoroborate (1.01 g, 0.1M) in liquid ammonia (50 ml) showed a cathodic range of -1.85V at the DME. The limit was associated with production of solvated electrons at the electrode.

During preparative electrolysis at more negative potentials, the mercury pool surface became covered with a dark grey crust and a suspension of a finely divided grey solid formed. Even before the addition of the ketone the solvated electrons were immediately destroyed and a blue solution was not formed.

On addition of ammonium chloride to the catholyte, the grey solid reacted vigorously with effervescence and a clear solution was produced.

(a) Reduction of Acetylcyclopropane and Pentan-2-one.

Galvanostatic reduction (100 mA) of acetylcyclopropane (0.042 g, 0.0005 mole), in 50 ml of solution, was carried out for 35 minutes (210 C passed; 4e reduction requires 193 C). During the electrolysis the potential of

the working electrode rose from -2.0V to -2.5V.

After extraction of the catholyte as described, the products were shown by g. l. c. to consist of pentan-2-one (62%), pentan-2-ol (18%), acetylcyclopropane (19%) and acetylcyclopropanol (1%).

Reduction of pentan-2-one under similar conditions gave only pentan-2-ol.

(b) Reduction of 1-acetyl-2,2-dimethylcyclopropane.

Controlled potential electrolysis of 1-acetyl-2,2-dimethylcyclopropane (0.28 g, 0.0025 mole) was carried out at -2.0V. The initial cell current was about 60mA but decreased rapidly as the mercury pool surface became contaminated.

After the passage of 575 C (4e reduction requires 964 C), electrolysis was stopped and the catholyte extracted as described previously. The mixture was found by g. l. c. to consist of 1-acetyl-2,2-dimethylcyclopropane (3) 5-methylhexan-2-one (4), 4,4-dimethylpentan-2-one (5) and their corresponding alcohols. After chromic acid oxidation, only the three ketones were observed.

Similar reductions were carried out under varied conditions as described in Table VI .

The platinum foil (area ca 20 cm²) and lead wire (area ca 8.0 cm²) electrodes gave a similar cathodic range to the mercury pool electrode, but cell currents were considerably lower. For a cell current of 50 mA, initial cathode potentials of about -2.0V, -2.7V and -3.0V were observed for mercury, platinum and lead electrodes respectively. The lead wire electrode appeared to become covered with a white crust during electrolysis, associated with a rapid fall in cell current. In order to maintain a current of 50mA, the measured potential increased to -6.3V. For this reason a pulse technique was employed, the potential being pulsed from -2.2V to 0.0V at 10 second intervals. At the latter potential, the electrode surface was regenerated. During this period an anodic current flowed, presumably due in part to oxidation of electrons, and this is included in the coulombic integral.

The cathodic range at a carbon paste electrode was only -1.1V and the preparative carbon rod electrode exhibited high currents at potentials more negative than this. However solvated electrons could not be observed until -3.3V and this potential was selected for the electrolysis. As some process other than the formation of solvated electrons was apparently occurring beyond -1.1V, more than the theoretical number of coulombs required was passed. Rapid decomposition of the carbon rod occurred.

Yields, calculated using nonane as the external standard, were between 75-100% based on starting material. The results are summarised in Table VI.

(ii) Tetraethylammonium Fluoroborate as Supporting Electrolyte.

A 0.1M solution of tetraethylammonium fluoroborate in liquid ammonia (50 ml) was prepared. The cathodic range (-1.9V) was slightly greater than that of butyltrimethylammonium fluoroborate at the DME. At potentials beyond the cathodic limit, solvated electrons were produced and, in the absence of ketone, a blue solution formed. Electrolysis at 100mA for 5 minutes resulted in a solution which took 10 minutes to decolorise.

In contrast to the butyltrimethylammonium case, no grey solid formed, although the surface of the mercury pool became tarnished.

(a) Reduction of Acetylcyclopropane and Pentan-2-one.

Galvanostatic reduction (100 mA) of acetylcyclopropane (0.084 g, 0.001 mole) in 50 ml of solution was carried out. The solution remained clear for about 35 minutes (210 C passed), after which time the blue colour of solvated electrons persisted. The electrolysis was continued for a further 45 minutes (480 C passed; 4e reduction requires 386 C). During the electrolysis, the cathode potential remained at about -2.1V.

The catholyte was worked up as usual. Analysis of the ether extract by g.l.c. (15% PEGA, 70°C) showed one major product and two minor products. The major product, which was unaffected by chromic

acid oxidation, was separated by preparative g.l.c. (15% DEGS, 60°C). It was identified as 3-methylhexan-3-ol (70-75% yield) on spectral evidence and by synthesis of an authentic sample δ (60MHz, CCl_4) 0.7-1.9 (m, 15H) 2.14 (s, 1H). The signal at δ 2.14 disappeared on shaking the sample with D_2O , and the presence of a hydroxyl group was supported by a broad peak at 3400 cm^{-1} in the i. r. spectrum. Treatment of the n. m. r. sample with the shift reagent $\text{Eu}(\text{FOD})$ (0.2 g) gave an expanded spectrum δ (100MHz, CCl_4) 2.2 (t, 3H, 6- CH_3) 4.24 (t, 3H, 1- CH_3) 5.2-5.6 (m, 2H, 5- CH_2) 6.25 (s, 3H, 3- CH_3) 6.73-7.6 (m, 4H, 2- and 4- CH_2); the assignments were supported by proton decoupling experiments.

The mass spectrum failed to show a parent ion m/e 116, but gave signals at 101 (P-Me), 87 (P-Et) and 73 (P-Pr). At low eV, a signal at 98 (P- H_2O) appeared.

The two minor components (15-20% yield) were identified as pentan-2-one and pentan-2-ol.

The reduction of pentan-2-one similarly yielded pentan-2-ol and 3-methylhexan-3-ol.

A series of experiments were carried out under similar conditions to study the effect on product distribution of changing one variable at a time. The experiments included lowering the supporting electrolyte concentration, using a mixture of supporting electrolytes, changing the electrode material and adding a proton donor (0.1M EtOH). Galvanostatic reduction (100 mA) of the substrate (0.001 mole) was carried out at a mercury pool electrode in a solution of tetraethylammonium fluoroborate (0.1M), unless otherwise indicated. The reduction was either taken to completion or stopped when 70% of the required number of coulombs had been passed. Yields were calculated using mesitylene as external standard.

The results of these experiments for the reduction of pentan-2-one and acetylcyclopropane are given in Tables VII and VIII respectively.

Further information on the reduction of acetylcyclopropane was obtained by sampling the reaction during electrolysis and analysing the

product mixture. The ketone (0.168 g, 0.002 mole) in 100 ml of solution was reduced at 100 mA for 140 minutes. (840 C passed; 4e reduction requires 750 C).

The samples were withdrawn as follows: the cell inlet tube was replaced by a piece of glass tubing which reached to the bottom of the cell and which was bent through 180° at the upper end. During the electrolysis, nitrogen was bubbled into the cell through this tube. The electrolysis was stopped at 5 minute intervals and the cell disconnected from the vacuum line. A pressure of nitrogen was applied at c'' (Diagram I), which forced catholyte solution (ca 2.0 ml) up the tube and into a sample bottle (10.0 ml) containing ammonium chloride. Ether (5.0 ml) was added to the samples, which were carefully concentrated and examined by g. l. c.

During the sampling procedure the level of solution in the working compartment fell, causing leakage of secondary compartment solution into the working compartment. In order to determine the effect of this on the product ratios, an experiment was carried out in which sampling was not commenced until half the required number of coulombs had been passed.

The results of both sampling experiments are shown in Table IX and Graphs I and II show the number of coulombs passed versus relative percentages of products.

(b) Reduction of 1-Acetyl-2,2-dimethylcyclopropane.

1-Acetyl-2,2-dimethylcyclopropane (0.28 g, 0.0025 mole) was reduced galvanostatically at 50 mA for 3 hours (540 C passed; 4e reduction requires 965 C). During the electrolysis, the potential of the mercury pool rose from -2.5V to -2.9V.

After work-up, the catholyte was examined by g. l. c. and showed two new peaks in addition to the products (4) and (5) described previously. The new products were unaffected by chromic acid oxidation, as shown by g. l. c., but the reaction solution acquired a yellow colour during the oxidation which was not previously observed. The g. l. c. /mass spectrum

(10% PEGA, 70°C) of both peaks gave signals at 129 (P-CH₃), 115, 97 and 73 (base peak).

The mixture was separated by preparative g.l.c. (15% DEGS, 60°C) into three colourless, liquid fractions, the first fraction consisting of already identified compounds (3), (4) and (5). Fractions two and three were shown by analytical g.l.c. to be pure samples of the new products.

The major product, fraction three, was identified as 3,6-dimethylheptan-3-ol. Its n.m.r. spectrum was not very informative: δ (100MHz, CCl₄) 0.85-1.6 (m, 19H) 2.15 (s, 1H). The signal at δ 2.15 was removed by shaking with D₂O and attributed to -OH, since a broad peak was observed in the i.r. spectrum at 3400 cm⁻¹. Addition of the shift reagent Eu(FOD) (0.2 g) to the n.m.r. sample gave a more easily interpreted spectrum δ (100MHz, CCl₄) 1.55 (d, 6H, 7- and 8-CH₃) 2.73 (m, 1H, 6-CH) 3.63 (t, 3H, 1-CH₃) 4.66 (m, 2H, 5-CH₂) 5.76 (s, 3H, 3-CH₃) 6.27 (m, 4H, 2- and 4-CH₂); the assignments were supported by proton decoupling experiments. The ¹³C n.m.r. spectrum showed 8 lines and assignments were made using off-resonance decoupling: δ (CDCl₃) 8.13 (1-CH₃) 22.65 (6- and 7-CH₃) 26.50 (6-CH) 30.00 (3-CH₃) 33.00 (5-CH₂) 34.26 (4-CH₂) 39.15 (2-CH₂) 72.89 (3-C). The combined spectral data suggested a molecular formula C₉H₂₀O (m/e 144) but a parent ion was not observed in the mass spectrum, the highest mass peak was P-CH₃ (accurate mass 129.128705, C₈H₁₇O requires 129.127933). Further fragmentation gave signals at P-C₂H₅ (accurate mass 115.112072, C₇H₁₅O requires 115.112284) and P-C₅H₁₁ (accurate mass 73.065375, C₄H₉O requires 73.065336), which all resulted from cleavage β to the O atom of 3,6-dimethylheptan-3-ol. Further fragmentation occurred at P-C₂H₅, H₂O (accurate mass 97.101506, C₇H₁₃ requires 97.101720) and at low eV a signal corresponding to P-H₂O (m/e 126) was observed, although the parent molecular ion was still not present.

The identity of fraction two as 3,5,5-trimethylhexan-3-ol readily

followed from that of fraction three. Its n. m. r. spectrum (60MHz, CCl_4) δ 0.8-1.81m) was simplified by addition of the shift reagent $\text{Eu}(\text{FOD})$ (0.2 g). δ 2.95 (s, 9H, 5- and 6- CH_3) 3.5 (t, 3H, 1- CH_3) 5.37 (s, 3H, 3- CH_3) 5.6-6.6 (m, 4H, 2- and 4- CH_2). Fragmentation in the mass spectrum was similar to that observed for 3,6-dimethylheptan-3-ol. The structures were confirmed by synthesis of authentic samples.

2. Attempted Alkylation of Acetylcyclopropane and Pentan-2-one Using Chemically Generated Solvated Electrons.

Solvated electrons were produced by dissolving alkali metals in liquid ammonia. Work-up was similar to that described for the electrochemical reductions. The products were analysed by g.l.c. (15% PEGA, 70°C) and identified by mixed injections with authentic samples.

(i) Sodium in Ammonia. Acetylcyclopropane (0.084 g, 0.001 mole) in a solution of tetraethyl ammonium fluoroborate (0.1M, 1.084 g) in liquid ammonia (50 ml) was reduced by the addition of small pieces of sodium (0.23 g, 0.01 g atom) which dissolved to give solvated electrons. The solution was stirred for 1.5 hours and worked-up as previously described.

Analysis of the product mixture after chromic acid oxidation showed peaks corresponding to pentan-2-one and acetylcyclopropane (1:2). There was no peak corresponding to the alkylated product 3-methylhexan-3-ol.

A similar reduction of pentan-2-one (0.086 g, 0.001 mole) afforded only pentan-2-ol, as indicated by g.l.c.

(ii) Lithium in Ammonia. Tetraethylammonium chloride was obtained as its monohydrate, and was dried for 48 hours at 100°C in vacuo before use, in order to remove the water of crystallisation. Lithium pellets (0.07 g, 0.01 g atom) were added to dry ammonia (50 ml) and the mixture

was stirred for 30 minutes to give a blue solution. The addition of tetraethylammonium chloride (1.8 g; slight excess) caused an instant decolorisation of the solution, and it became apparent that the lithium had only partially dissolved. Acetylcyclopropane (0.084 g, 0.001 mole) was added and the mixture was stirred for 1.5 hours, during which time lithium chloride precipitated (solubility of LiCl in ammonia is 0.54 g/100 g at -34°C). Some lithium remained undissolved.

Analysis of the products indicated some pentan-2-one and mainly unreacted acetylcyclopropane.

(iii) Potassium in Ammonia. Addition of potassium (0.39 g, 0.01 g atom) to dry ammonia (50 ml) gave initially a blue solution of solvated electrons, but after stirring for about 30 minutes the solution decolorised and a grey precipitate of potassamide formed.

In a further experiment potassium (0.095 g, 0.0025 g atom) was added to a solution of tetraethylammonium chloride (0.1M, 0.414 g) in dry ammonia (25 ml) containing pentan-2-one (0.086 g, 0.001 mole). The potassium dissolved to give a blue solution which decolorised after about 30 minutes. A white suspension, possibly of potassium chloride (solubility of KCl in ammonia is 0.213 g/100 g at -34°C) or of potassamide was formed. After stirring for 1 hour the mixture was quenched with an excess of ammonium chloride and was worked-up as usual. The product mixture (40% yield) was shown by g.l.c. analysis to be a mixture of pentan-2-one (28%) and pentan-2-ol (72%).

3. Attempted Alkylation of Pentan-2-one by other Supporting Electrolytes.

The galvanostatic reduction (100 mA) of pentan-2-one (0.086 g, 0.001 mole) was carried out for 30 minutes (180 C passed; 2e reduction requires 193 C) in the presence of various supporting electrolytes. These were diethyldimethylammonium iodide, tributylethylammonium fluoroborate, triethylmethylammonium iodide, tributylmethylammonium fluoroborate, ethyltripropylammonium fluoroborate, tetramethylammonium

fluoroborate and tetrapropylammonium fluoroborate.

Owing to low solubilities, saturated solutions of tetramethylammonium (ca 0.02M), tetrapropylammonium (ca 0.02M), and tributylmethylammonium (ca 0.075M) fluoroborates were used. Solutions were otherwise 0.1M.

The use of iodides was avoided when possible owing to formation of nitrogen triiodide as a black solid at the anode during electrolysis. The solid detonated on dismantling the electrode and was considered dangerous. When the use of an iodide was unavoidable, the nitrogen triiodide was decomposed by an aqueous solution of sodium sulphite. Fluoroborates were prepared by precipitation from a saturated solution of the iodide with aqueous fluoroboric acid.

Solvated electrons were observed beyond the cathodic limit in all cases except that of tetramethylammonium fluoroborate, when only amalgam formation occurred. A platinum electrode was used instead of mercury in this case.

Tetrapropylammonium fluoroborate gave a slightly larger cathodic range than the other supporting electrolytes (-2.0V at the DME) and a reduction wave for the ketones was just visible.

Possible products were 2-methylpentan-2-ol from methyl alkylation, 3-methylhexan-3-ol from ethyl alkylation, 4-methylheptan-4-ol from propyl alkylation and 4-methyloctan-4-ol from butyl alkylation. Authentic samples were prepared, or obtained, and all were found to give peaks on g.l.c. under the usual conditions. 2-Methylpentan-2-ol and pentan-2-ol both showed identical retention times, so analysis was carried out after chromic acid oxidation in experiments where confusion could arise.

In all cases except two, the supporting electrolytes showed similar behaviour to the butyltrimethylammonium case on reduction. The solvated electrons were rapidly destroyed and a grey solid formed. Only pentan-2-ol was formed in these reductions.

In order to remove possible complications arising from quaternary ammonium amalgam formation, the reduction was also carried out at a platinum electrode in 0.1M butylmethylammonium fluoroborate solution.

using acetylcyclopropane as substrate. The stability of solvated electrons seemed greater than at a mercury cathode, but no alkylated products were formed (see Table VIII.)

In the case of diethyldimethylammonium iodide and tributylethylammonium fluoroborate however, the solvated electrons were stable enough to give a blue solution, although the stability was less than in the tetraethylammonium case, as shown by the shorter time taken to decolorise a solution resulting from the passage of 100mA for 5 minutes (in the absence of ketone). The tributylethylammonium salt particularly resembled the tetraethylammonium fluoroborate, in that the reaction mixture remained very clean during the reduction; in this case a high yield of ethyl alkylated product was obtained (>80%) but there was no evidence for butyl alkylation. A similar result was obtained using acetylcyclopropane as substrate. Reduction of pentan-2-one in the presence of diethyldimethylammonium iodide afforded a trace (<1%) of methyl and ethyl alkylated products.

4. Electrochemical Reduction of Oct-4-yne.

A solution of oct-4-yne (2mM) in liquid ammonia containing THF as a co-solvent was electro-inactive at a HMDE. A preparative reduction was carried out beyond the potential of electron dissolution. The acetylene (0.22 g, 0.002 mole) was reduced galvanostatically (100mA) at a mercury pool in a 0.1M solution of tetraethylammonium fluoroborate in liquid ammonia (50 ml) containing THF (15 ml). The cathode potential remained at about -2.1V during the reduction and the catholyte turned blue shortly after the start of the electrolysis. After about 100 minutes (600 C passed; 2e reduction requires 386 C), the solution was quenched with ammonium chloride and extracted into ether. The extract was concentrated by distillation of the ether through a Vigreux column and examined by g.l.c. (15% PEGA, 50°C). Peaks corresponding to unreacted oct-4-yne and THF were obtained. The mass spectrum of the product mixture showed a highest mass peak (m/e 110) corresponding to oct-4-yne, suggesting that reduction of the acetylene had not taken place.

The reduction was also carried out under more extreme conditions, a current of 300mA being passed for 1 hour in an undivided cell. Extensive contamination of the mercury pool cathode occurred and its potential rose from -5.0 to -8.0V but g.l.c. and mass spectral analysis of the reaction mixture suggested no reduction had occurred.

Reduction of Oct-4-yne by Solvated Electrons in the Presence of Ethanol.

Galvanostatic reduction (100mA) of oct-4-yne (0.001 mole) was carried out in a 0.1M solution of tetraethylammonium fluoroborate in liquid ammonia (100 ml) containing ethanol (5 ml). After 2 hours (720 C passed; 2e reduction requires 193 C) the catholyte had not turned blue due to an excess of electrons. The reduction solution was extracted into ether and the concentrated extract examined by g.l.c. Two peaks were observed in addition to peaks corresponding to oct-4-yne and ethanol. Mass spectrum/g.l.c. (propylene carbonate, 50°C) indicated that both peaks had molecular ions m/e 112, suggesting that 2e reduction to olefins had taken place. G.l.c. peak integration indicated a 5:1 isomer ratio, with the combined yield being about equal to that of recovered oct-4-yne.

5. Related Chemical Syntheses

Preparation of 1-Acetyl-2,2-dimethylcyclopropane¹⁶⁹

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Dried, recrystallised trimethyloxosulphonium iodide (39.0 g, 0.175 mole) was stirred into dimethylsulphoxide (130 ml) under dry nitrogen. Sodium hydride (4.2 g, 0.175 mole) was added slowly, followed by addition of mesityl oxide (16.7 g, 0.17 mole) over a period of 15 minutes. The temperature was never allowed to rise above 40°C during the additions. Stirring was continued for 3 hours and then left overnight. The mixture was then poured onto ice and the organic layer was extracted with petroleum-ether (b.p. 30-40°C). The extract was washed with water, dried (MgSO₄) and concentrated on a rotary evaporator. Distillation of the product afforded 1-acetyl-2,2-dimethylacetylcyclopropane (8.27g, 44%), b.p. 45°C/14 mm.

The product was further purified before use by preparative g.l.c. (SE30, 75°C) to give material exhibiting only one peak on analytical g.l.c. (15% PEGA, 70°C).

Grignard Synthesis of Tertiary Alcohols.

Dry, clean magnesium turnings (4.0 g, 0.166 g atom) were placed in a 3-necked flask equipped with a mechanical stirrer, condenser (CaCl₂ drying tube) and addition funnel. The magnesium was covered with dry ether and a few drops of ethyl bromide were added. The mixture was stirred until reaction commenced. The application of heat and addition of a small crystal of iodine was usually necessary to start the reaction. Ethyl bromide (20.0 g, 0.1835 mole), in an equal volume of dry ether, was then added and the mixture was stirred until all the magnesium had reacted.

3,6-Dimethylheptan-3-ol. 5-Methylhexan-2-one (18.2 g, 0.159 mole) was then added to the Grignard reagent. After refluxing for 1 hour, the mixture was poured onto ice and neutralised with dilute aqueous hydrochloric acid. The organic layer was extracted into ether (200 ml), washed with water, dried (MgSO₄), and concentrated. 3,6-Dimethylheptan-3-ol (18.5 g; 80%), b.p. 170°C, was obtained by distillation from calcium hydride.

3,5,5-Trimethylhexan-3-ol. (17.5 g; 76%), b.p. 148°C, was prepared from ethyl magnesium bromide and 4,4-dimethylpentan-2-one (18.2 g, 0.16 mole) in a similar manner.

3-Methylhexan-3-ol (13.9 g; 75%), b.p. 140°C, was prepared using magnesium (4.0 g, 0.166 g atom), propyl bromide (22.58 g, 0.18 mole) and butan-2-one (11.5 g, 0.16 mole) in a similar manner.

4-Methyloctan-4-ol (19.0 g; 82%), b.p. 75°C/15 mm, was synthesised from magnesium (4.0 g, 0.166 g atom), butyl bromide (25.12 g, 0.16 mole) and pentan-2-one (13.73 g, 0.18 mole) in a similar manner.

III. Electrode Reductions of Organic Compounds

Analytical Studies: Polarography and Cyclic Voltammetry

A series of electro-reductions of organic compounds was studied by polarography and/or cyclic voltammetry using a dropping mercury electrode (DME), hanging mercury drop electrode (HMDE) or polished platinum disc electrode (PDE). Tetraethylammonium or butyltrimethylammonium fluoroborates were usually used as supporting electrolytes, although in some cases lithium or potassium salts were employed. During the studies various reference electrodes were assayed. These consisted of a silver wire immersed in a saturated solution of silver chloride in a solution of the electrolyte, a silver wire immersed in liquid ammonia saturated with silver chloride and potassium chloride, and, most usually, a lead wire in a 0.05M solution of lead nitrate in liquid ammonia. Also several cell designs were assayed before the final construction, previously described, was selected for use. In order to eliminate any discrepancies in results which may have arisen from variations in the conditions used, a series of cyclic voltammograms were recorded under identical conditions. A solution of the depolariser (2mM) in 0.1M tetraethylammonium fluoroborate was prepared and CV was conducted at a HMDE at a sweep rate of 250 mV s^{-1} using a counting resistor of 47 K-ohms and a recorder γ -axis sensitivity of 40 mV cm^{-1} . Potentials were measured vs Pb/0.05M Pb^{2+} .

Peak reversibility was estimated by measurement of the anodic and cathodic peak separations ($E_{p_a} - E_{p_c}$) and by measurement of the anodic to cathodic peak currents ($\frac{i_{p_a}}{i_{p_c}}$). The peak heights were measured using the time-base mode of operation of the recorder. A potential sweep was carried out to 100mV beyond the cathodic peak potential and the current/time decay curve was recorded. This was used as a base-line from which to measure the peak height of the anodic peak (and, in the case of a second electron transfer, the peak height of the second cathodic peak). The anodic peak was estimated by reversing the direction of the potential sweep at about 100mV beyond the cathodic peak potential. An example of the use of the technique is given for benzophenone (Fig. 15.1).

A summary of the CV data obtained using the standard conditions described above for the following compounds is given in Table X.

1. The Reduction of Benzophenone

Cyclic voltammograms of benzophenone were recorded at a HMDE and PDE in solutions containing butyltrimethylammonium (Fig. 15.1), tetraethylammonium (Fig. 15.3), potassium (Fig. 15.2) and lithium (Fig. 15.5) salts. Polarograms were also recorded in some cases (Fig. 15.6). The effect of using mixtures of quaternary ammonium salts was investigated and also the influence of ethanol (Fig. 15.7) and acetonitrile (Fig. 15.8) addition was noted. Wave clipping was used to study an anomalous wave observed at the HMDE (Fig. 15.4). A summary of the CV data is given in Table XI.

2. The Reduction of Benzoylcyclopropane

Benzoylcyclopropane was reduced at a HMDE, and PDE in the presence of tetraethyl- (Fig. 16.1) and butyltrimethyl- (Fig. 16.2) ammonium salts. The effect of ethanol on the cyclic voltammogram was investigated (Fig. 16.2).

3. The Reduction of Acetophenone

A cyclic voltammogram and polarogram of acetophenone was recorded in the presence of tetraethyl- (Fig. 17.1) and butyltrimethyl- (Fig. 17.2) ammonium salts. The effect of ethanol addition on the former was investigated.

4. The Reduction of Azobenzene

Azobenzene is sparingly soluble (<2mM) in liquid ammonia, and was therefore sometimes added to the cell dissolved in a small volume of THF. Cyclic voltammograms were recorded at a PDE and HMDE in the presence of potassium, butyltrimethylammonium and tetraethylammonium salts (Figs. 18.1, 18.2 and 18.3). The effect of ethanol (Fig. 18.3) and acetonitrile on the cyclic voltammogram was noted. In some instances, the addition of ethanol resulted in the formation of anomalous waves (Fig. 18.4) at a HMDE. The effect of wave clipping and the addition of phenylhydrazine and hydrazobenzene was investigated.

5. The Reduction of Stilbene

Liquid cis-stilbene appeared to readily dissolve in liquid ammonia to give a 2mM solution but the solid trans-isomer was only sparingly soluble. Cyclic voltammograms of both isomers were recorded at either a HMDE or PDE in solutions of tetraethyl- (Fig. 19.1) or butyltrimethyl- (Fig. 19.2) ammonium salts. The effect of second cycles and of holding the potential between the two reduction waves before initiating an anodic sweep was recorded (Fig. 19.3 and 19.4). A mixture of the isomers was also studied by cyclic voltammetry (Fig. 19.4b) and the effect of ethanol on the cyclic voltammogram was investigated (Fig. 19.5).

6. The Reduction of Diphenylacetylene

Diphenylacetylene was studied by polarography (Fig. 20.1) and cyclic voltammetry (Fig. 20.2) in a solution of tetraethylammonium fluoroborate. The effect of ethanol addition on the latter was noted (Fig. 20.3). Second cycle voltammetry and wave clipping were also carried out (Fig. 20.5).

Preparative Studies: Controlled Potential Reductions

Controlled potential electrolyses were carried out in conjunction with the analytical studies previously described.

A mercury pool cathode (volume 2.0 ml; area ca 5.0 cm²) was usually employed and potentials are quoted versus the Pb/0.05M Pb(NO₃)₂ reference electrode. In all cases a 3-compartment cell was used.

The same general procedure was used to separate the reduction products. At the end of the electrolysis, ammonium chloride (an excess, ca 1.0 g) was added to the catholyte. The anode and reference compartments were removed from the cell and ether (200 ml) was slowly added to the cathode compartment as ammonia evaporated. The ethereal solution was washed with brine, dried over anhydrous magnesium sulphate and concentrated on a rotary evaporator.

1. Reduction of Benzophenone in Liquid Ammonia

Reduction of benzophenone (0.182 g, 0.001 mole) was carried out at a mercury cathode in a solution of butyltrimethylammonium fluoroborate (0.1M, 2.168 g) in liquid ammonia (100 ml). In a typical reduction at the potential of the second wave (-1.6V), an initial cell current of 90mA flowed, decreasing to 3mA after about 5 hours (139 C passed; 2e reduction requires 193 C). The catholyte became initially blue-green but after a few hours the blue colour disappeared to give a light yellow solution. Work-up in the usual manner afforded a brown oil (0.18 g). T.l.c. of the crude product (alumina; eluent 70:30 petrol ether) indicated two components with retention times similar to those of benzophenone and the corresponding alcohol, diphenylcarbinol. This was in accordance with the n.m.r. spectrum (CCl₄), which showed signals corresponding to unreacted benzophenone δ 7.2-8.0 (m) and diphenyl carbinol δ 2.3 (s, 1H, -OH) 5.84 (s, 1H, CH) 7.36 (s, 10H, aromatic) in about equal amounts. Other signals in the regions δ 0.8-1.4 (m, ca. 3-H) 3.1-3.9 (broad m, ca 1-H) 4.7-5.3 (broad m, <1-H)

were unassigned.

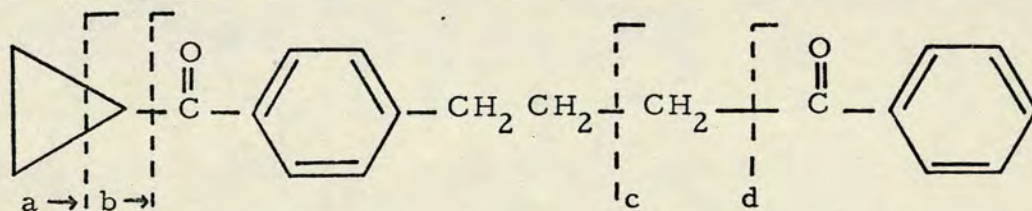
A similar product mixture, as indicated by its n. m. r. spectrum, was obtained when reduction was carried out in the presence of tetraethylammonium fluoroborate as supporting electrolyte.

A larger scale reduction of benzophenone (0.91 g, 0.005 mole) was continued overnight, during which time some leakage of the secondary compartment into the catholyte occurred. The cell current decreased from 200mA to 6mA (1400 C passed; 2e reduction requires 965 C) and a white solid precipitated. The extracted reduction mixture (0.78 g) gave an n. m. r. spectrum corresponding to pure diphenyl carbinol with none of the unassigned signals previously observed.

2. Reduction of Benzoylcyclopropane in Liquid Ammonia

The reduction of benzoylcyclopropane (1.46 g, 0.01 mole) was carried out at a mercury pool cathode containing a solution of butyltrimethylammonium fluoroborate (0.1M) as supporting electrolyte. The ketone solidified on addition to the catholyte but dissolution was achieved on stirring. A controlled potential of -1.8V caused the catholyte to turn reddish-brown and a tarry material deposited on the cathode, causing a premature fall in the cell current. This was partially remedied by increasing the area of the mercury pool. The electrolysis was terminated after about 7 hours when the cell current had fallen from 180mA to 18mA (1450 C passed; 2e reduction requires 1930 C). The catholyte was light brown in colour and a white solid was present, but this dissolved on addition of ammonium chloride (1.0 g). The cathode solution was extracted into ether in the usual manner to yield, on concentration, a brown oil (1.1 g). The n. m. r. spectrum (60MHz, CDCl_3) of the product mixture was complex and showed signals at δ 0.0-3.4 (m) 3.85 (d) 5.7 (weak) 6.9-8.0 (m), the ratio of aromatic to aliphatic protons being about 2:3. Examination of the mixture by t. l. c. (alumina III; eluent 5:3 ether-petrol) indicated numerous components, some of which were separated by wet column chromatography (alumina III; eluent initially 2:3 ether-petrol, followed by an increasing proportion of ether, and finally

chloroform). The total material eluted from the column (0.6 g) represented about 50% recovery, suggesting a considerable portion of the crude product was highly polar. The first fractions collected afforded a colourless liquid, which was shown to be the ring cleaved product, butyrophenone (0.01 g, 0.7%), by its n.m.r. spectrum (60MHz, CCl_4) δ 0.8-1.2 (t, 3H, CH_3), 1.4-2.1 (sextet, 2H, CH_2) 2.7-3.1 (t, 2H, CH_2), 7.0-8.15 (m, 5H, aromatic). The following fractions were identified as unreacted benzoylcyclopropane (0.2 g, 13.7%) by their n.m.r. spectra (60MHz, CCl_4) δ 0.7-1.6 (m, 4H, cyclopropyl CH_2) 2.4-2.9 (m, 1H, cyclopropyl CH) 7.2-8.2 (m, 5H, aromatic). Elution with ether afforded the major component, a white crystalline solid, m.p. 91° (from ether), which was believed to be p-(3-benzoylpropyl)-benzoylcyclopropane formed by head to tail coupling of one molecule of benzoylcyclopropane and one molecule of the corresponding ring cleaved ketone. This compound (0.13 g, 9%) gave a parent ion in the mass spectrum m/e 292, corresponding to $\text{C}_{20}\text{H}_{20}\text{O}_2$, the molecular formula being supported by elemental analysis. (Found: C, 82.43; H, 6.92. $\text{C}_{20}\text{H}_{20}\text{O}_2$ requires C, 82.19; H, 6.848). The major peaks in the mass spectrum at m/e 264, 251, 120 and 105 could be explained by the cleavages indicated below.



$$a = m/e \ 264$$

$$c = m/e \ 120$$

$$b = m/e \ 251$$

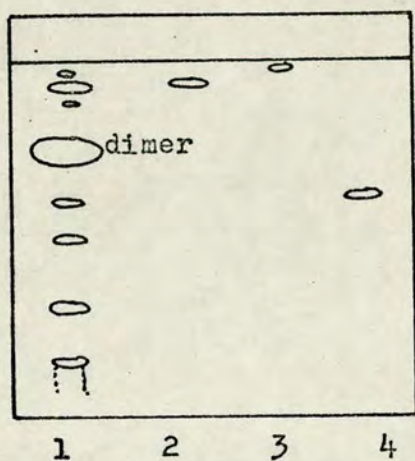
$$d = m/e \ 105$$

The n.m.r. spectrum (100 MHz, CCl_4) showed signals at δ 0.6-1.25 (m, 4H, cyclopropyl CH_2) 1.9-2.22 (doublet of quintets, 2H, CH_2 , $J = 6\text{Hz}$) 2.4-3.0 (m, 1H, cyclopropyl; two triplets, 4H, CH_2 , $J = 6\text{Hz}$) 7.1-7.5 (m, 5H, aromatic) 7.75-7.95 (m, 4H, aromatic).

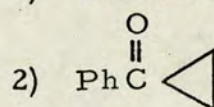
Further elution with ether yielded phenylcyclopropyl carbinol

(0.1 g, 7%), as indicated by n.m.r. spectroscopy (60MHz, CCl_4)
 δ 0.2-1.4 (m, 5H, cyclopropyl) 2.77 (s, 1H, -OH) 3.73-4.0 (1H, d, CH) 7.17 (s, 5H, aromatic). Only 80 mg of unidentified material was eluted by chloroform.

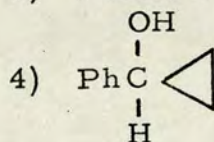
In addition to these components there was evidence of a compound containing an olefinic proton, as shown by a signal in the n.m.r. spectrum at δ 5.7, both in the product mixture and the fractions separated from the column prior to elution of dimer. Comparison of the t.l.c. behaviour of the crude reaction mixture with authentic samples is indicated below.



1) Reaction mixture



3) PhCOPr



Attempts to analyse the less volatile components by g.l.c. /mass spectrum were unsuccessful. Even on a very non-polar column (1% SE 30, 210°) the dimer had a retention time of 30 minutes.

A similar product mixture resulted from reduction at the potential of the first wave, although there was no evidence for phenylcyclopropylcarbinol formation in the n.m.r. spectrum or by t.l.c. Reduction by solvated electrons also gave the same products as judged by n.m.r. spectroscopy.

When the reduction was carried out in the presence of ethanol (5% by volume) or acetamide (0.2M), a much cleaner reaction took place, the major product being phenylcyclopropylcarbinol. Also reduction in the presence of tetraethylammonium fluoroborate (0.1M) as supporting electrolyte gave a product mixture whose n.m.r. spectrum indicated

only benzoylcyclopropane and the corresponding alcohol, no signals corresponding to dimer being observed.

3. Reduction of Acetophenone in Liquid Ammonia

Acetophenone (1.2 g, 0.01 mole) was reduced at the potential of the second wave (-1.7V) at a mercury pool cathode in a solution of butyltrimethylammonium fluoroborate (0.1M) in liquid ammonia. An initial cell current of 100mA decreased to 6mA (690 C passed; 2e reduction requires 1930 C). The solution became pale yellow and a white solid, which dissolved on addition of ammonium chloride, precipitated. The catholyte was extracted with ether in the usual manner and the extract was concentrated to yield a brown oil (0.9 g). The n.m.r. spectrum of the product mixture (60MHz, CCl_4) δ 0.7-1.3 (weak multiplet) 1.42 (s), 1.55 (s) 1.7-2.1 (weak multiplet) 2.46 (s) 3.0 (s) 3.3 (s) 3.5 (s) 3.75 (s) 4.5-4.9 (broad multiplet) 6.9-7.9 (m) suggested the presence of acetophenone, 1-phenylethanol and the corresponding pinacol. Unassigned signals were also present. A white solid (0.1 g) crystallised from the oil and was identified as the pinacol by n.m.r. spectroscopy.

The mixture was fractionated by wet column chromatography (Alumina III; eluent 50:50 ether-petrol, followed by ether, and finally ethanol). Three compounds were separated. These, in order of elution, were unreacted acetophenone (0.32 g, 26.6%) (60MHz, CCl_4) δ 2.38 (s, 3H, CH_3) 7.0-7.9 (m, 5H, aromatic), 1-phenylethanol (0.01 g, 1.3%) (60MHz, CCl_4) δ 1.1-1.4 (d, 3H, CH_3) 2.35 (s, 1H, -OH) 4.35-4.9 (q, 1H, CH) 7.4 (s, 5H, aromatic) and the pinacol, which was eluted by ethanol, (0.18 g, total yield 0.28 g, 23%) (60MHz, CDCl_3) δ 1.5 (s, 6H, CH_3) 2.68 (s, 2H, -OH) 7.18 (s, 10H, aromatic). The compounds were identified by comparison of their n.m.r. spectra with authentic samples. The low yield of alcohol obtained was surprising as the n.m.r. spectrum of the product mixture indicated about equal amounts of 1-phenylethanol and acetophenone, by comparison of their methyl proton signals. However g.l.c. analysis (15% PEGA, 155°C) gave peaks for alcohol and starting ketone which supported the results from the

chromatographic separation. A suitable column was not found for g.l.c. estimation of the pinacol.

Controlled potential reductions were also carried out at the potential of the first wave and by electrochemically generated solvated electrons, using tetraethylammonium fluoroborate as the supporting electrolyte. Similar product mixtures were obtained although in the presence of this supporting electrolyte the ratio of alcohol to pinacol was greater, shown by comparison of the aromatic proton signals in the n.m.r. spectrum.

Controlled Potential Reduction of Acetophenone in Liquid Ammonia / Acetonitrile

Reductions of acetophenone at a mercury pool were carried out in solutions containing 10% and 50% (by volume) of dry acetonitrile. Butyltrimethylammonium fluoroborate (0.1M) was used as supporting electrolyte and the electrode potential was maintained at -1.9V during the electrolysis.

The product mixtures from both reductions showed signals in the n.m.r. spectrum (60MHz, CCl_4) δ 1.6 (s, 3H, CH_3) 2.57 (s, 2H, CH_2) which were attributed to 3-hydroxy-3-phenylbutyronitrile by comparison with an authentic sample. Signals were also present which corresponded to unreacted ketone and the pinacol. The relative proportion of hydroxynitrile to pinacol was higher when reduction was carried out in 50% acetonitrile and in this case a small amount of 3-phenylbutyronitrile was indicated by g.l.c. analysis (10% APL, 175°C). An attempt to obtain an accurate product analysis by g.l.c. was not successful as the relative proportion of the hydroxynitrile suggested by g.l.c. (after sensitivity corrections) was much lower than that indicated by the n.m.r. spectrum of the mixture. Also the pinacol could not be detected under the g.l.c. conditions tried.

4. Reduction of Azobenzene in Liquid Ammonia

The reduction of azobenzene was carried out at a platinum foil

electrode (area ca 25 cm²) in a solution of potassium fluoroborate (0.1M). Prior to addition of the substrate, the catholyte was treated with electrochemically generated solvated electrons by maintaining a cell current of 100mA for 5 minutes. The solution was then stirred until the blue colour had disappeared. Methyl chloride was bubbled through the cathode compartment until about 5 ml had condensed. This caused a reduction in the cathodic limiting potential from about -2.0V to -1.3V at a platinum disc electrode (Fig.4.6).

Azobenzene (0.182 g, 0.001 mole) dissolved in THF (0.5 ml) was added to the cell to give a red solution and was reduced at the potential of the second wave (-1.1V). An initial cell current of 36mA decreased to 18mA (250 C passed; 2e reduction requires 193 C), the red colour of the solution being less intense at the end of the electrolysis. After addition of ammonium chloride (0.5 g), the catholyte was extracted into ether. Examination of the concentrated extract (0.18 g) by n.m.r. spectroscopy (60MHz, CCl₄) suggested the presence of unreacted azobenzene δ 7.3-8.1 (m, aromatic) and hydrazobenzene δ 5.44 (s, 2H, NH) 6.7-7.35 (m, 10H, aromatic) in about equal amounts.

The reduction was also carried out in the absence of methyl chloride to give a reddish-brown cathode solution (100 C passed) the colour of which was unaltered by rapidly bubbling methyl chloride through the catholyte. However when methyl iodide (5 ml) was added in one portion, the red colour immediately discharged to give a pale yellow solution which was worked up as described previously. The n.m.r. spectrum (60MHz, CCl₄) of the crude product (0.18 g) showed signals corresponding to azobenzene, hydrazobenzene, N-methylhydrazobenzene δ 3.0 (s, 3H, N-Me) and N,N'-dimethylhydrazobenzene δ 2.9 (s, 6H, N-Me) in the approximate ratio of 1 : 0.04 : 0.12 : 0.24. The identity of signals corresponding to the mono- and di-alkylated products was based on literature values.

5. Reduction of Diphenylacetylene in Liquid Ammonia

Reduction of diphenylacetylene (0.356 g, 0.002 mole) was

achieved by maintaining a potential of -1.8V at a mercury cathode in a solution of tetraethylammonium fluoroborate (0.1M) in liquid ammonia. An initial cell current of 170mA decreased rapidly but was restored by swirling the cell contents, thereby presumably aiding dissolution of the diphenylacetylene. During the reduction, the solution turned dark grey and electrolysis was terminated after the passage of 600 C ($4e$ reduction requires 772 C). After work-up in the usual manner, a white crystalline product (0.3 g) was obtained, whose n. m. r. spectrum (60MHz , CDCl_3) showed signals at δ 2.92 (s) 7.02 (s) $7.1\text{-}7.55\text{ (m)}$. Examination of the product by g. l. c. (15% PEGA, 200°C) showed three peaks with retention times corresponding to 1, 2-diphenylethane, recovered diphenylacetylene and trans-stilbene. The components were separated by preparative g. l. c. (15% DEGS, 180°C $20\text{ lb/sq}^{11}\text{ He}$), the first fraction, a liquid, consisting of 1, 2-diphenylethane as shown by its n. m. r. spectrum (60MHz , CCl_4) δ $2.9\text{ (s, 4H, CH}_2\text{)}$ $7.1\text{ (s, 10H, aromatic)}$. Two solid fractions were identified by their n. m. r. spectra (60MHz , CCl_4) as diphenylacetylene δ $7.1\text{-}7.6\text{ (m)}$ and trans-stilbene δ 7.0 (s, 2H, CH) $7.05\text{-}7.5\text{ (m, 10H, aromatic)}$. Standardisation of a weighed sample of the product mixture against benzonitrile and estimation of product yields by g. l. c. peak integration (after relative sensitivity corrections) gave a product analysis corresponding to 1, 2-diphenylethane (48%), diphenylacetylene (28%) and trans-stilbene (24%) in an overall yield of $90\text{-}100\%$, representing a current efficiency of about 75% .

A similar reduction was carried out at the potential of the first wave (-1.42V). A lime-green colour appeared in the vicinity of the electrode but the final solution was brown in colour. The reduction was terminated (489 C passed; $2e$ reduction requires 386 C) and the catholyte worked-up as described previously to give a white solid (0.2 g). Analysis by g. l. c. and peak area integration indicated a product mixture containing 1, 2-diphenylethane (31%), diphenylacetylene (28.5%) and trans-stilbene (40.5%) in an overall yield of 77% and current efficiency of about 60% .

In a further experiment, diphenylacetylene (0.0005 mole dissolved

in 0.5 ml THF prior to addition to the cell) was reduced at a platinum foil electrode in the presence of potassium iodide (0.1M) as supporting electrolyte. Before electrolysis was commenced, the catholyte was pre-treated with solvated electrons (-3.0V maintained for 5 minutes). During reduction of the acetylene a white solid precipitated from solution. Product analysis indicated that both 1, 2-diphenylethane and trans-stilbene had been produced.

Reduction of Diphenylacetylene in Ammonia/THF

Owing to the low solubility of diphenylacetylene in liquid ammonia, a reduction was carried out in a solution containing 25% THF as co-solvent, conditions otherwise being similar to those previously described. The potential was maintained at -1.4V and an initial cell current of 60mA decreased to 5mA (673 C passed; 2e reduction requires 386 C). The product mixture (0.35 g), obtained in the usual manner, was shown by g.l.c. analysis to consist of 1, 2-diphenylethane (72.5%), diphenylacetylene (19.7%) and trans-stilbene (7.8%) in an overall yield of 50%.

6. Reduction of cis-Stilbene in Liquid Ammonia

cis-Stilbene (0.18 g, 0.001 mole), dissolved in THF (0.5 ml), was added to a solution of tetraethylammonium fluoroborate (0.1M, 1.084 g) in liquid ammonia (50 ml) in the cathode compartment of a three-compartment cell. Reduction at a mercury pool cathode was carried out at a potential pulsed from -1.5V to -1.0V at 1 second intervals for 1 hour. The initial cell current was 120mA (cathodic) and 60mA (anodic). The solution turned brown at the more cathodic potential but the colour was discharged when the potential was reduced to -1.0V. A white solid precipitated during the reduction. The catholyte was worked-up as usual and the ether extract was examined by g.l.c. (15% PEGA, 200°C) after the addition of a weighed sample of benzonitrile as external standard. One major peak corresponding to trans-stilbene (81%, based on starting material) was obtained. Its identity was

confirmed by n. m. r. spectroscopy of the concentrated extract (60MHz, CCl_4) δ 7.0 (s, 2H, CH) 7.05-7.6 (m, 10H, aromatic). A very minor peak in the chromatogram corresponded to either recovered cis-stilbene or 1,2-diphenylethane; these compounds were shown by injection of authentic samples to have identical retention times.

A similar reduction was carried out at -1.5V without applying a potential pulse profile. The cell current rapidly decreased but was restored by swirling the cell contents. After about 1.5 hour the cell current had decreased to 6.0mA, the solution was dark brown and a white solid had precipitated (65 C passed; 1e reduction requires 96.5 C). The potential was then reduced to -1.0V causing an anodic current (6mA) to flow. When the current had fallen to 2mA, the reduction was terminated and the catholyte extracted into ether. G.l.c. analysis indicated trans-stilbene (63% based on starting material) and either cis-stilbene or 1,2-diphenylethane. The latter product (ca 15% yield) was identified from the n. m. r. spectrum (60MHz, CCl_4) of the concentrated extract, the yield being estimated by integration against the signals of trans-stilbene. The product yields represent a current efficiency of about 70%.

Table I

Variation of Cathodic Potential Range in Acetonitrile

with the Supporting Electrolyte Cation

<u>Origin of Data</u>	<u>Supporting Electrolyte</u>	<u>Cathode</u>	<u>Cathodic Range (V)</u>
Fig. 1b	^d Et ₄ NBF ₄	DME	-3.18 ^a
ref. 162	Et ₄ NCF ₃ SO ₃	DME	-2.16 ^a
Fig. 2 (and 5.4)	^d Et ₄ NClO ₄	Pt	-3.07 ^b
ref. 163	Et ₄ NClO ₄	Pt	-2.9 ^b
ref. 164	Bu ₄ NBF ₄	DME	-2.8 ^b
ref. 163	Bu ₄ NClO ₄	Pt	-2.7 ^b
Fig. 3a	LiClO ₄	DME	-2.0 ^a
Fig. 3b	LiClO ₄	Pt	-3.14 ^a
ref. 165	LiClO ₄	Pt	-3.2 ^b
ref. 165	LiClO ₄	Pt	-3.0 ^c
ref. 165	LiClO ₄ (+LiH)	Pt	-3.5 ^c
ref. 64	Li ⁺	Pt	-3.1 ^b
ref. 64	K ⁺	Pt	-3.0 ^b

(a) vs. Ag/0.1M Ag⁺

(b) vs. SCE

(c) vs. Ag/0.01M Ag⁺

(d) After cathodic pre-treatment to remove acrylonitrile. Reference electrode comparisons¹⁶⁶: Ag/0.1M AgNO₃ + 0.336V rel. to SCE;

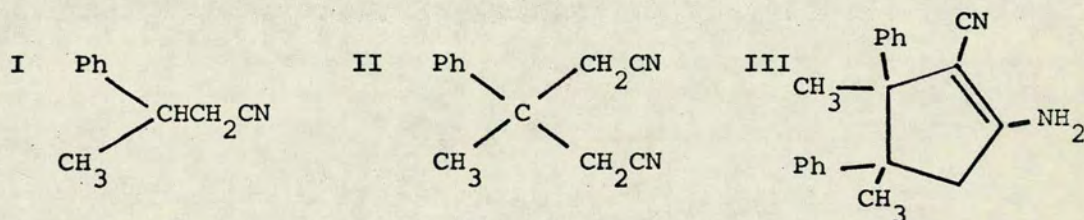
Ag/0.01M AgNO₃ + 0.291V rel. to SCE (slight variation with Salt bridge).

Table II

Reduction of Acetophenone in Acetonitrile: Product Distribution

Unless otherwise indicated, reduction was conducted at -3.0V at a mercury pool cathode. Product yields are based on separation by column chromatography.

Expt.	PhCOCH ₃ /mol	Yields %		Initial Current/mA	Coulombs/% of theoretical for 2e reduction
		I	II + III ^c		
1	0.04	31 ^a	-	55	54
2	0.04(Pt)	22 ^a	-	-	47
3	0.01	51	37	90	excess
4	0.01	34	45	90	57
5	0.01(-2.5V)	14	42	17	80
6	0.01	11	35	24	82
7	0.02	14	34	40	65
8	0.01 ^b	0	0	45	8



^a estimated by g.l.c. (standardisation using n-C₁₈H₃₈)

^b pinacol, 1-phenylethanol and 3-methylcinnamionitrile identified

^c yields calculated assuming II is the major product.

Table III

Solubilities of Inorganic Salts in Liquid Ammonia at 25°C

(g/100g NH₃)¹⁶⁷

<u>Cation</u>	<u>Anion</u>						
	Cl ⁻	Br ⁻	I ⁻	ClO ₄ ⁻	NO ₃ ⁻	CO ₃ ²⁻	NH ₂ ⁻
NH ₄ ⁺	102.5	237.9	368.4	137.9	390.0	0.0	-
Li ⁺	-	-	-	-	243.66	-	-
Na ⁺	3.02	137.95	161.9	-	97.6	-	0.004
K ⁺	0.04	13.5	182.0	-	10.4	0.0	3.6
Ag ⁺	0.83	5.92	206.84	-	86.04	-	-

Solubilities of Organic Compounds in Liquid Ammonia

Hydrocarbons - Alkanes (i); alkenes and alkynes (s.s);

benzene (s). Toluene forms two layers below 15°C.

Alcohols - Polyhydric and simple alcohols (s); phenols (m).

Carboxylic acids - Converted to ammonium salts. Low molecular weight (s).

Esters - Low molecular weight (s).

Aldehydes and ketones - (m). Some ketones and aldehydes react with ammonia to form addition compounds.

Ethers - Diethyl ether (m); higher molecular weight (s.s).

Amines - Low molecular weight (s), RNH₂ > R₂NH > R₃N.

i (insoluble); s.s. (slightly soluble); m (moderately soluble);
s (soluble).

Table IV

Solubilities (M) of Quaternary Ammonium Salts in Liquid Ammonia

<u>Cation</u>	I	<u>Anion</u>	
		BF_4^-	TSO^-
Me_4N^+	0.0023 ^a	-	-
Et_4N^+	0.01 ^a	0.660	0.390
Pr_4N^+	0.0083 ^a	-	-
Bu_4N^+	0.0039 ^a 0.0060	0.0690	-
$\text{Et}_2\text{Bu}_2\text{N}^+$	0.033 ^a	-	-
BuMe_3N^+	0.10 ^a 0.420	1.060	0.0140
BuEt_3N^+	0.031 ^a	-	-
BuPr_3N^+	0.0063 ^a	-	-
Bu_3MeN^+	0.081 ^a 0.10	0.180	-
Bu_3EtN^+	0.059 ^a 0.280	0.160	-

^a at -78°C^{96}

Otherwise at -36°C (measured according to the procedure described in the Experimental).

Table V
Cathodic Ranges in Liquid Ammonia

<u>Figure</u>	<u>Cation</u>	<u>Cathode</u>	<u>Cathodic Limit (V)</u>		
			ref. a	ref. b	ref. c
9a	Et ₄ N ⁺	DME	-1.9	-2.1	-
9b		HMDE	-1.85	-	-
9c		Pt	-1.6 to -1.95	-	-
9d		Pt*	-1.5		
-	BuMe ₃ N ⁺	DME	-	-2.1	-2.2
10a		HMDE	-1.8		
10b		Pt	-1.95		
10c		Pt*	-1.5		
11a	Bu ₄ N ⁺	DME	-2.0		
11b	Pr ₄ N ⁺	DME	-1.95		
11c	Me ₄ N ⁺	DME	-1.75		
12a	Li ⁺	DME	-	-2.0	-
12b		Pt	-	-2.3	-
13a	K ⁺	HMDE	-1.1		
13b		Pt	-2.0		

*contaminated

ref. a Pb/0.05M Pb(NO₃)₂

ref. b Ag/satd. AgCl/satd. KCl in NH₃

ref. c Ag/satd. AgCl in 0.1M BuMe₃NBF₄.

Table VI

Electro-reduction of 1-Acetyl-2,2-dimethylcyclopropane in the Presence
of Butyltrimethylammonium Fluoroborate

1-Acetyl-2,2-dimethylcyclopropane (0.0025 mol) reduced in 0.1M BuMe₃NBF₄ (2e reduction requires 482 C.) The ratio of (4)/(5) was measured after chromic acid oxidation of alcohols.

<u>Cathode</u>	<u>Electrolysis Conditions</u>	<u>Total Coulombs</u>	<u>Relative %</u>			<u>Ratio (4)/(5)</u>
			(3)	(4)	(5)	
Hg	P -2.0V (60mA)	575	16.5	57.0	26.5	2.15
Hg	P -2.3V (300mA)	575	10.3	59.1	30.6	1.90
Hg	G 50mA (-2.0V)	540	10.1	61.3	28.6	2.10
Hg ¹	G 50mA (-2.0V)	540	6.2	61.3	32.5	1.90
Hg ²	G 50mA (-2.0V)	540	9.0	74.6	16.4	4.50
Pt	P -2.7V (50mA)	575	40.0	38.0	22.0	1.70
Pb	G 50mA (-3.0V)	540	6.5	50.0	43.5	1.15
Pb ³	P -2.2V (25mA)	340 ⁴	50.0	28.0	22.0	1.30
C	P -3.3V (120mA)	1350 ⁵	1.1	63.9	35.0	1.80

¹ Br⁻ counter ion

² +EtOH (10 ml)

³ pulsed

⁴ anodic current during the second pulse included

⁵ high background current included.

P potentiostatic, voltage (initial current)

G galvanostatic, current (initial voltage)

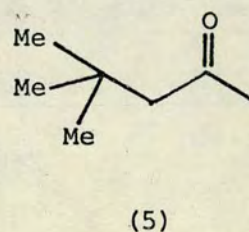
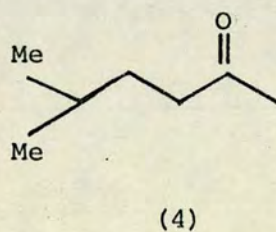
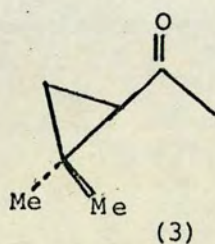


Table VII

Electro-reduction of Pentan-2-one in Liquid Ammonia in the Presence
of Tetraethylammonium Fluoroborate

Unless otherwise indicated galvanostatic (100 mA) reduction of pentan-2-one (0.001 mole) was conducted in a solution of Et_4NBF_4 (0.1M) at a Hg pool cathode.

<u>Reduction Conditions</u>	<u>Relative %</u>			<u>Overall Yield %</u>
	MeCOPr	$\begin{array}{c} \text{OH} \\ \\ \text{MeC-Pr} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{OH} \\ \\ \text{MeC-Pr} \\ \\ \text{Et} \end{array}$	
2F mol ⁻¹ passed	-	66	34	70
2F mol ⁻¹ passed 0.02M Et_4NBF_4	18	60	22	68
1.4F mol ⁻¹ passed	27	63	10	70
1.4F mol ⁻¹ passed +0.1M EtOH	20	80	-	70
1.4F mol ⁻¹ passed Pt cathode	56	40	5	60

Table VIII

Electro-reduction of Acetylcyclopropane in Liquid Ammonia in the
Presence of Tetraethylammonium Fluoroborate

Unless otherwise indicated galvanostatic (100 mA) reduction of acetylcyclopropane (0.001 mole) was conducted in a solution of Et_4NBF_4 (0.1M) at a Hg pool cathode until $4F \text{ mol}^{-1}$ had been passed.

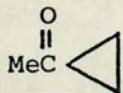

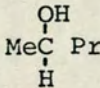
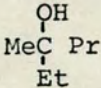
<u>Reduction Conditions</u>	<u>Relative %</u>				<u>Overall Yield %</u>
					
2.8F mol ⁻¹ passed	-	37	36	27	65
as indicated above	-	9	29	62	80
Pt cathode	-	45	12	43	62
0.1M BuMe ₃ NBF ₄	5	75	20	-	75
0.1M BuMe ₃ NBF ₄ Pt Cathode	22	72	6	-	60
0.05M Et ₄ NBF ₄	-	37	1	52	76
0.05M BuMe ₃ NBF ₄					

Table IX

Electro-reduction of Acetylcyclopropane (0.002 mole) in Liquid Ammonia
in the Presence of Tetraethylammonium Fluoroborate - Sampling Experiments

<u>Time</u> (min.)	<u>Coulombs</u>	<u>Relative %</u>			
		$\begin{array}{c} \text{O} \\ \parallel \\ \text{MeC} \end{array} \triangleleft$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{MeCPr} \end{array}$	$\begin{array}{c} \text{OH} \\ \\ \text{MeC-Pr} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{OH} \\ \\ \text{MeC-Pr} \\ \\ \text{Et} \end{array}$
11	66	86	14	0	0
21	126	73	27	0	0
31	186	53	45	2	0
41	246	23	74	3	0
51	306	16	80	4	0
62	372	6	85	9	0
78	468	0	68	27	5
95	570	0	5	53	42
107	642	0	2	54	44
140	840	0	2	54	44
53	318	13	87	0	0
65	390	0	100	0	0
76	456	0	91	3	6
108	648	0	24	19	57
125	750	0	0	30	70

Table X

Comparison of CV Data for the Reduction of Organic Compounds in

Liquid Ammonia

The compounds (2 mM) were reduced in a solution of Et_4NBF_4 (0.1M) at a HMDE. Potentials are measured vs. $\text{Pb}/0.05\text{M Pb}(\text{NO}_3)_2$ at a sweep rate of 250 mV s^{-1}

Figure	Compound	Wave I				Wave II				$E_{p(II)} - E_{p(I)}$ (V)
		$-E_{p_c}$ (V)	i_{p_a} i_{p_c}	$E_{p_a} - E_{p_c}$ (mV)	i_d (μA)	$-E_{p_c}$ (V)	i_{p_a} i_{p_c}	$E_{p_a} - E_{p_i}$ (mV)	i_d (μA)	
15.3	PhCOPh	0.87	1.0	65	3.8	1.52	0.55	-	3.3	0.65
16.1	PhCO ∇	1.15	1.0	55	3.7	1.75	0.55	-	3.3	0.60
17.1	PhCOCH ₃	1.14	0.8	60	3.7	1.76	-	-	-	0.62
18.3	PhN=NPh	0.46	1.15	60	3.9	1.05	-	-	3.4	0.59
19.2	<u>cis</u> PhCH=CHPh	1.43	0.92	105	5.28	1.69	0.35	80	5.3	0.26
20.2	PhC \equiv CPh	1.48	1.0	50	2.38	1.67	-	-	5.98	0.19

Table XI

CV Data for the Reduction of Benzophenone in Liquid Ammonia

Figure	Supporting Electrolyte Cation	Cathode	wave I			wave II			Ep _{II} -Ep _I or E _{1/2} (II)-E _{1/2} (I) (V)
			-Ep _c (V)	ip _a ip _c	Ep _a -Ep _c (mV)	-Ep _c (V)	ip _a ip _c	Ep _a -Ep _c (mV)	
-	BuMe ₃ NBF ₄	HMDE	0.87	0.94	70	1.52	0.65	70	0.65
15.1	"	PDE	0.87	1.0	70	1.5	0.81	60	0.63
15.6b ⁽¹⁾	"	DME	1.52	-	-	2.2	-	-	0.68
-	Et ₄ N ⁺	HMDE	0.87	1.0	65	1.52	0.55	-	0.65
15.3	"	PDE	0.87	1.0	60	1.53	0.46	-	0.66
15.2 ⁽²⁾	K ⁺	PDE	-1.265	1.0	60	1.83	1.0	60	0.565
15.5 ⁽²⁾	Li ⁺	Pt wire	-1.36	1.0	70	1.78 (ads)	-	-	0.42
15.6 ⁽¹⁾	"	DME	-1.28	-	-	1.66	-	-	0.38

Unless otherwise indicated potentials are measured vs. Pb/0.05M Pb(NO₃)₂.

CV data recorded at 250 mV s⁻¹.

(1) vs. Ag/satd. AgCl in supporting electrolyte solution.

(2) vs. Ag/Satd. AgCl/satd. KCl in liquid ammonia.

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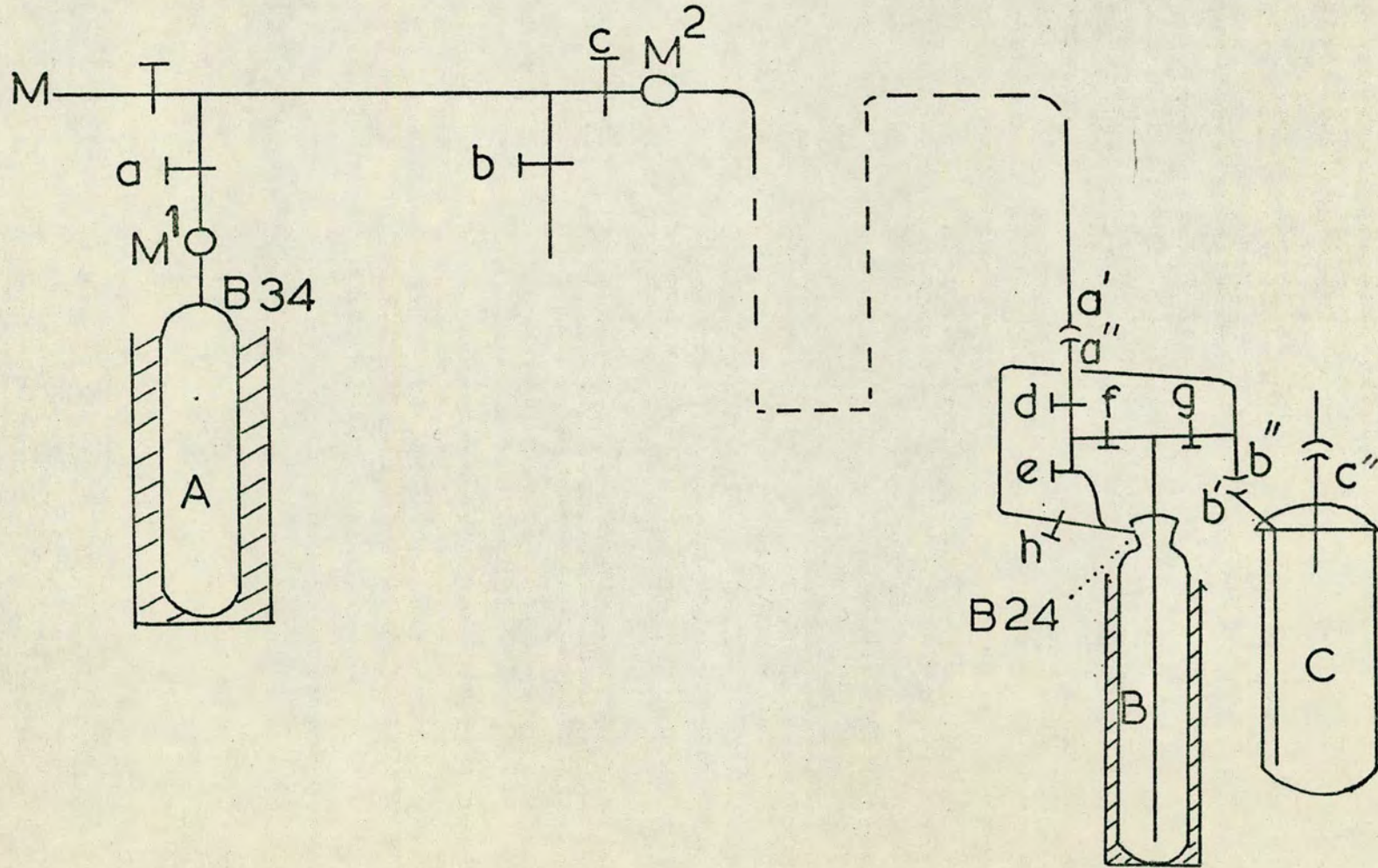
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DIAGRAM I



KEY TO DIAGRAM I

a b c High vacuum 2mm stopcocks
d Rotaflo tap TF2/13
e f g h J. Young taps ORT/4 silicone
M Mercury bubbler or nitrogen inlet
M¹ M² Manometers
a' b' S13 cup joints
a'' b'' c'' S13 ball joints
B19 B24 B34 Cone and socket joints
———— Glass tubing
- - - - - Flexible polythene tubing
a' attached to a'' for ammonia distillation
a' attached to c'' during cell operation