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1) Survey of previous literature.

Electrosynthesis in organic chemistry may be said to have its origin in the discovery, usually attributed to Kolbe[1], that ethane is produced at the anode during the electrolysis of a solution of potassium acetate.

Somewhat earlier, in 1834, Faraday[2] had found that combustible gases were evolved at the anode during the electrolysis of potassium acetate solutions. He stated that these were carbonic oxide and carburetted hydrogen, but he did not investigate further the nature of the hydrocarbon.

Kolbe's discovery was made during attempts to prepare the free radical methyl, and he considered that the gases evolved at the anode consisted of methyl and carbon dioxide in the approximate proportion of 1:2 by volume. He found also that the hydrocarbon methyl corresponded in all properties to the gas obtained from cyanide of ethyl by the action of potassium. It was similar to, but not identical with marsh gas. Later, Frankland[3] showed that methyl with identical properties could be obtained by the reaction of zinc, water and ethyl iodide. It was Schorlemmer[4] in 1864 who showed that the methyl of the aforementioned authors was identical with the hydride of ethyl, i.e. ethane.

The credit for the discovery of the formation of ethane by the electrolysis of acetates is, however, usually given to Kolbe and the reaction is known as the Kolbe Reaction or Kolbe Electrosynthesis.

The importance of this reaction as a method of synthesis in organic chemistry was early recognized and Kolbe's work was followed by that of many other

investigators, mainly along three lines:

1) Attempts to extend the Kolbe reaction to other organic acids.
2) More detailed investigation of the electrolysis of salts of acetic acid and of other fatty acids.
3) Attempts to explain the mechanism of the electrosynthesis process.

An important step forward in the extension of the method of electrosynthesis was made in 1891 by Crum-Brown and Walker[5], who succeeded in bringing about a synthesis of a number of dibasic acids. By electrolysing the ethyl potassium salt of a lower dibasic acid (e.g.potassium ethyl succinate) they found that at the anode the diethyl ester of a higher dibasic acid (e.g. diethyl adipate) was produced. The higher acid thus obtained contained double the number of CH_2 groups present in the dibasic acid they had started from. This method has proved of great value in synthesizing long-chain dibasic acids.[6]

The paper of Crum-Brown and Walker is also of special importance in the study of the mechanism of electrosynthesis reactions. Kolbe had originally supposed that the formation of ethane by the electrolysis of potassium acetate was due to the oxidation of acetic acid by oxygen developed at the anode

$$2\ CH_3COOH + O = C_2H_6 + 2\ CO_2 + H_2O$$

Crum-Brown and Walker suggested a different mechanism for the anode reaction in the electrolysis of organic acids, viz. the reaction between discharged anions, e.g. in the case of acetates

$$2\ CH_3COO = C_2H_6 + 2\ CO_2$$

Interest in the mechanism of electrosynthesis reactions increased after the publication of the work of Crum-Brown and Walker, and many attempts were made to decide between the respective merits of the "oxidation" and "discharged ion" theories to account for the undoubtedly complex phenomena which occur at the anode.

A fresh stimulus on the theoretical side was provided in 1918 by Fichter and Krummenacher[7], who revived the earlier idea of Schall[8] that acid peroxides may be formed as intermediate products at the anode during the electrolysis of solutions of salts of organic acids. Fichter[9] in fact extended this "peroxide theory" to organic electrochemical oxidations in general.

In addition to the work already mentioned many other papers were published in the period 1891 to 1925 dealing with the various reactions and phenomena occurring at the anode during processes of electrosynthesis. Many of these papers will be found in the references given in the published work forming the main part of this thesis. A few of the more outstanding of these papers can be mentioned in this brief historical survey, since they relate more particularly to the general purpose of the work submitted in this thesis, which has been concerned largely with the electrolysis of acetate solutions..

Murray[10] was the first to make a detailed study of the electrolysis of acetate solutions, and examined the effect of concentration of acetate, current density, temperature etc. on the amount of ethane produced. Hofer and Moest[11] investigated the effect of adding alkalis and inorganic salts to the acetate solutions during electrolysis, and found that under these conditions the yield of ethane is considerably reduced and alcohol is the chief product. Foerster and Piguet[12] studied the effect of varying the metal of the anode,

2) General purpose of the investigation.

In spite of the large amount of experimental work dealing with the electrolysis of organic acids and their salts, a brief resumé of which up to about 1925 has been given in the preceding section, there was no general agreement regarding the mechanism of the various reactions occurring at the anode. On the theoretical side controversy centred mainly round the respective merits of the "oxidation" and "discharged ion" theories in accounting for the experimental facts. In the more recent work the revival of the "peroxide" theory by Fichter introduced an additional cause for differences of opinion.

The general purpose of the investigation forming the subject of Part A of this thesis, was to make a further study of the processes of electrosynthesis and to attempt to discriminate more clearly between the various theoretical explanations of the reactions occurring at the anode.

It was decided to make a more detailed investigation of the original Kolbe reaction using salts of acetic acid, mainly for three reasons.

Firstly, for this acid there already existed a considerable amount of experimental data.

Secondly, the main products of the electrosynthesis in this case are gaseous, and the course of the reaction lends itself to being followed by convenient analytical methods.

Thirdly, the decomposition of acetyl peroxide, which is of interest for the electrosynthesis process, had not been previously studied to any extent. Indeed, the experimental evidence regarding the controlled decomposition of the peroxides of aliphatic acids in general was very meagre compared with the data available for benzoyl and other aromatic peroxides (cf. Gelissen and Hermanns, Ber., 1926, 59, 662).

The study of the decomposition of acetyl peroxide was therefore of direct interest in the general problem of the thermal decomposition of diacyl peroxides.

The experimental work, which was carried out during the period 1925 - 1937, followed three main lines of investigation:

1) The improvement of the gas-analytical methods and the carrying out of a more detailed examination of the gases evolved at the anode during the electrolysis of acetate solutions under various conditions.

2) A more comprehensive study of the anode potential changes during the electrolysis, and a comparison of these with the gas-analysis data.

3) A more detailed investigation of the decomposition reactions of acetyl peroxide under various conditions and of the possible intermediate formation of this substance at the anode during the electrolysis of acetate solutions.

3) Results obtained.

a) List of published papers.

An account of the experimental work and of the main results obtained is given in the following nine published papers, copies of which are attached.

1. The mechanism of Kolbe's electrosynthesis.
   (with D.A. Fairweather) J.Chem. Soc., 1926, 3111 - 3121.
2. The decomposition of acetyl peroxide.
   J.Chem. Soc., 1928, 2040 - 2045.
3. Formation of methane during the electrolysis of potassium acetate.
   (with S.N. Shukla) Trans. Faraday Soc., 1931, 35 -40.
4. The analysis of mixtures of hydrogen, methane, and ethane.
   (with S.N. Shukla) J.Chem. Soc., 1931, 368 -370.
5. Discharge potential of the acetate ion.
   (with S.N. Shukla) Trans. Faraday Soc., 1931, 722 - 730
6. Formation of methane during the electrolysis of potassium acetate.
   (with S.N. Shukla) Trans. Faraday Soc., 1932, 457 - 462
7. Decomposition of acetyl peroxide.
   (with G.L.E. Wild) J.Chem. Soc., 1935, 207 -210.
8. Influence of the electrode surface on anodic processes.
   (with J. Weiss) Trans. Faraday Soc., 1935, 1011 -1017
9. Thermal and photochemical decomposition of acetyl peroxide.
   (with G.L.E. Wild) J.Chem.Soc., 1937, 1132 - 1136

b) Summary of experimental results.

The main experimental results can be summarized as follows:

1. The electrolytic oxidation of acetic acid is complete and not partial under ordinary conditions and occurs to a considerable extent at low anode potentials. (Paper 1)

2. The critical anode potential for the formation of ethane in the electrolysis of aqueous potassium acetate solutions using a smooth platinum anode is 2.14 volts. This potential is independent of the size of the anode and is not much affected by the concentration of the acetate solution or by increase of temperature. (Papers 1 and 5)

3. In non-aqueous solvents the formation of ethane in general occurs more readily and is not so dependent on the nature of the anode material. (Papers 1 and 6)

4. The change in the anode process brought about by the addition of metallic salts to the acetate solution has been shown to be connected with changes in the nature of the anode surface, probably due to the formation of oxide layers. (Paper 8)

5. Using a more accurate gas-analysis technique (paper 4) a new type of anode reaction leading to the formation of considerable amounts of methane has been found. (Papers 3 and 6)

6. The conditions favourable to the formation of methane appear to be low current density and high concentration of the electrolyte, both in aqueous and in non-aqueous solutions. (Papers 3,5 and 6)

7. With a smooth platinum electrode methane commences to be formed at the same critical anode potential

of 2.14 volts which is characteristic of the electro-synthesis reaction. (Paper 5)

8. The thermal decomposition of acetyl peroxide vapour at 100 deg. C follows very largely the reaction

$$(CH_3COO)_2 \longrightarrow C_2H_6 + 2\ CO_2$$ (Paper 9)

9. Thermal decomposition of the peroxide in the liquid state or in solution at temperatures up to 100 deg. C is a more complex process resulting in the formation of more methane than ethane even at relatively low temperatures. The decomposition in hexane solution is of the first order with respect to the peroxide. (Papers 2, 7 and 9)

10. In the photochemical decomposition of acetyl peroxide in solution reaction according to the scheme mentioned in (8) occurs to a greater extent than in the thermal decomposition, but even so more methane than ethane is produced. The photochemical decomposition of the solid peroxide, however, approximates more closely to the ethane reaction. (Papers 2 and 9)

c) General conclusions.

From a study of the previous literature and the additional experiments which have been described it is concluded that the reaction between discharged ions affords the most satisfactory although perhaps incomplete explanation of Kolbe's electrosynthesis. In the case of the electrolysis of acetate solutions the evidence in favour of this view seems very considerable. In the interaction of the discharged acetate radicals some sort of momentary loose union may well take place, but the assumption of the intermediate formation of the chemically known peroxide is not necessary. That a small portion of the acetate radicals may unite to form the more stable peroxide would not be surprising and is not excluded. Acetyl peroxide can decompose in a variety of ways under conditions which are not necessarily comparable with the conditions existing at the surface of the anode during electrolysis, and it is doubtful whether the results of experiments on the thermal decomposition have any direct bearing on the mechanism of the anodic process. In the controlled decomposition of the peroxide at least two simultaneous or consecutive reactions appear to take place.

B. Studies on Absorption Spectra of Solutions.

1) Introduction.

2) General purpose of the investigation.

3) Results obtained.
   a) List of published papers.
   b) Summary of experimental results and general conclusions.

1) Introduction.

In the voluminous literature dealing with the electronic absorption spectra of molecules there are very few data from which a reliable comparison can be made of absorption spectra in the gaseous and dissolved states. A comparison of this sort is desirable for various reasons.

In examining the effect of various solvents on the absorption spectrum of a dissolved molecule the spectrum of the gaseous substance forms a useful reference standard. For this purpose it is preferable that the absorption spectrum of the gas should be measurable at low pressures and at temperatures comparable with those of the solution. Furthermore, the comparison of the absorption spectra should be based on the complete extinction coefficient curves, so that the solvent effects can be evaluated both for the position of the absorption band (i.e. λ max or ν max) and for the band strength. The latter parameter is defined by $\int \varepsilon \, d\nu$, and if the width of the extinction coefficient curve in the different solvents is constant one can replace $\int \varepsilon \, d\nu$ by ε max.

An accurate comparison of the absorption curves of substances in the gaseous and dissolved states is also of interest in considering the primary process of light absorption by dissolved molecules. The nature of the primary absorption process and of the electronic transitions involved can be determined directly only with dilute gaseous systems in which discontinuous spectra with regions of band structure are found. In solution there is usually a smoothing out of any fine structure observed in the gaseous spectrum, and recourse must therefore be had to absorption measurements of the gaseous substance and a comparison of the extinction coefficient curves in the two states.

2) General purpose of the investigation.

The general purpose of this investigation was to make a more detailed study of

1. The absorption curves of simple dissolved molecules for which absorption data in the gaseous state were available.
2. The effect of the nature of the solvent on the absorption spectra of dissolved molecules.
3. The nature of the primary absorption process in solutions.

The study of the absorption spectra of halogen solutions seemed particularly desirable from the above-mentioned points of view because the theoretical treatment of the absorption spectra of the gaseous halogens is reasonably complete and these substances have frequently been used in the study of photochemical reactions.

The absorption spectra of iodoform and of other tri-iodides in solution afforded an interesting case of complicating solvent effects of a chemical nature and seemed worthy of further study.

The absorption spectra of ions in aqueous solution have been interpreted as electron affinity spectra and are of interest in relation to the photochemical processes taking place when such solutions are irradiated. Since the study of the absorption spectra of ions had been concerned mainly with anions it was decided to investigate in more detail the absorption spectrum of the ferrous cation in aqueous solution.

3) Results obtained.

a) List of published papers.

1. Absorption spectra of iodine solutions and the influence of the solvent.
   Trans. Faraday Soc., 1935, 1432 - 1438

2. Electron affinity spectrum of ferrous ion in aqueous solution.
   (with R.H. Potterill and J. Weiss)
   Proc.Roy.Soc., A., 1936, 561 - 570

3. The ultra-violet absorption spectra of iodoform and of other tri-iodides in solution.
   (with R.H. Potterill)
   Trans. Faraday Soc., 1937, 363 - 371

4. The continuous absorption spectrum of bromine in solution.
   (with C.L. Child)
   Trans. Faraday Soc., 1938, 1506 - 1515.

b) Summary of experimental results and general conclusions.

1. Measurements have been made of the extinction coefficient curves of solutions of bromine and of iodine in various organic solvents, and the curves have been compared with those of gaseous bromine and iodine. (Papers 1 and 4)

2. In inert and non-polar solvents the solvent does not produce any marked change in shape or position of the halogen absorption curve, but the amount of absorption by the dissolved halogen is increased compared with that of the gaseous substance. (Papers 1 and 4)

3. In polar but chemically inert solvents the shape of the absorption curve is similar to that in non-polar solvents, but the wave-length of maximum absorption is more or less displaced towards the ultra-violet. For solutions of iodine in a series of similar solvents the displacement increases with increasing dipole moment of the solvent. (Paper 1)

4. In solutions of bromine and iodine in alcohol and other "reactive" solvents the wave-length of maximum absorption is much more displaced toward the ultra-violet. With such solutions chemical reactions occur on standing which lead to more pronounced alterations of the absorption curve. (Papers 1 and 4)

5. The various types of interaction which can occur between halogen molecules and solvent molecules give rise to different types of "solvent effects" in the absorption curves of halogen solutions. In the absence of any marked solvent effects the absorption

curves of the halogens in the gaseous and dissolved states are very similar, and the primary absorption process in both states is probably the same.

(Papers 1 and 4)

6. Comparison of the absorption curves of iodoform and of other tri-iodides with that of the tri-iodide ion in solution shows that while similarities occur in all these curves, these do not amount to actual identity. It is not necessary to postulate a similarity in structure between CHI_3 and the I_3' ion.

(Paper 3)

7. The ultra-violet absorption spectrum of ferrous salts in aqueous solution is very sensitive to traces of ferric salts. The characteristic absorption curve of the Fe^{++} ion can be considered as an electron affinity spectrum. (Paper 2)

Appendix.

August Kekulé and the Benzene Problem.
Annals of Science, 1939, 34 -46.

This paper on certain aspects of Kekulé's contributions to the structure of benzene and its derivatives is appended as supporting evidence of published work.

Explanatory Note
on part played by collaborators.

The work submitted in this thesis (Parts A and B, and Appendix) has all been carried out since obtaining my last degree in any university, viz. the Ph.D. of the University of Edinburgh in 1925.

In Part A the work described in paper 2 was carried out entirely by myself. The work of paper 1 was done in collaboration with D.A. Fairweather, who carried out the experimental work on propionates, while I performed the experiments on acetates. The theoretical part was written jointly. The theoretical part of paper 8 was written in collaboration with J. Weiss, the experimental part is solely due to me. The work described in the remaining six papers of Part A was carried out with the assistance of research students working under my sole direction. Most of the experimental work was performed by my students, but I was largely responsible for writing the papers.

In Part B the work described in paper 1 was performed entirely by myself. The absorption measurements described in paper 2 were carried out by me with the assistance of a research student, R.H. Potterill. The photochemical experiments on ferrous salts in paper 2 were performed by J. Weiss, and are not included in the work submitted. The theoretical part of paper 2 is the joint work of J. Weiss and myself. The work described in papers 3 and 4 was carried out with the assistance of research students, working under my sole direction. I am responsible for the theoretical part.

The historical paper in the Appendix was written entirely by myself.

J. Walker

A. 1.

THE MECHANISM OF KOLBE'S ELECTROSYNTHESIS.

BY

DAVID ALEXANDER FAIRWEATHER

AND

OSWALD JAMES WALKER.

Reprinted from the Journal of the Chemical Society, December, 1926.



Reprinted from the Journal of the Chemical Society, 1926.

CCCCXVIII.—*The Mechanism of Kolbe's Electrosynthesis.*

By David Alexander Fairweather and Oswald James Walker.

Since Kolbe's discovery of the production of ethane at the anode during the electrolysis of a solution of potassium acetate (*Annalen*, 1849, **69**, 279), many investigations have been made with a view to determine the nature of the undoubtedly complex process involved. Two rival theories have emerged: (1) The "oxidation" theory, which supposes that all the discharged anions react with water to give the acid, which is then oxidised by atomic oxygen to the synthetic product; and (2) the "discharged ion" theory, which supposes that two discharged anions unite directly. The following equations represent these reactions:

$$\left.\begin{array}{l} 2CH_3\cdot CO\cdot O\cdot + H_2O = 2CH_3\cdot CO_2H + O \quad . \quad . \quad . \quad . \quad . \quad (a) \\ 2CH_3\cdot CO_2H + O = CH_3\cdot CH_3 + 2CO_2 + H_2O \quad . \quad . \quad . \quad (a') \end{array}\right\}$$

$$2CH_3\cdot CO\cdot O\cdot = CH_3\cdot CH_3 + 2CO_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

In two recent contributions to this subject (Gibson, J., 1925, **127**, 475; Robertson, *ibid.*, p. 2057) it is claimed that the oxidation theory has been proved to hold, not only for the ethane synthesis, but also for the Crum Brown and Walker synthesis of dibasic acids. The conclusions drawn in these papers do not seem to be entirely sound, and, moreover, fresh experimental evidence has now been obtained which demonstrates beyond all doubt that synthesis is due solely to the direct interaction of the discharged ions.

Concerning the intrinsic probability of the oxidation theory, it must be admitted that it would be somewhat surprising if the carboxylic hydrogen atom of a fatty acid were attacked by an oxidising agent in preference to the hydrogen atoms of the hydrocarbon residue, since one is accustomed to regard a carboxyl group as being very stable towards oxidising agents. The oxidation theory, in fact, could scarcely have been considered seriously had it not been shown by Gordon (*J. Physical Chem.*, 1914, **18**, 55) that comparatively large quantities of ethane and methane are formed when acetic acid is oxidised in dilute solution and at a moderate temperature with potassium persulphate.

Referring to the well-established fact that an anode of smooth platinum must acquire a definite potential before any appreciable quantity of ethane is formed, Gibson deduces that at this potential either (*a*) the acetate ion is first discharged, or (*b*) the acetic acid in becoming oxidised to ethane, begins to act as a depolariser. This view requires some modification, since the so-called "discharging potential" of organic anions must, in reality, be a depolarisation potential. It may be assumed that the first reaction at the anode, *viz.*, the neutralisation of the electric charges on the ions takes place with infinite velocity. Any subsequent chemical reactions in which the discharged ions may be involved, will however, take place with a finite velocity dependent on the concentration of the reacting substances and on the temperature. Thus no matter what views may be held as to the mechanism of ethane formation, there must necessarily exist in the neighbourhood of the anode an accumulation of the unstable substance $CH_3 \cdot CO \cdot O$. Some at least of these discharged ions react with water, giving atomic oxygen. We thus have two unstable products at the anode either of which may cause a back *E.M.F.* The point in the anodic potential–current curve at which the current begins to increase rapidly is therefore the point at which these substances have attained concentrations sufficiently high to allow of their being removed with appreciable rapidity. This depolarisation may conceivably be effected in five ways :

(1) $O + O = O_2$.
(2) $2CH_3 \cdot CO_2H + O = CH_3 \cdot CH_3 + 2CO_2 + H_2O$.
(3) $CH_3 \cdot CO_2H + 4O = 2CO_2 + 2H_2O$.
(4) $2CH_3 \cdot CO \cdot O \cdot + 7O = 4CO_2 + 3H_2O$.
(5) $2CH_3 \cdot CO \cdot O \cdot = CH_3 \cdot CH_3 + 2CO_2$.

Gibson's second alternative is therefore capable of extension, and his conclusion that the particular reaction studied, *viz.*, the formation of trichloromethyl trichloroacetate, is an oxidation reaction

can scarcely be held as valid, since it is largely based on the fact that the potential at which this ester was observed to be first formed is not the discharging potential of the trichloroacetate ion.

Both Gibson and Robertson record a sharp fall in the amount of oxygen evolved in unit time at or about the synthetic potential, and entirely upon this evidence Robertson bases his conclusion that the synthesis of ethyl succinate is an oxidation reaction (*loc. cit.*, p. 2064). Such a fall was not observed by us. In any case, if equations (a) and (a′) be added together, equation (b) is obtained, *i.e.*, the amount of oxygen liberated must be independent of the mode of ethane formation. On either theory, the net result evidently is that one molecule of ethane is produced from two discharged ions without either liberating or using up any oxygen. The amount of evolved oxygen depends on the concentration of active oxygen at the anode, since it is produced by the reaction $O + O = O_2$. If with rising anode potential the amount of oxygen evolved in unit time decreases, the concentration of atomic oxygen must also be decreasing; but since the anode potential is rising, it cannot be the atomic oxygen alone which is responsible for the back *E.M.F.* observed—this must also be due to the discharged ions themselves.

Since the oxidation theory involves the partial oxidation of the acid, it is of interest to inquire to what extent complete oxidation to carbon dioxide and water takes place. Murray (J., 1892, **61**, 34) pointed out that the readiness with which complete oxidation takes place is inconsistent with the oxidation theory. From Robertson's figures it may be shown that about 30 to 40% of the oxygen developed at the anode is used for complete oxidation between the potentials of 2·02 and 2·30 volts, *i.e.*, *before* any synthesis commences. This theory therefore requires the extremely unlikely assumption that partial oxidation necessitates a higher potential (and therefore greater concentrations of reacting materials) than complete oxidation.

No positive evidence whatever would therefore appear to have been put forward in support of the oxidation theory. On the other hand, the recent work of Salauze (*Bull. Soc. chim.*, 1925, **37**, 522), who obtained good yields of ethane by electrolysis of a methyl-alcoholic solution of an acetate, proves that under these conditions the discharged ions do indeed interact directly.

In order to collect further data bearing upon the phenomenon of electrosynthesis, the electrolysis of solutions of acetates and propionates has been studied with regard to the effect of concentration and temperature of the solution, current density, anode potential, nature of solvent, and material of anode.

Experimental.

The apparatus used was of the same type as that employed b Gibson and by Robertson. The anode and cathode gases wer collected together and transferred to a Bone and Wheeler ga analysis apparatus by means of a Dittmar pipette filled wit mercury. A complete analysis of each gas sample was made. Th potentials given are on the hydrogen standard, and were obtaine by calculation after direct comparison with a normal calom electrode.

Experiments with Solutions of Potassium Acetate.—All aceta solutions were made *N* with respect to the free acid to preven the solution becoming alkaline during the course of an experimen *N*-Potassium acetate solution was electrolysed, three anodes smooth platinum of different sizes being used with the same smoot platinum cathode. From Fig. 1 it will be seen that the values *C.D.* and anode potential for all three anodes can be represente on one smooth curve, and that the ratio of ethane to hydroge increases regularly with increasing anode potential independentl of the size of the anode. Murray states (*loc. cit.*, p. 25) tha " although the yield of ethane is increased by increasing the curren or by employing a smaller anode, the variation is not to be accounte for by a change in current density alone. There are apparentl some other factors influencing the electrolysis." The factor whic Murray neglected appears to be the anode potential : between th limits of 2·7 volts, below which no formation of ethane takes plac and 3·0—3·1 volts, above which the yield of ethane can no longe be increased, the amount of ethane formed does increase with th *C.D.* When, however, the ethane : hydrogen ratio has reached it maximum value of nearly 0·9, the *C.D.* can be increased enormousl without affecting the yield of ethane.

An increase in the concentration of the electrolyte scarcel affects the formation of ethane above 2·7 volts, as will be see from the data obtained with a 3*N*-solution, which are show graphically in Fig. 2. Ethane formation takes place, however, somewhat lower anode potentials the more concentrated the sol tion, as is shown in Table I.

Table I.

Concentration	3*N*	4*N*	5*N*
Anode potential	2·68	2·66	2·62
$C_2H_6 : H_2$	0·11	0·11	0·12

The values of *C.D.* and of the ethane : hydrogen ratio for th two concentrations of acetate have been plotted against one anoth in Fig. 3. Up to *C.D.*'s of about 20 milliamp./sq. cm. the rat

increases rapidly. These results indicate that a certain minimum concentration of discharged ionic products is necessary before any appreciable formation of ethane takes place.

A *N*-solution of potassium acetate was also electrolysed at 50° and 95°, the electrolysis cell being immersed in thermostats kept at these temperatures: an increase in temperature did not greatly influence the *P.D.* at which ethane formation commenced; as will be seen, however, from Fig. 2, the amount of ethane formed is less at the higher temperatures.

Experiments with Solutions of Potassium Propionate.—Preuner and Ludlam (*Z. physikal. Chem.*, 1907, **59**, 682) showed that with a 0·5*N*-solution of potassium propionate a polished platinum anode must acquire potentials of 2·58 volts and 2·70 volts, referred to a

FIG. 1.

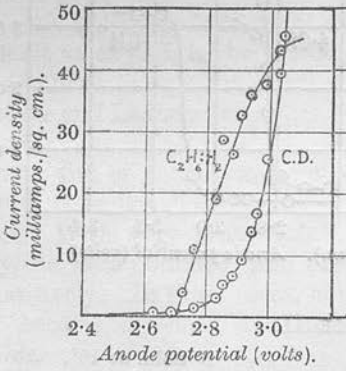
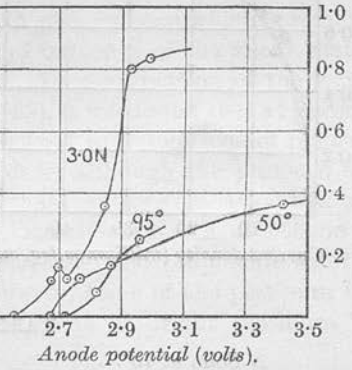


FIG. 2.



(*The right-hand scale of ordinates represents the ratio* $C_2H_6 : H_2$ *and relates to both diagrams.*)

hydrogen electrode in the same solution as standard, for ethylene and butane formation, respectively. It seemed desirable to ascertain the effect of other factors on the products of electrolysis. All solutions were *N* with respect to free propionic acid.

N-Potassium propionate solution was electrolysed with smooth platinum electrodes. At low anode potentials, the gases evolved consisted mainly of hydrogen and oxygen with a little ethylene, but no butane. As the *P.D.* was raised the ethylene increased rapidly, reaching a maximum, after which butane made its appearance. Simultaneously with the increase of ethylene, the oxygen began to decrease, finally reaching a minimum. About 1% of carbon monoxide was always present. The results obtained with an anode of 7·2 sq. cm. surface are given in Table II. It is seen that the ethylene : hydrogen ratio begins to increase rapidly at 2·60 volts and tends to reach an asymptotic value of about 0·60

at 2·95 volts. Table III shows the results obtained with a 4*N*-solution using the same electrodes. The corresponding curve is of the same shape as with the *N*-solution, but is displaced 0·15 volt to the left, the ethylene formation commencing at a lower potential.

A *N*-solution was also electrolysed at 50°, using a smooth platinum anode of 0·165 sq. cm. surface. From Table IV it is seen that although there is more ethylene at low potentials at this temperature, the increase with rise of anode potential is more gradual and the ethylene : hydrogen ratio does not increase much beyond 0·

FIG. 3.

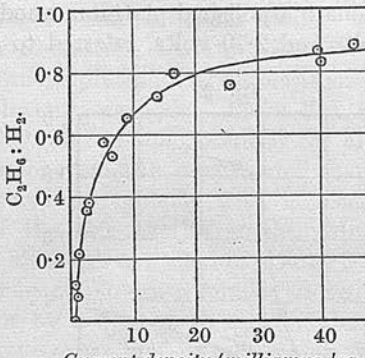


FIG. 4.

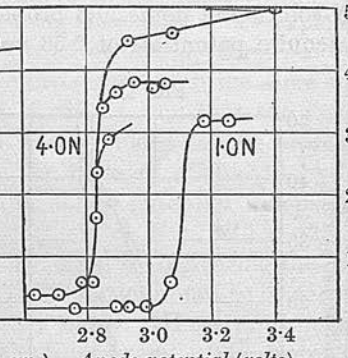


TABLE II.

N-Soln. at 10°. Anode = 7·2 sq. cm.				*N*-Soln. at 10°. Anode = 7·2 sq. cm.			
A.P.	*C.D.*	C_2H_4/H_2.	O_2/H_2.	*A.P.*	*C.D.*	C_2H_4/H_2.	O_2/H_2.
2·36	0·06	0·01	0·23	2·75	2·64	0·24	0·12
2·48	0·08	0·02	0·29	2·78	8·06	0·33	0·067
2·54	0·17	0·01	0·37	2·79	—	0·41	0·043
2·60	0·35	0·04	0·365	2·83	—	0·47	0·030
2·66	0·61	0·07	0·32	2·89	—	0·55	0·022
2·71	0·93	0·13	0·23	2·92	—	0·58	0·024

TABLE III.

4*N*-Soln. at 10°. Anode = 7·2 sq. cm.			
A.P.	*C.D.*	C_2H_4/H_2.	O_2/H_2.
2·35	0·01	0·01	0·37
2·46	0·07	0·03	0·36
2·54	0·13	0·10	0·30
2·60	0·31	0·29	0·14
2·63	0·82	0·43	0·047
2·71	5·56	0·58	0·018
2·75	8·33	0·59	0·011

TABLE IV.

N-Soln at 50°. Anode = 0·165 sq. cm.			
A.P.	*C.D.*	C_2H_4/H_2.	O_2/H_2.
2·56	2·7	0·04	0·28
2·63	6·1	0·09	0·24
2·68	12·1	0·16	0·17
2·75	28·5	0·25	0·10
2·79	46·1	0·28	0·077
2·86	84·8	0·34	0·055
2·95	158·2	0·38	0·042
3·07	249·7	0·40	0·031
3·15	304·2	0·41	0·029

Complete oxidation is, on the whole, more vigorous at 50° and also more free oxygen is evolved above 2·75 volts than at 10°. It appears that the increase of temperature increases the rate of reaction of the discharged ions with water more than it increases the rate of their interaction.

Fig. 4 shows the relation between the anode potential and the percentage of butane (after removal of carbon dioxide) for the two concentrations. With *N*-solution, butane begins to be formed in appreciable quantity at 3·05 volts and reaches a maximum of 3·2% at 3·15 volts. No greater quantity was obtained with *P.D.*'s up to 4·6 volts. With 4*N*-solution, three anodes were used, in order to cover the desired range of *C.D.*'s. The amount of butane increases suddenly at about 2·8 volts and reaches a maximum of 5·0% with the smallest anode. At 50°, no butane was formed even at high potentials.

Nature of the Anode Material.—A phenomenon which is somewhat difficult to explain is the profound influence of the anode material on synthesis in aqueous solution. In confirmation of the work of Preuner and Ludlam (*loc. cit.*, p. 689), it was found that at platinised platinum anodes no synthesis occurred with solutions of potassium acetate and of potassium propionate, although the presence of up to 10% of carbon dioxide showed that complete oxidation had taken place. With very large *C.D.*'s, small quantities of ethane and ethylene were obtained from the acetate and propionate solutions, respectively. In these cases, however, some of the platinum black had become detached and small spots of bright platinum were visible.

With gold anodes, we could detect no trace of synthetic product. With a *N*-solution of potassium acetate, the current increased regularly with increasing anode potential, whilst the gas evolved at 3·1 volts still consisted of hydrogen and oxygen with about 3% of carbon dioxide. The propionate solution gave a gas of similar composition at *P.D.*'s between 3 and 5·3 volts. The anode suffered considerable disintegration, and the solution became brown with dispersed gold.

Fichter and Krummenacher (*Helv. Chim. Acta*, 1918, **1**, 148) suggested that the ability of a metal to promote the Kolbe synthesis was connected with its oxygen overvoltage, and Gibson (*loc. cit.*, p. 484) also discusses this view. It seems more reasonable, however, to approach the problem from the point of view adopted by Preuner and Ludlam. The discharged ions may be supposed to react either with water to give acid and oxygen or with themselves to effect synthesis. Synthesis cannot occur unless there is a sufficient concentration of discharged ions at the anode. We are thus led to

the conclusion that the velocity of the reaction of discharged io with water at surfaces of platinised platinum and of gold is mu greater than at one of smooth platinum, so that their concentrati does not attain a value sufficiently high to give synthesis.

Experiments with Non-aqueous Solvents.—The nature of t anode would be expected to have little effect when the solvent such that reaction with the discharged ions cannot take pla Hofgartner (*Monatsh.*, 1911, **32**, 523) obtained ethane : hydrog ratios as high as 0·97 by electrolysing an 8·8% solution of potassiu acetate in glacial acetic acid with a smooth platinum anode. Wi the same anode material, Salauze (*loc. cit.*) obtained by electroly of acetates in methyl-alcoholic solution 95% of the possible ethan and showed that in this solvent the nature of the anode, provid that it is not attacked, has much less influence than in aqueo solution.

The following experiment shows the effect of the addition water on the electrolysis of 4·9 g. of potassium acetate and 1·52 of acetic acid in 100 c.c. of methyl-alcoholic solution. A platinis platinum anode of 0·165 sq. cm. surface and a smooth platinu cathode were used, and the current was maintained at the consta value of 25 milliamp. in each determination.

CH_3OH (c.c.)	100	95	90	80	0
H_2O (c.c.)	0	5	10	20	100
C_2H_6/H_2	0·71	0·58	0·22	0	0

It will be seen that ethane formation is inhibited by the presen of water. The way in which the effect due to the anode materi is dependent on the solvent is further shown by electrolysing solution of anhydrous sodium acetate in glacial acetic acid with a anode of (1) smooth platinum and (2) gold. The ratios of etha to hydrogen in the evolved gases were 0·86 and 0·77, respectivel Synthesis therefore takes place readily at a gold anode in th solvent.

It has been shown that the yield of butane from the electroly of aqueous solutions of potassium propionate is very small. B using an anhydrous solvent, however, much better yields can b obtained. A *N*-solution of potassium propionate in equal volum of methyl alcohol and propionic acid was electrolysed with a smoot platinum anode at 100 milliamp. until the liquid was saturated wit the gases, which were then found in the following proportion C_2H_4, 12·3; C_4H_{10}, 36·0; O_2, 0·5; CO, 0·5; H_2, 50·7%. A simil experiment with a gold anode gave a gas of approximately the sam composition. It need scarcely be pointed out that this constitute a valuable method for the preparation of butane.

We have stated that the bends in current–anode potenti

curves must be due to depolarisation. Now in anhydrous solution this depolarisation must be effected exclusively by union of the discharged ions to give synthesis. It was therefore considered of interest to examine the electromotive phenomena at the anode under these conditions, and potential–current density curves were constructed for a smooth platinum anode in a methyl-alcoholic solution of potassium propionate (N) and propionic acid (N), care being taken to exclude traces of water. The propionate solution itself was used as a buffer solution between the cell and the potassium chloride solution leading to the calomel electrode. As shown in Fig. 5, depolarisation evidently occurs at 2·6—2·7 volts. Owing to the great solubility of the gases in methyl alcohol, it was not possible to obtain for analysis representative samples at the various anode potentials.

FIG. 5.

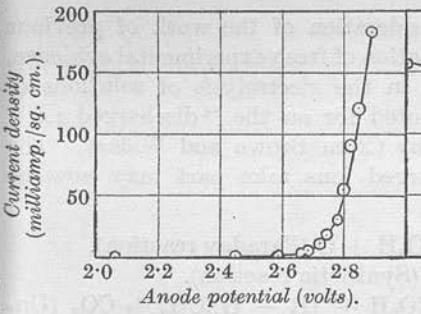
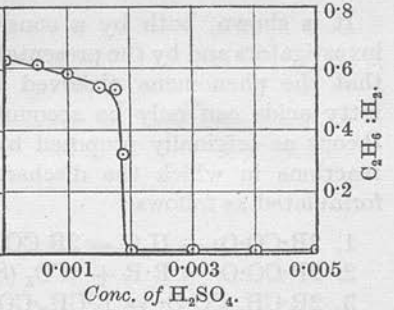


FIG. 6.



The Electrolytic Oxidation of Acetic Acid.—It might be held that, although the discharged ions interact in non-aqueous solutions, synthesis in aqueous solutions may be due either partly or entirely to oxidation of the free acid. It was thought that if in a solution of acetic acid the acetate ions could be prevented from discharging, whilst at the same time the oxidation conditions were maintained unaltered, it would be possible to ascertain conclusively whether or no ethane is obtained by oxidation of the acid. These conditions have been realised in the following experiment. A concentrated aqueous solution of acetic acid ($15N$) was electrolysed with the addition of varying small quantities of sulphuric acid, smooth platinum electrodes being used and a constant current of 35 milliamp. Each electrolysis was allowed to proceed for about 24 hours to ensure saturation of the liquid with the gases evolved.

The results are shown graphically in Fig. 6, in which the ethane : hydrogen ratio is plotted against the concentration of sulphuric acid in g.-equivs. per litre. It will be seen that the critical concentration of sulphuric acid is $0{\cdot}002N$, and that the formation of

ethane is then almost completely prevented. This concentrati
evidently corresponds to a critical concentration of dischar
acetate ions, below which synthesis cannot take place. The ion
ation of the acetic acid, already small owing to the high conc
tration of the solution, is still further reduced by the sulphu
acid; the current is then partly carried by the SO_4'' and HS
ions. These, after discharge, react with water to give ato
oxygen, which, however, does not oxidise the acetic acid to etha
Little oxygen was evolved in any of the experiments; it was u
up in oxidising the acetic acid to carbon dioxide and water, 20—2
of carbon dioxide being present even in absence of ethane. T
experiment shows beyond doubt that ethane is produced by t
interaction of discharged acetate ions, and that electrolytic oxyg
when it oxidises acetic acid, does so completely and not partly.

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Conclusion and Summary.

It is shown, both by a consideration of the work of previ
investigators and by the presentation of fresh experimental eviden
that the phenomena observed in the electrolysis of solutions
fatty acids can only be accounted for on the "discharged io
theory as originally proposed by Crum Brown and Walker. T
reactions in which the discharged ions take part may now
formulated as follows:

1. $2R{\cdot}CO{\cdot}O{\cdot} + H_2O = 2R{\cdot}CO_2H + O$ (Faraday reaction).
2. $2R{\cdot}CO{\cdot}O{\cdot} = R{\cdot}R + 2CO_2$ (Synthetic reaction).
3. $2R{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot} = R{\cdot}CH_2{\cdot}CO_2H + (R - H){:}CH_2 + CO_2$ (U
saturated product).
4. $2R{\cdot}CO{\cdot}O{\cdot} = R{\cdot}CO_2R + CO_2$ (Ester formation).
5. $R{\cdot}CO{\cdot}O{\cdot} + OH = R{\cdot}OH + CO_2$ (Alcohol formation).
6. $R{\cdot}CO{\cdot}O{\cdot} + nO = xH_2O + yCO_2$ (Complete oxidation).

The conditions which favour reactions 2 and 3 are precisely th
which retard or prevent reaction 1.

The main points which have been put forward in support of t
above theory may be summarised as follows:

1. The arguments advanced by Gibson and by Robertson
favour of the oxidation theory are largely fallacious.

2. The electrolytic oxidation of acetic acid has been shown
be complete and not partial under ordinary conditions. Compl
oxidation takes place to a considerable extent at low an
potentials.

3. The presence of a definite concentration of the dischar
anions themselves is indispensable for synthesis.

4. In confirmation of the results of other workers, it has be

shown that synthesis can and does take place in non-aqueous solutions to which the oxidation theory is not applicable.

The authors wish to thank Professor Sir James Walker, F.R.S., for his helpful criticism and advice during the course of this work, and also Messrs. Brunner Mond and Co., Ltd., for a grant which defrayed part of the expense incurred.

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A. 2.

THE DECOMPOSITION OF ACETYL PEROXIDE AND THE MECHANISM OF KOLBE'S ELECTROSYNTHESIS.

BY

OSWALD JAMES WALKER.

Reprinted from the Journal of the Chemical Society, August 1928



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CCLXV.—*The Decomposition of Acetyl Peroxide and the Mechanism of Kolbe's Electrosynthesis.*

By Oswald James Walker.

The earlier idea of Schall (*Z. Elektrochem.*, 1896, **3**, 83), that acid peroxides are formed as intermediate products at the anode during the electrolysis of fatty acids, has in recent years been taken up by Fichter (*Trans. Amer. Electrochem. Soc.*, 1924, **45**, 131; *J. Chim. phys.*, 1926, **23**, 493), who has extended the peroxide theory to electrochemical oxidation in general. It is the purpose of this paper to show that the experimental justification for this view is unsound and that there is no necessity to assume that acetyl peroxide is formed during the electrolysis of acetates.

Whatever view we adopt regarding the mechanism of Kolbe's reaction we must assume that free $CH_3 \cdot CO \cdot O$ radicals are present at some stage in the process. If we accept the discharged-ion theory, *i.e.*, that the $CH_3 \cdot CO \cdot O$ radicals result simply from the discharge of acetanions and not from a dehydration of acetic acid by oxygen (compare Fairweather and Walker, J., 1926, 3111 *), the question still arises: Do the $CH_3 \cdot CO \cdot O$ radicals unite to form acetyl peroxide which then decomposes into carbon dioxide and ethane; or do they decompose "unimolecularly," so to speak, into carbon dioxide and free CH_3 radicals, which then unite to form ethane?

The first view may be tested, as Fichter suggested, by preparing the pure acetyl peroxide and causing it to decompose. The application of results of such experiments to the Kolbe reaction at the anode may, however, not be conclusive. For even assuming that acetyl peroxide decomposes on heating entirely into carbon dioxide and ethane, it does not follow that in the anode process, in which

* The values of the anode potential in that paper are through a regrettable error in the calculation all 0·56 volt too high. This in no way affects the reasoning in the paper, which is concerned only with the relative values of the potentials.

these gases are obtained from discharged acetanions, the $CH_3 \cdot CO$ radicals must have first united to form a peroxide. On the contrary, one may argue that acetyl peroxide, when heated, breaks up into two $CH_3 \cdot CO \cdot O$ groups, which then react as in the electric process (compare Wieland and Fischer, *Annalen*, 1925, **446**, 6 It will be seen, however, from the experimental part that a simp decomposition of acetyl peroxide according to the equati $(CH_3 \cdot CO \cdot O \cdot)_2 = C_2H_6 + 2CO_2$ does not take place.

Fichter (*Helv. Chim. Acta*, 1927, **10**, 869) claims to have obtain direct evidence for the peroxide theory, since he has shown th in the electrolysis of a solution of potassium hexoate small quantiti of hexoyl peroxide are formed when the temperature is kept ve low. This experiment shows that when the conditions are mad very favourable the discharged acyl radicals unite to a small exte to form the acid peroxide, but one is not justified in concludi that the Kolbe synthesis, which is the main reaction, has proceed through the intermediate stage of peroxide. In fact, the difficul of isolating from the electrochemical products any peroxide temperatures at which these peroxides are by no means unstab cannot be reconciled with this view. A further difficulty aris when one considers that by electrolysing a solution of an aceta at about 100° considerable quantities of ethane are obtaine although acetyl peroxide decomposes well below this temperatu (see experimental part). Also Gibson (*Proc. Roy. Soc. Edin.*, 192 **44**, 151) has shown that hexachloroethane is formed in th electrolysis of trichloroacetic acid, of which the peroxide is appa ently incapable of existence.

The decomposition of acetyl peroxide, on which Fichter large bases his theory, has really not been studied to any extent (f the previous literature on the subject, see Fichter, *Helv. Chim. Ac* 1918, **1**, 151). It was decided, therefore, to investigate the natu and composition of the gases obtained by the decomposition acetyl peroxide under various conditions.

EXPERIMENTAL.

Acetyl peroxide was prepared from acetic anhydride and sodiu peroxide by the method of Gambarjan (*Ber.*, 1909, **42**, 4010). Th ethereal solution of peroxide was dried over calcium chloride, t ether evaporated at the ordinary temperature, and the crystalli residue of peroxide washed with ether; it was then sufficiently pur m. p. 26·5° (Nef gives 30°, and Colson 27°). Analysis: A mixtu of 0·1—0·2 g. of the peroxide, 50 c.c. of water, 10 c.c. of glaci acetic acid, and 10 c.c. of a 20% solution of potassium iodide w kept for 24 hours (the liberation of iodine takes place slowl

compare Clover and Richmond, *Amer. Chem. J.*, 1903, **29**, 183) and the iodine was then titrated with $N/10$-thiosulphate. Independently prepared samples of the peroxide were found to contain 99·6, 99·8, and 99·4% of $(CH_3{\cdot}CO{\cdot}O{\cdot})_2$.

In all the experiments that follow, the gases evolved were collected over mercury and analysed in the usual manner in a Bone and Wheeler apparatus containing mercury.

Decomposition of Pure Acetyl Peroxide.—When acetyl peroxide is heated gradually above its melting point the liquid commences to evolve gas at 60—70°, and at 80° the evolution proceeds briskly. The decomposition takes place gently without the violent explosion that occurs when the substance is heated rapidly. The composition of the gas (% vol.) evolved at 80° is: CO_2, 58·7, 61·0; C_2H_4, 1·1, 1·6; O_2, —, 2·3; CO, 1·6, 3·0; CH_4, 34·0, 28·8; C_2H_6, 4·6, 3·4.

The proportion of methane formed is greater than in the explosive decomposition of acetyl peroxide investigated by Fichter (*Helv. Chim. Acta*, 1918, **1**, 152), which did not lead to a simple disintegration according to the equation $CH_3{\cdot}CO{\cdot}O{\cdot}O{\cdot}OC{\cdot}CH_3 = C_2H_6 + 2CO_2$. He also found considerable quantities of methane and ascribed its formation to a sort of "cracking" process, due to the violence of the explosion and the high temperature of the decomposition, which he supposes does not occur in the slow molecule-by-molecule decomposition at the anode.

A further experiment, in which the decomposition was carried out quantitatively and as slowly as possible, showed that the absolute yield of ethane, calculated on the weight of peroxide used, is very small. In a small, weighed tube 0·0500 g. of acetyl peroxide was gently heated till decomposition commenced at 61°. The heating was continued, at 65—75°, for about 4 hours, 11·0 c.c. of gas (measured at 13° and 754 mm.) being collected. The residue weighed 0·0257 g., and the amount of undecomposed peroxide in it, estimated by liberation of iodine from potassium iodide, was 0·0170 g. The decomposed peroxide (0·0330 g.) therefore produced 10·4 c.c. of gas (reduced to N.T.P.) having the following percentage composition by volume: CO_2, 58·3; O_2, 0·2; CO, 0·9; CH_4, 38·6; C_2H_6, 1·9. This corresponds to 1·0 molecule of carbon dioxide, 0·65 molecule of methane, and 0·04 molecule of ethane from 1 molecule of peroxide. The formation of ethane is therefore certainly not the main reaction.

Decomposition of Solutions of Acetyl Peroxide.—When a solution (100 g.) of acetyl peroxide (14·4 g.) in water containing acetic acid (27·7 g., to increase the solubility) was gradually warmed, effervescence set in at about 75° and between 80° and 90° there was a brisk

evolution of gas. The gases evolved at about 80° were collec and analysed (expts. *a* and *b*).

Acetyl peroxide dissolved in	CO_2.	C_2H_4.	O_2.	CO.	CH_4.	C_2H
a. Aqueous acetic acid	76·0	1·2	3·1	1·4	16·0	2·
b. „ „	75·0	—	1·4	1·4	20·8	1·
c. Ethyl alcohol	50·5	—	—	2·2	45·8	1·
d. „ „	51·0	—	—	1·7	45·6	1·

Here again the amount of ethane formed is small compared w that of methane and there is relatively more carbon dioxide.

A solution of 0·15 g. of acetyl peroxide in 0·4 c.c. of alcohol w heated gradually in a water-bath. Gas evolution commenced about 60°. The gas evolved between 60° and 70° was collec after passing through a cooled tube to condense any alcohol vapo it consisted mainly of carbon dioxide and methane in nearly eq volumes, with only a very small amount of ethane (see expts. *c* a *d* in the table).

From these experiments, it is evident that the decomposition acetyl peroxide does not take place to any large extent accord to the equation $(CH_3{\cdot}CO{\cdot}O{\cdot})_2 = C_2H_6 + 2CO_2$, and hence th is no reason to suppose that in the electrolysis of acetates, wh the gases evolved at the anode are essentially carbon dioxide a ethane, acetyl peroxide has been formed at the anode. It m also be emphasised that methane is not present in the anode gas although it appears to be one of the necessary products in t decomposition of acetyl peroxide. The only electrolytic formati of methane from acetates is recorded by Baur (*Z. Elektrochem.*, 19 29, 105), who used commutated direct current.

There is the possibility that the methane obtained in the abo experiments from aqueous solutions of acetyl peroxide may ha come from decomposition not of the peroxide itself but of t peracid which is got from it by hydrolysis. It has been shown Clover and Richmond (*loc. cit.*, p. 184) that a solution of ace peroxide kept for 24 hours undergoes the change:

$$CH_3{\cdot}CO{\cdot}O{\cdot}O{\cdot}CO{\cdot}CH_3 + H_2O = CH_3{\cdot}CO{\cdot}O{\cdot}OH + CH_3{\cdot}CO{\cdot}OH$$

A solution of the peroxide which had been kept for a week liberat almost the whole of the required amount of iodine immediat after the addition of potassium iodide, showing that the chan from peroxide to peracid was practically complete (since the form liberates iodine only very slowly). The solution of peracid w heated gradually and at about 40° gas evolution commenced. T gas evolved between 75° and 80° consisted mainly of oxygen wi about 10% of carbon dioxide and no trace of ethane or methan Hence the decomposition of the peroxide does not proceed throu the peracid stage.

In the search for a method whereby acetyl peroxide might be decomposed at lower temperatures than those employed so far, the action of ultra-violet light on the peroxide was investigated: the peroxide decomposed, and larger quantities of ethane were obtained than by any of the previous methods. A solution of acetyl peroxide in aqueous acetic acid was placed in a quartz tube surrounded by a water-cooled quartz condenser and was exposed at a distance of 3 or 4 inches to the light of a mercury vapour lamp. A gas was slowly evolved and after 7 or 8 hours about 5 c.c. had collected. The composition of the gas is shown in the table (expts. *a* and *b*).

	Acetyl peroxide.	CO_2.	C_2H_4.	O_2.	CO.	CH_4.	C_2H_6.
a.	Dissolved in aqueous acetic acid	75·4	—	1·2	1·4	4·8	17·3
b.	,, ,, ,, ,,	68·5	—	1·4	1·3	11·8	17·1
c.	Solid	66·8	—	1·3	1·2	5·6	25·1
d.	,, ...	68·4	2·1	0·7	1·3	3·9	23·6
e.	,, ...	67·4	2·0	0·5	1·4	4·4	24·4

In experiments *c*, *d*, and *e*, solid acetyl peroxide was exposed to the ultra-violet light for about 3 hours. The amount of ethane formed was much greater than in the thermal decomposition. Even in this case, however, there is no reason to suppose that the main reaction consists in a simple breaking up of the acetyl peroxide into ethane and carbon dioxide.

Conclusion.

The results of the experiments described in this paper make it appear extremely unlikely that the formation of ethane and carbon dioxide at the anode in the electrolysis of acetates proceeds through the intermediate stage of acetyl peroxide. The view that the discharged acetate ions, which must necessarily be very unstable radicals, react together to give the above-mentioned products still affords the most satisfactory, although perhaps incomplete, explanation of Kolbe's electrosynthesis. In the interaction of these radicals some sort of momentary loose union may well take place prior to a more far-going disruption, but the assumption of the actual formation of the chemically known peroxide is unnecessary and also experimentally unsound. That a small portion of the acetate radicals might unite to form the more stable peroxide would not be surprising, and this possibility is not excluded.

The main arguments against the peroxide theory may be summed up as follows:

(1) The thermal decomposition of acetyl peroxide, both in the pure state and in solution, does not indicate a reaction according to the equation $(CH_3{\cdot}CO{\cdot}O)_2 = C_2H_6 + 2CO_2$.

(2) Methane, which is not found in the anode gases during the

electrolysis of acetates, is always present among the decomposit products of acetyl peroxide, often in large amounts.

(3) Peroxides have not as yet been isolated by electrochem means, even at low temperatures at which the peroxides are c paratively stable.

I should like to thank Professor Sir James Walker, F.R.S., his helpful advice during the course of this work.

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A. 3.

Formation of Methane During the Electrolysis of Potassium Acetate, and the Mechanism of Kolbe's Electrosynthesis.

BY

S. N. SHUKLA AND O. J. WALKER.

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FORMATION OF METHANE DURING THE ELECTROLYSIS OF POTASSIUM ACETATE, AND THE MECHANISM OF KOLBE'S ELECTROSYNTHESIS.

By S. N. Shukla and O. J. Walker.

Received 22nd September, 1930.

Most of the controversy concerning the mechanism of Kolbe's electrosynthesis has centred round the respective merits of the so-called "discharged ion" and "oxidation" theories to account for the undoubtedly complex phenomena which occur at the anode.[1] In recent years, much

[1] Gibson, *J. Chem. Soc.*, **127**, 475, 1925; Fairweather and Walker, *J. Chem. Soc* 3111, 1926; Fichter, *J. Soc. Chem. Ind.*, 347, 1929.

valuable work has been done by Fichter and his co-workers, particularly with the object of showing that peroxides are formed as intermediate products at the anode. The intermediate formation of acetyl peroxide during the electrolysis of potassium acetate can be interpreted in terms of both of the above theories, and the proof of the formation of peroxides will not afford a certain criterion to distinguish between the two views. Although the peroxide theory has been accepted by Fichter, it has been criticised, amongst others, by Müller[2] and by Walker,[3] who showed that one of the strongest arguments against it, in the case of the electrolysis of acetates, was the absence of methane in the anode gases, in spite of its presence amongst the decomposition products of acetyl peroxide, often in large amounts. When this criticism was made, no evidence had been obtained for the formation of methane in the direct current electrolysis of aqueous potassium acetate solutions, although Baur[4] obtained methane from acetate solutions using commutated current, and Petersen[5] from the electrolysis of fused acetates. Evidence has now been obtained that methane is actually formed at the anode during the electrolysis of aqueous acetate solutions under certain conditions. The possibility of methane being present in the anode gases was indicated, in the first place, by the fact that during the course of a large number of analyses, in which the anode gases were analysed separately from the hydrogen, the explosion analysis of the combustible constituent gave results, which in many cases did not agree with the assumption that it was purely ethane. The values of C/A, where C is the contraction on explosion and A the amount of absorption by potash, lay in general between 1·25 and 2·0, which are the theoretical values for pure ethane and methane respectively.

It seems surprising, in view of the large number of investigations on Kolbe's reaction, that the presence of methane should have been overlooked. It should be remembered, however, that previous analyses of the gaseous products of electrolysis have been confined almost entirely to the mixed anode and cathode gases, *i.e.* to a mixture containing a large proportion of hydrogen. If it is assumed that only ethane and hydrogen are present in the combustible residue after removal of the other constituents (and this has usually been done either directly or implicitly), then the presence of any methane, particularly in relatively small amounts, may easily remain undetected, since $2CH_4$ is equivalent to $C_2H_6 + H_2$, *i.e.* the CH_4 simply acts as a mixture of C_2H_6 and H_2. Moreover, previous analyses have usually been made with gases obtained by electrolysing at comparatively high *C.D.* and as will be shown later, the amount of methane formed is appreciable only at low *C.D.*'s.

In order to make certain, however, that the combustible gas does contain methane as well as ethane, it was decided to remove the ethane from the mixture by cooling it with liquid air, and to burn the uncondensed methane separately. This was done by transferring the combustible residue, after the removal of carbon dioxide and oxygen, from the Bone and Wheeler apparatus to an evacuated tube cooled in liquid air. After standing for some time, any uncondensed gas was pumped off by means of a Töpler pump. The presence of methane would be proved if this uncondensed residue were found to be a combustible gas giving a ratio of $C/A = 2·0$ on explosion.

In a large number of analyses this was found to be the case. The following values, for example, of C/A were obtained from the explosion of

[2] Muller, *Z. Electrochem.*, **28**, 103, 1922.
[3] Walker, *J. Chem. Soc.*, 2040, 1928.
[4] Baur, *Z. Electrochem.*, **29**, 105, 1923.
[5] Petersen, *Z. Electrochem.*, **20**, 328, 1915.

the residue of the gas evolved at the anode in the electrolysis of potassium acetate solutions, after removal of CO_2, O_2, and of ethane as described above: 1·96, 2·01, 1·93, 1·99, 1·99, 1·92, 1·93, 1·89, 2·00, 2·10 (average = 1·97). Explosion of the condensed gas separately gave $C/A = 1·25$. These results show conclusively that methane is present in these cases in the anode gases from the electrolysis of potassium acetate.

The preliminary experiments indicated that the current density was an important factor, methane being found in general only in the anode gases obtained by electrolysis with low current density. In order to investigate more closely the conditions under which methane is formed, solutions of potassium acetate (containing an equivalent amount of free acetic acid) of different concentrations were electrolysed at various current densities at the ordinary temperature. A platinum wire anode, length 4·4 cm. and diameter 0·1 cm., was used and the anode gases were collected separately. The analyses were carried out in a Bone and Wheeler apparatus over mercury. After removal of carbon dioxide and oxygen, the combustible residue was transferred to the liquid air cooling apparatus mentioned in the preceding paragraph, and the uncondensed portion pumped off and measured. Preliminary measurements with known mixtures of pure methane and ethane showed that the contraction after cooling with liquid air was a sufficiently accurate measure of the amount of ethane present in the mixture. In many cases the condensed ethane was also pumped off, collected separately and exploded. In the analysis of the anode gases, the residual gas not condensed by liquid air was not assumed to be entirely methane, since the presence of more or less accidental amounts of nitrogen had to be allowed for, due to air dissolved in the original electrolyte or admitted during the course of the analysis. The uncondensed gas was therefore exploded and the methane determined from the explosion results, the value of C/A acting as a check on the analysis.

The results are given in Table I.

It will be seen, firstly, that the quantity of methane is appreciable only when the electrolysing current has a value below about 15 m.a., corresponding with a current density of about 10 m.a./sq. cm. The results with the N solutions show this particularly well. In a few cases, small amounts of methane were obtained with comparatively high current densities. Secondly, the proportion of methane to ethane for a given current density is greater the more concentrated the solution. In the most favourable case, using a 3·5 N solution, almost twice as much methane as ethane is formed. Thirdly, methane is formed apparently only along with ethane. From the results with 0·5 N and 1·0 N solutions, it is evident that no methane is evolved as long as oxygen is the main gaseous product. These results may be summed up by saying that methane is formed within a definite limit of current density.

The formation of methane under certain conditions at the anode has thus been established, but it is difficult to see in what way the methane can have been formed. One must admit that in these cases the argument that the products of the electrolytic reaction are not the same as those of the thermal decomposition of acetyl peroxide, does not hold, and the peroxide theory provides, therefore, a possible partial explanation. It must be emphasised, however, that at ordinary current densities, such as are used in the electrolytic preparation of ethane, no appreciable amount of methane is produced, and one must suppose that under these conditions the acetyl peroxide decomposes in a different manner. If the methane is

produced by thermal decomposition of ethane [6] due to a region of higher temperature at the anode surface, then one would expect the proportion of methane to ethane to increase with the current density, since the temperature effect at the anode surface would then be greater. As seen from the last column in Table I., however, the ratio CH_4/C_2H_6 decreases with increasing *C.D.* In this connection, it is interesting to note that in many reactions in which a disruption of the acetic acid molecule or of the acetate radicle takes place, methane occurs amongst the reaction products,

TABLE I.

Concentration of Electrolyte.	Current Milliamps.	Per Cent. CO_2.	Per Cent. O_2.	Per Cent. CH_4.	Per Cent. C_2H_6.	Per Cent. Residue.	$\frac{CH_4}{C_2H_6}$
0·5*N* CH_3COOK (+ 0·5*N* CH_3COOH)	1	4·2	83·3	0	3·3	9·2	0
	2	4·9	87·7	0	1·7	5·7	0
	3	6·3	87·3	0	1·0	5·4	0
	4	7·4	87·0	0	0·5	5·1	0
	5	9·9	82·3	0	1·3	6·5	0
	6	38·4	15·3	9·0	34·2	3·1	·26
	7	50·4	4·4	7·7	35·9	1·6	·22
0·5*N* CH_3COOK (+ 0·5*N* CH_3COOH)	5	34·8	5·6	14·5	35·8	9·3	·41
	10	32·8	1·8	11·1	47·9	6·4	·23
	15	41·6	2·9	6·6	44·4	4·5	·15
	25	43·2	1·8	3·2	48·2	3·6	·07
	50	46·9	1·4	0·6	46·2	4·9	·01
	100	47·9	1·8	0	46·5	3·8	0
1·0*N* CH_3COOK (+ 1·0*N* CH_3COOH)	1	11·5	76·5	0	2·3	9·8	0
	2	13·9	76·7	0	1·6	7·8	0
	3	40·6	14·0	17·7	23·6	4·1	·75
	4·3	56·4	1·7	8·8	31·3	1·8	·28
	5	56·6	1·1	7·7	32·9	1·7	·23
	6	57·3	0·9	6·3	34·4	1·1	·18
	10	56·9	0·5	3·7	37·5	1·4	·10
	15	55·4	1·0	2·1	40·2	1·3	·05
	25	53·6	0·8	1·6	42·3	1·7	·04
	35	55·9	0·7	1·2	40·6	1·6	·03
	50	56·6	0·9	1·0	39·7	1·8	·02
	100	58·5	0·6	0·5	39·5	0·9	·01
	300	54·8	0·8	0·6	42·2	1·6	·01
3·5*N* CH_3COOK (+ 3·5*N* CH_3COOH)	1·5 – 2·0	67·3	0·4	19·8	10·5	2·0	1·89
	4·0 – 6·0	66·0	0·4	15·3	16·3	2·0	·94
	8	59·5	1·0	5·1	32·1	2·3	·16
	10	55·4	0·6	0	36·9	7·1	0
	15	50·5	1·0	0	42·8	5·7	0
	25	48·9	1·8	0	44·7	4·6	0
	200	59·4	0·3	0	40·3	0	0

e.g. fusion of acetate with soda-lime, action of persulphate on acetate, action of barium peroxide on acetic anhydride, decomposition of acetyl peroxide, photolysis of acetates.

It has already been pointed out that the intermediate formation of acetyl peroxide may be admitted according to both the discharged ion and oxidation theories. Since a certain amount of misunderstanding appears to have arisen in the recent literature, regarding the interpretation of the evidence for and against these theories, this opportunity is taken to discuss

[6] Fichter, *Helv. Chim. Act.*, 13, 98, 1930.

the subject further. Wieland and Fischer [7] state that it is of no importancc which view we adopt, since the end result is the same. Fichter [8] says the same thing: "We fail to see the difference between the chemical oxidation of an acid and the discharge of its anions at the anode. Both reactions are identical and consist in a loss of one negative charge per equivalent." Further,[9] in comparing Kolbe's reaction with the action of fluorine on acetates, he says: "The anodic reaction can be formulated as a simple oxidation; the reaction with fluorine on the other hand as a reaction between ions. It is solely a question of convenience, and one which does not suppose any change in the mechanism of the reaction." Yet in spite of this, he states elsewhere [10]: "The purely chemical imitation of the Kolbe electrosynthesis of hydrocarbons by means of gaseous fluorine, proves conclusively that synthesis is due to oxidation." Now admittedly the *net* result of the two theories is the same, and this obviously must be the case since they are both put forward to explain the same set of facts. But it is quite incorrect to assume that the mechanism of the reaction must be the same. In fact, it simply ignores one of the most important questions at issue, *viz.*, whether oxygen is necessarily formed as an intermediate stage at the anode.

It is by no means clear whether those who uphold the oxidation theory consider that the oxygen is produced from discharge of the CH_3COO' ion and reaction with water

$$2CH_3COO + H_2O = 2CH_3COOH + O \quad . \quad . \quad (1)$$

or by discharge of oxygen or hydroxyl ions. The latter mechanism is highly improbable, when one considers the ease with which ethane formation occurs in non-aqueous solvents and, also, the change to the Hofer and Moest reaction when the electrolyte is made alkaline. Work at present in progress shows that the abnormally high value of 2·54 volts for the so-called discharge potential of the acetate ion [11] is not correct, or that, at any rate, ethane is evolved below this potential. If one supposes that the oxygen is produced by the action of discharged acetate radicles on water, then the difficulty of explaining the reaction in non-aqueous solvents still arises. Moreover, it is not clear whether it is to be supposed that the acetic acid which is oxidised according to the equation

$$2CH_3COOH + O = C_2H_6 + 2CO_2 + H_2O \quad . \quad . \quad (2)$$

is simply the acid in the solution immediately in contact with the anode, or whether it is what one might call "nascent" acetic acid produced by reaction 1. There is no reason to suppose that the freshly-formed acetic acid at the anode has properties differing from those of the acetic acid in the solution which is not oxidised to ethane and carbon dioxide.[12] The electrolysis of concentrated acetic acid solutions, containing small quantities of sulphuric acid, shows clearly that the ethane reaction does not take place when oxygen evolution is increased.[13]

It remains now to dispose of certain criticisms which have been made of the discharged ion theory, since they have been repeated several times;

[7] Wieland and Fischer, *Ann.*, **446**, 60, 1925.
[8] Fichter, *J. Amer. Electrochem. Soc.*, 274, 1929.
[9] Fichter, *J. Chim. Physique*, **23**, 494, 1926.
[10] Fichter, *Helv. Chim. Act.*, **9**, 697, 1926.
[11] Preuner and Ludlam, *Z. physikal. Chem.*, **59**, 682, 1907.
[12] Fairweather and Walker, *loc. cit.*, 3119.
[13] See also Schall and Thieme-Wiedtmarckter, *Z. Elektrochem.*, **35**, 343, 1929.

quite recently again by Fichter.[1] It is maintained that, if this theory is correct, we should expect Kolbe's reaction to take place the more readily the greater the dissociation of the salt used, whereas experiments show that salts of the strong sulpho-aliphatic acids do not give a Kolbe synthesis. Moreover, a solution of a benzoate which contains benzoate ions does not give diphenyl on being electrolysed. It must be remembered that the concentration of the discharged ions at the anode is the predominant factor, and only to a lesser extent is the result due to the concentration of the undischarged ions in the solution, in so far as they affect the composition of the electrolyte. Further, the failure to find any representative of the aromatic series of acids which would undergo a Kolbe reaction in an aqueous solution of its salts, does not mean that the anions of such acids are not discharged at the anode, as is implied by Fichter. It is obvious that the discharge of an anion is not necessarily followed by reaction to give the Kolbe synthesis. The discharged anions can react in several ways, *e.g.* with one another, with the solvent or with substances in solution; the particular way in which they will react will depend on a large number of factors, *e.g.* their concentration at the anode, their chemical nature, the concentration of the solution, temperature, nature of anode, etc. The fact that the Kolbe synthesis is far from being general is not surprising, and constitutes no argument against the discharged ion theory.

Another argument given several times by Fichter[1] against the discharged ion theory is that "one molecule of propionate, or one anion of propionic acid, requires sometimes one and sometimes two electric units for its discharge." This statement is quite wrong. It is obvious that one gram-ion of a monobasic acid like acetic or propionic acid always requires one Faraday for its discharge. It is stated that a propionate in yielding ethylene apparently consumes two Faradays per molecule, whereas an acetate in yielding ethane consumes only one, but this is due to the fact that the equation

$$2CH_3 . CH_2 . COO' + 2F = CH_2 : CH_2 + CO_2 + CH_3CH_2COOH \quad (3$$

is expressed incorrectly, as follows

$$CH_3 . CH_2 . COO' + 2F = CH_2 : CH_2 + CO_2 + H \quad . \quad (4$$

"Equation" (4) naturally gives a surplus of 1 Faraday on the left-hand side because it has been obtained by subtracting CH_3CH_2COO' from the left-hand side of equation (3) and only CH_3CH_2COO from the right-hand side. This is equivalent to saying that the equation $2OH' + 2F = HOH + O$ can be written $OH' + 2F = H + O$.

Summary.

(1) It has been shown that under certain conditions methane is present along with ethane amongst the anode gases produced during the electrolysis of aqueous potassium acetate solutions.

(2) The conditions favourable to the formation of methane appear to be low current density and high concentration of the electrolyte.

(3) The mechanism of Kolbe's electrosynthesis and the recent work of Fichter are discussed.

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A. 4.

THE ANALYSIS OF MIXTURES OF HYDROGEN, METHANE, AND ETHANE.

BY

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AND

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XLVIII.—*The Analysis of Mixtures of Hydrogen, Methane, and Ethane.*

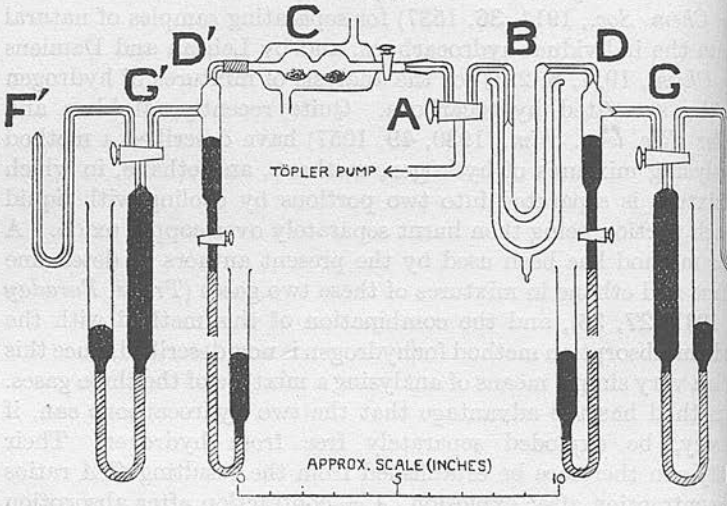
By Oswald James Walker and Soorya Narayan Shukla.

The principle of analysing gaseous mixtures by fractional distillation at low temperatures was applied by Burrell and Seibert (*J. Amer. Chem. Soc.*, 1914, **36**, 1537) for separating samples of natural gas into the individual hydrocarbons, and by Lebeau and Damiens (*Ann. Chim.*, 1917, **8**, 221) for the analysis of mixtures of hydrogen with the saturated hydrocarbons. Quite recently, Mulders and Scheffer (*Rec. trav. chim.*, 1930, **49**, 1057) have described a method of analysing mixtures of hydrogen, methane, and ethane, in which the mixture is separated into two portions by cooling with liquid air, each portion being then burnt separately over copper oxide. A similar method has been used by the present authors to determine methane and ethane in mixtures of these two gases (*Trans. Faraday Soc.*, 1931, **27**, 35), and the combination of this method with the palladium-absorption method for hydrogen is now described, since this affords a very simple means of analysing a mixture of the three gases. The method has the advantage that the two hydrocarbons can, if necessary, be exploded separately free from hydrogen. Their identity can therefore be established from the resulting C/A ratios (C = contraction after explosion, A = contraction after absorption by caustic potash), a point of special importance when unknown mixtures which may contain one or both of these hydrocarbons are being analysed. Moreover, the analyses to be described have been carried out on fairly small amounts of the mixture—about 5—10 c.c. in most cases—and are as accurate as those of Mulders and Scheffer, who used a total volume of some 30—40 c.c. for each analysis. The actual measurements of the quantities of gas before and after the various operations were made in a Bone and Wheeler apparatus of the usual type, in which the pressure of the gas at constant volume is observed, and the gas sample was transferred to and from the separation apparatus by means of small tubes inverted over mercury in a crucible.

Apparatus.—The form of separation apparatus is shown in Fig. 1. It consists of a Töpler pump connected by means of the three-way

stopcock A to (1) the U-tube B, which can be cooled by imme of the h in a vacuum vessel containing liquid air, for removal of the et contract and (2) the palladium bulbs C, containing 2—3 g. of "oxid Scheffer palladium sponge for removal of the hydrogen. The tubes B amounts C are connected respectively to the mercury traps D and D' work to transferring pipettes G and G', and the bent capillary tubes F a uite a dipping into mercury troughs. The hydrogen-absorption appa robably is similar to that described by Grice and Payman (*Fuel*, 192 nd the 236), but improved by the introduction of the mercury trap a or a sec the use of the steam-jacket for heating to 100°. The activity o The p palladium is renewed from time to time by heating in a cruci passed t contact with air. A ground-glass joint was originally used in nto C th

FIG. 1.



of the rubber connexion between C and D', but the latter, if ut the waxed, is just as satisfactory and renders the apparatus less his is n ceptible to strain. The rubber tubing between the mercury f the re and their reservoirs should, of course, be long enough to allo e essen the mercury level in the trap being adjusted when the apparat ubject evacuated. f the th

Analysis of a Mixture containing Hydrogen, Methane, and Eth nd me After being measured in the Bone and Wheeler burette, the tituent sample is transferred (*via* the small inverted tube) through F t % of t transferring pipette G. The apparatus is evacuated by mea mounts the pump through A as far as the stop-cock of G, and the U then immersed in liquid air by raising the Dewar vessel. A is closed, and the sample transferred to B. After 5 mins., conne is made to the pump again, and the uncondensed portion, consi

THE S
INO

C_2

Taken.
14·2
45·6
17·3
10·6
41·3
40·4
29·2

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the fi

of the hydrogen and the methane, pumped off and measured. The contraction gives the amount of ethane in the sample. Mulders and Scheffer (*loc. cit.*) noted that the condensed portions contained small amounts of dissolved methane, and found it necessary for exact work to carry out a second fractionation. We find, however, that quite accurate results can be obtained with one fractionation, probably owing to the use of smaller amounts of the gaseous mixture, and the increase in accuracy does not justify the extra time required for a second fractionation.

The palladium tube is then evacuated as far as G′, and steam passed through the jacket of the tube C. The sample is introduced into C through F′ and G′, as in the former case, and allowed to remain in contact with the palladium at 100° for 15—20 mins. The steam is then replaced by cold water, and when the tube C is cold, the residual methane can be pumped off and measured. The difference between this reading and the previous one gives the amount of hydrogen. The amounts of the three constituents in the mixture can thus be determined by means of two simple operations : a complete analysis can be carried through after a little practice in 1½ hours. The following table shows the type of result obtainable. The mixtures were made up from the pure constituents. As a check,

C_2H_6, %.		H_2, %.		CH_4, %.	
Taken.	Found.	Taken.	Found.	Taken.	Found.
14·2	14·2	53·9	52·6	31·9	33·2
45·6	45·7, 46·1, 44·9	31·4	30·5, 31·3, 31·5	22·9	23·8, 22·6, 23·6
17·3	17·3, 17·1, 17·4	64·0	63·0, 63·6, 63·1	18·7	19·7, 19·3, 19·5
10·6	10·5	39·0	38·9	50·4	50·6
41·3	41·2, 41·8	40·0	40·4, 40·1	18·7	18·4, 18·1
40·4	39·7	42·2	42·6	17·4	17·7
29·2	29·5	54·4	53·6	16·4	16·9

The residual methane can be exploded, and the ethane condensed in the first stage can also be pumped off and exploded separately, but the results show that for ordinary accuracy and rapid working this is not necessary. In presence of nitrogen, however, explosion of the residual gas after the removal of ethane and hydrogen would be essential. Since the methane is determined by difference, it is subject to the largest error, the mean errors in the determination of the three constituents being : Ethane $\pm$ 0·8%, hydrogen $\pm$ 1·1%, and methane $\pm$ 2·6%. The percentage by volume of any constituent seldom differs from the calculated percentage by more than 1% of the total mixture, which is satisfactory in view of the small amounts of the gas used.

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A.5.

ANODE PHENOMENA IN THE ELECTROLYSIS OF POTASSIUM ACETATE SOLUTIONS. PART II. DISCHARGE POTENTIAL OF THE ACETATE ION

BY

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AND

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By Soorya N. Shukla and Oswald J. Walker.

Received 13th July, 1931.

In 1898 Bose [1] found that the decomposition potential of a 3·5 *N* aqueous solution of potassium acetate between smooth platinum electrodes was 2·05 volts. Preuner and Ludlam [2] measured the potential difference at a platinum anode during the electrolysis of a 0·5 *N* solution of potassium acetate (0·5 *N* also with respect to added acetic acid), and found a break in the current-potential curve not at 2·05 volts but at 2·54 volts. They also showed that at this potential ethane began to be evolved amongst the anodic gases, while the percentage of oxygen began to diminish. Fairweather and Walker [3] confirmed the existence of a definite potential for the formation of ethane in the electrolysis of a *N* solution of potassium acetate, but found the value to be about 2·15 volts. It has been generally assumed that Preuner and Ludlam's potential of 2·54 volts represents the "discharge potential" of the acetate ion at a smooth platinum electrode, though it has been pointed out by Gibson [4] that the evolution of ethane at this potential might also mean that at 2·54 volts the anode has acquired an oxidising potential high enough to allow the reaction to proceed. It is possible, however, to ascribe the evolution of oxygen below this potential to the primary discharge of acetanions followed by a secondary reaction of the discharged ions with water. For the present, therefore, we shall refer to this "discharge potential" as the "critical" potential for the formation of ethane, without making any assumptions as to its actual meaning.

Preuner and Ludlam's value, while it has been generally accepted as being correct, is much higher than that of other investigators, and makes the "discharge" potential of the acetate ion abnormally high in comparison with that of other anions. It was decided to make a more detailed study of the effect of concentration of acetate and of temperature on the value of the potential. Moreover, it was shown recently by the present authors [5] that at low-current densities methane is also evolved along with ethane at the anode, and in investigating the conditions most favourable for the formation of methane the effect of varying anode potential is also of interest. The objects of this investigation were therefore :—

(1) To determine the "critical" potential for the formation of ethane during the electrolysis of aqueous potassium acetate solutions of varying concentration and at different temperatures.

(2) To see whether this potential is also a critical potential for the formation of methane which takes place along with that of ethane.

The determination of the critical potential was carried out by two methods, following the procedure of Preuner and Ludlam. Firstly measurements were made of the current strength and of the anode potential during the electrolysis, and the resulting values plotted on

[1] Bose, *Electrochem.*, 5, 153, 1898. [2] *Z. physikal. Chem.*, 59, 682, 1907.
[3] *J.C.S.*, 3111, 1926; see also Walker, *J.C.S.*, 2040, 1928 (footnote).
[4] *Proc. Roy. Soc., Edin.*, 44, 140, 1924; see also *J.C.S.*, **127**, 475, 1925.
[5] *Trans. Far. Soc.*, **27**, 35, 1931, referred to in text as Part I.

current density-anode potential graph. The critical potential is indicated by a break or point of inflexion on the curve. Secondly, samples of the anode gases were collected at different anode potentials and the particular potential found at which ethane is first evolved. In many cases the gas samples were obtained during electrolyses in which the anode potential was measured directly as in the first method, but it was found to be more convenient, when the relationship between current density and anode potential had been determined for a given concentration of electrolyte, simply to collect the gas at a definite current density, from which the anode potential could be obtained. The values of critical potential found by both of these ways coincided in nearly every case, and this can be taken therefore as a good example of a case where a break in the current potential curve does mark the commencement of a new reaction at the anode. As will be seen from the current density-anode potential curves, and more readily from the log *C.D.*—anode potential curves, the break in the curve does not consist of a sudden sharp rise in the current density at a given potential, but rather of a small region in which the rate of increase of anode potential with current density becomes more rapid.

Experimental.

Apparatus.—The electrolyses were carried out in an H-shaped glass vessel, similar to that described by Gibson, in which the anode and cathode gases were collected in different compartments separated from one another by a thick plug of glass-wool. The anode consisted of a smooth platinum wire, 4·4 cm. long and 0·1 cm. in diameter, and the cathode was a thin foil of platinum of 2 sq. cm. surface area. A glass tube containing the same solution as the electrolysis vessel was pressed close up to the wire anode and connected through a solution of normal KCl to a normal calomel electrode, so that measurements were made of the *P.D.* of the cell

$$+ \text{Pt.} \mid CH_3COOK \text{ sol.} \mid N\,KCl \mid HgCl_2,\ N\,KCl \mid Hg -$$

of which the mercury is the negative electrode. By adding 0·283 volts, the potential difference between the anode and the solution (the anode potential, *A.P.*) on the hydrogen scale is obtained. All the values in the tables refer to this scale. No correction was made for liquid junction potentials, which are of the order of 0·01 volts when calculated by the formula of Lewis and Sargent.

A variable E.M.F. was applied across the terminals of the electrolysis vessel and successive readings of the polarising current and anode potential taken, time being allowed for these to become constant after every increase of the applied E.M.F. In the preliminary experiments the solution was stirred during the anode potential measurements, but it was found that sufficiently reproducible results could be obtained with the stirring produced by the gases evolved—additional stirring simply has the effect of slightly lowering the anode potential for a given current density. The first measurements were carried out at room temperature, which varied throughout the course of the whole work between 10° and 20° C., but was fairly constant during any single experiment. However, in order to obtain more uniform curves and in order to study the effect of temperature variation, measurements were also made in which the electrolysis vessel was placed in a thermostat at temperatures of 5° ± 1°; 20° ± 0·1°; 35° ± 0·1° and 50 ±0·1° respectively. Except where otherwise stated the solutions of potassium acetate contained an equivalent amount of added acetic acid to prevent the solution becoming alkaline during the course of the electrolysis.

Relation between Current Density and Anode Potential.

The values of current density and anode potential for solutions of potassium acetate of various concentrations at room temperature are plotted in Fig. 1. From these it will be seen that the current begins to rise rapidly at potentials between 2·0 and 2·3 volts and that on the whole the steepness of the curves decreases with increasing concentration of the electrolyte. In the case of the $N/5$ solution there is a noticeable break or point of inflexion in the curve at about 2·2 volts, which is not very apparent on the other curves. If, however, the log of current density is plotted against the *A.P.* as has been done in Fig. 1*a*, the existence of a change in the slope of the straight line at about 2·15 volts is noticeable in almost every case. These

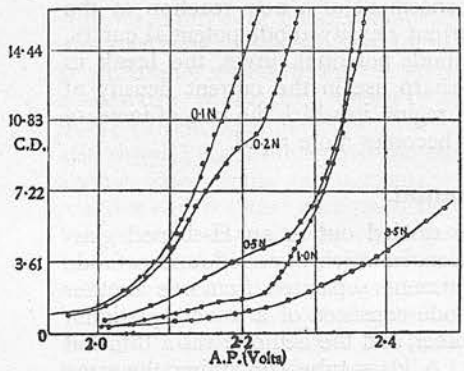


FIG. 1.

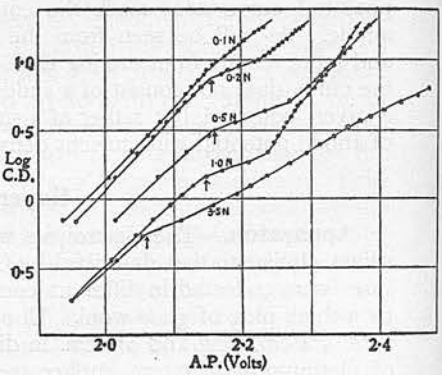


FIG. 1A.

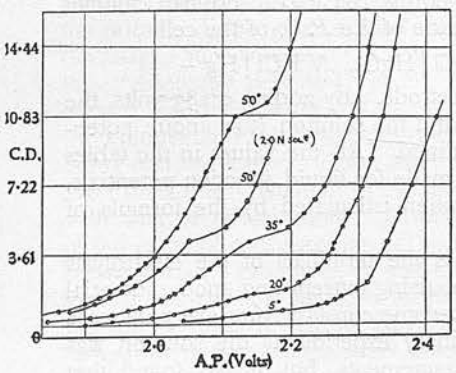


FIG. 2.

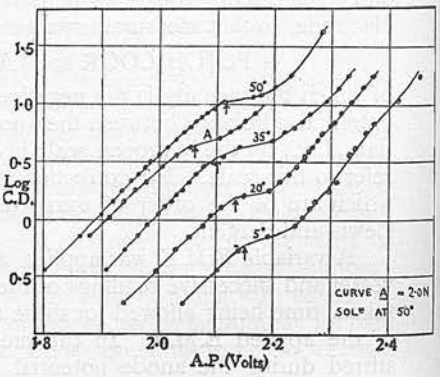


FIG. 2A.

experiments were performed at room temperature and not at a definite constant temperature. In the curves obtained from the experiments carried out in the thermostat, the existence of a break at 2·1-2·2 volts is very marked, as will be seen from Fig. 2 and particularly from Fig. 2*a*, in which the values for N potassium acetate at various constant temperatures are plotted. They contain also the curves for the $2N$ solution at 50°. The breaks in the logarithmic curves consist of a decrease in the slope of the straight line within a small range of anode potential, the slope then resuming its original value. Within this small potential range the anode potential increases much more rapidly with increasing current density. Up to the

critical potential, *i.e.*, the potential at which the slope of the logarithmic curve changes, the relationship between the current density I and anode potential P is of the form,

$$P = a + b \log (I + c),$$

where a, b, and c are constants. Logarithmic relationships of this type have been found to hold for the evolution of hydrogen at certain cathodes and of oxygen at platinum anodes.[6] For two cases in which a large series of

TABLE I.

Conc. of Electrolyte.	Temp. °C.	Current Density Millamp. (per sq. cm.).	Anode Potential (volts).	Percentage of				Ratio $\frac{CH_4}{C_2H_6}$.
				CO_2.	O_2.	CH_4.	C_2H_6.	
0·2 *N*	10-20	3·61	2·09	2·5	93·5	0	0	—
		4·33	2·11	2·8	92·4	0	0	—
		5·05	2·12	33·7	41·0	2·6	15·9	0·16
		5·78	2·13	50·5	12·5	3·0	27·8	0·11
		7·22	2·15	49·2	4·3	3·3	36·8	0·09
1·0 *N*	5	0·72	2·19	16·3	72·4	0	0	—
		0·90	2·24	47·5	4·2	11·5	31·1	0·37
		1·26	2·26	56·9	1·3	6·4	31·3	0·21
		1·81	2·30	58·5	1·4	6·4	30·0	0·21
		3·61	2·33	55·8	1·2	3·5	34·9	0·10
1·0 *N*	20	1·44	2·13	20·0	70·0	0	0	—
		1·81	2·19	53·6	5·8	14·5	19·3	0·75
		3·61	2·25	53·3	1·7	5·2	35·7	0·15
1·0 *N*	35	1·81	2·04	13·8	80·7	0	0	—
		3·61	2·11	40·5	53·1	0	0	—
		5·05	2·20	57·9	7·4	8·3	17·6	0·47
1·0 *N*	50	10·82	2·12	32·7	55·8	0	0	—
		11·55	2·16	73·8	2·1	6·2	13·6	0·45
		18·05	2·23	75·4	1·5	3·7	14·1	0·26
2·0 *N*	50	1·44	1·94	27·9	65·4	0	0	—
		3·61	2·03	57·0	37·2	0	0	—
		5·05	2·11	74·0	2·1	8·3	11·8	0·70
		7·22	2·15	74·1	1·4	8·4	12·6	0·66
3·5 *N*	20	0·18	1·98	40·5	42·6	0	0	—
		0·36	2·04	46·1	1·5	32·8	9·3	3·53
		1·44	2·22	61·8	1·1	23·5	8·6	2·74
3·5 *N*	50	0·72	1·89	62·9	32·3	0	0	—
		1·44	1·95	68·9	23·3	0	0	—
		1·81	1·98	80·2	1·3	10·0	5·7	1·77

measurements are available in the region of *C.D.*, during which oxygen is evolved, *viz.* (1) for the *N*/10 solution at room temperature and (2) for the *N* solution at 50° the relationship holds almost exactly. The actual values of a, b, and c in these two cases are: (1) 1·922, 0·217, and 0·460, and (2) 1·870, 0·223, and 0·121, respectively. The maximum difference between observed and calculated values of the anode potential is 0·01 volt, but the difference is in general very much less, about 0·002-0·005 volt.

[6] Glasstone, "The Electrochemistry of Solutions," page 381, 1931.

The values of the critical potential to the nearest 0·01 volt determined as the potential in the log *C.D./A.P.* curve at which the slope of the line changes, have been tabulated in Table II. These potentials are indicated

TABLE Ia.

Conc. of Electrolyte.	Current Density Milliamp. (per sq. cm.).	Anode Potential (Volts).	Percentage of		Ratio CH_4/C_2H_6.
			CH_4.	C_2H_6.	
0·5 *N* (room temp.)	2·88	2·15	0	0	—
	3·61	2·19	0	0	—
	4·33	2·23	9·0	34·2	0·26
	5·05	2·27	7·7	35·9	0·22
1·0 *N* (room temp.)	0·72	2·07	0	0	—
	1·44	2·15	0	0	—
	2·17	2·23	17·7	23·6	0·75
	3·61	2·26	7·7	32·9	0·23

on the curves by an arrow. In the case of the 3·5 *N* solution at 20° and 50° there was no definite critical potential on the curve. Before comparing these results with those obtained by the gas analysis method, the details of the latter method will be described.

Relation between Anode Potential and Composition of Anode Gases.

Samples of the gas evolved at the anode while the anode potential was kept constant at various values on either side of the critical potential were analysed for the following constituents: carbon dioxide, oxygen, carbon

TABLE II.

Concentration of Electrolyte.	Temperature °C.	Critical Potentials.	
		Graphical Method.	Gas Analysis Method.
0·2 *N*	About 20	2·16	2·11
0·5 *N*	,,	2·16	2·21
1·0 *N*	,,	2·15	2·19
3·5 *N*	,,	2·06	—
1·0 *N*	5	2·15	2·21
,,	20	2·13	2·16
,,	35	2·10	2·16
,,	50	2·12	2·14
2·0 *N*	50	2·07	2·07
3·5 *N*	20	—	2·01
,,	50	—	1·96
	Average	2·12	2·16 (neglecting last two values)

monoxide, methane and ethane. The analyses were carried out by means of a Bone and Wheeler apparatus with mercury as the confining liquid, and the separation of methane from ethane was effected by means of liquid

air as already described by us.[7] The results of various experiments are shown in Table I., in which, to save space, only the percentages of carbon dioxide, oxygen, ethane and methane are given, since they illustrate the course of the main anodic reactions. The residue consisted of small amounts of carbon monoxide and of nitrogen from dissolved air. Table IA. contains some of the results of the previous paper (Part I.), for which anode potential measurements are now available, and therefore only the percentages of ethane and methane are reproduced.

From the results of Tables I. and IA. the critical potential, *i.e.*, the potential at which evolution of ethane commences, has been calculated and the values are tabulated, along with the values obtained by the graphical method, in Table II. The critical potential has been taken as the mean of the last measured potential at which no ethane is evolved and the first measured potential at which ethane is formed, *e.g.*, in the case of the N solution at 20° no ethane is evolved at 2·13 volts, and 19·3 per cent. of ethane was found at 2·19 volts. The evolution of ethane must commence somewhere between these two potentials and therefore the mean of the two values, *viz.* 2·16 volts may be taken as the most accurate value of the critical potential.

Critical Potential for the Formation of Ethane.

In Table II. the values of the critical potential determined by the two methods are compared. It will be seen that the values obtained by both methods agree very well and that for very widely differing conditions of temperature and concentration of acetate there is very little variation in the potential at which ethane commences to be formed. The average value is 2·14 volts and is therefore considerably lower than Preuner and Ludlam's value of 2·54 volts. The variation from the mean value is seldom as large as 0·1 volt. Preuner and Ludlam, using the Nernst logarithmic expression, calculated the potential for a solution normal with respect to acetate ions, from their value of 2·54 volts obtained with a solution half normal with respect to both acetate and acetic acid, and obtained a value of 2·26 volts. From our results it is seen that in the concentration range 0·2 to 2·0 N there is very little variation in the critical potential. If this potential be assumed to be the discharge potential of the acetanions and to follow the Nernst concentration expression, no appreciable variation within this range is to be expected since a tenfold increase in the concentration, even assuming complete dissociation of the acetate, will decrease the discharge potential by about 0·06 volt only. With concentrations from 2·0 N upwards, however, there does appear to be a definite decrease of the potential, in agreement with the results of Fairweather and Walker,[3] who found that for 3, 4 and 5 normal solutions ethane formation takes place at lower anode potentials the more concentrated the solution. It is also seen that variation of the temperature does not greatly influence the potential at which evolution of ethane commences. As the temperature is increased, there is a small lowering of the critical potential, which is more marked in the more concentrated solutions.

Interpretation of the Critical Potential.

It has thus been established that at a smooth platinum anode a break in the current potential curve and the commencement of ethane evolution both occur at a potential of 2·14 volts, and that this potential is only

[7] Walker and Shukla, *J.C.S.*, 368, 1931; see also Part I.

slightly influenced by the temperature and by the concentration of acetate in the solution. At this anode potential a new reaction evidently begins to take place and the potential may be explained in three ways:

(1) Potential at which the reaction,

$$2CH_3COOH + O = C_2H_6 + 2CO_2 + H_2O \quad . \quad . \quad (1)$$

commences.

(2) Discharge potential of the acetanions.

(3) Potential at which discharged acetate ions cease to react with water and commence to react with one another.

The first interpretation has generally been favoured by the supporters of the oxidation theory of Kolbe's reaction, but this view is in our opinion open to certain objections (see Part I.). Preuner and Ludlam adopted the second view and considered it to be evidence for the discharged anion theory that evolution of ethane does not commence till a definite potential is reached. Their value of 2·54 volts has been generally given in the literature and text-books as the discharge or decomposition potential of the acetate ion. If this view is correct the evolution of oxygen below the critical potential must be ascribed to the discharge of hydroxyl or oxygen ions. There is, however, no conclusive evidence for this assumption, which is also open to criticism (see Part I.), and it seems just as probable that below the critical potential acetate ions are being discharged, and that the change in the anode reaction consists merely in the change from

$$2CH_3COO + H_2O = 2CH_3COOH + O \quad . \quad . \quad (2)$$

to

$$2CH_3COO = C_2H_6 + 2CO_2 \quad . \quad . \quad . \quad (3)$$

In fact the nature of the break in the current-potential curve might be taken to support this view, since it does not consist of a sudden rise in the current such as occurs in the discharge of a new ion species at a definite potential, *e.g.* in the cathodic discharge of metallic ions. A definite decision as to the meaning of the critical potential is not possible, however, and all one can say is that at that potential, whether it is a true discharge potential or not, a new reaction occurs. The results described do show, however, that the primary factor in determining the commencement of the anodic process is the anode potential, and not the particular value of the current density which is only of secondary importance. For example in the concentration range 0·2 to 2·0 *N* between 5° and 50° ethane evolution may commence at current densities between 0·9 and 11·6 milliamperes per sq. cm., depending on the particular conditions, whereas the anode potential at which the ethane reaction begins is constant at about 2·14 volts. It is possible that the anode potential corresponds to a definite concentration of discharged ions at the anode surface, and that not until this concentration of discharged ions is reached can they react together to form ethane. A large concentration of acetate in the solution, and low temperature both favour the formation of ethane, and that is because both these factors have the effect of increasing the anode potential for a given current density. Increase in current density after the critical potential has been reached will still further increase the anode potential and therefore increase the yield of ethane (*cf.* Fairweather and Walker, *loc. cit.*[3], page 3114).

Formation of Methane.

So far only the formation of ethane has been considered, but the experiments described in this paper also provide further information re-

garding the production of methane. The most convenient method of comparing the various experiments is to examine the ratio of methane to ethane. The results of Table I. confirm the observations previously made that the first appearance of methane in the anode gases occurs along with that of ethane, and it may now be said that both these hydrocarbons commence to be formed at the same critical potential of 2·14 volts, at which the amount of oxygen evolved drops to a small percentage. Whereas, however, the amount of ethane formed above this anode potential increases with increasing current density until it reaches a maximum value of about 90 per cent. of that theoretically possible,[3] the amount of methane appears to be at a maximum at the point where it is first formed and rapidly decreases with increasing current density, as is clearly seen from Tables I. and Ia. In the results given in Part I.,[5] the highest value of the methane/ethane ratio was 1·89. In the further experiments of Table I. values as high as 3·5 have been obtained. The following series of electrolyses at low current densities of a 3·5 *N* solution at about 10° illustrate even more clearly the decrease of the CH_4/C_2H_6 ratio with increasing current density (Table III.).

TABLE III.

Conc. of Electrolyte.	Current Density in (Milliamp. per sq. cm.).	Percentage of.				Ratio CH_4/C_2H_6.
		CO_2.	O_2.	CH_4.	C_2H_6.	
3·5 *N* (about 10° C)	0·18	35·6	1·2	41·5	9·8	4·3
	0·29	33·8	2·6	46·1	9·4	4·9
	0·72	55·0	0·5	32·2	7·9	4·1
	1·44	53·0	0·8	29·8	9·9	3·0
	2·17	73·0	0·2	15·8	8·6	1·84
	3·61	66·9	0·9	16·8	11·5	1·45
	7·22	70·0	0·7	4·1	21·1	0·19
	10·82	64·7	1·8	2·2	27·6	0·08
9·9 *N* (about 10° C)	0·72	0	1·5	65·8	22·0	2·99
	1·81	0·3	0	12·3	79·2	0·16

In order to see whether the ratio methane/ethane could be still further increased by increasing the acetate concentration a 9·9 *N* solution of potassium acetate (without added acetic acid) was electrolysed using a large platinum foil anode (14 sq. cm. surface area, waxed on one side) so that even smaller current densities might be used. The results are given in Table III. At a current density of 0·07 milliamps. per sq. cm. only three times as much methane as ethane was obtained, but the solution was appreciably alkaline through hydrolysis in this case, as is seen from the absence of carbon dioxide. It appears, therefore, from all the experiments made that the ratio methane/ethane has a maximum value at the critical potential, the maximum being greater the higher the concentration of the solution. The effect of acetate concentration is best seen by comparing values of the ratio taken from Table I. at the lowest current density in each case at which hydrocarbons are formed, *i.e.*, at a potential just slightly higher than the critical potential:

Conc. of sol.	0·2 *N*	0·5 *N*	1·0 *N*	3·5 *N*
A.P.	2·116	2·19-2·23	2·23	2·04
CH_4/C_2H_6	0·16	0·41-0·26	0·75	3·5-4·9

Conclusion and Summary.

The conditions for the formation of ethane and methane at a smooth platinum anode during the electrolysis of aqueous potassium acetate solutions have been more closely defined as a result of the experiments described in this paper. The results may be summarised as follows :—

(1) Below an anode potential of 2·14 volts oxygen and carbon dioxide are the main gaseous products, and no hydrocarbons are evolved.

(2) At the critical potential of 2·14 volts methane and ethane commence to be formed along with a larger amount of carbon dioxide, and the proportion of oxygen begins to decrease rapidly. There is not sufficient evidence to show whether this critical potential represents a true discharge potential of the acetanion.

(3) For concentrations of acetate below 2·0 *N* the critical potential is independent of concentration, but with more concentrated solutions the value decreases. The critical potential decreases slightly with increase of temperature.

(4) At the critical potential the ratio methane to ethane is at a maximum, and then decreases rapidly with increasing current density, so that methane is formed only within a limited range of current density. The maximum value of methane/ethane increases with the concentration of acetate. With a 3·5 *N* solution under the most favourable conditions a value of nearly 5 : 1 was obtained.

Of particular interest is the question of how the methane is formed. Certain possibilities were indicated in Part I., but a more detailed discussion of the problem will be held over until the conclusion of some further experiments now in progress on the influence of dissolved substances and of the solvent on the formation of methane.

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A.6.

ANODE PHENOMENA IN THE ELECTROLYSIS OF POTASSIUM ACETATE. PART III. FORMATION OF METHANE

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ANODE PHENOMENA IN THE ELECTROLYSIS OF POTASSIUM ACETATE. PART III. FORMATION OF METHANE.

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It has recently been shown that under certain conditions appreciable quantities of methane are formed at a smooth platinum anode during the electrolysis of aqueous potassium acetate solutions, and that the conditions favourable for the formation of that hydrocarbon appear to be low current density and high concentration of acetate.[1] In a further investigation of the conditions favourable for methane formation the effect of (1) the nature of the solvent, and of (2) the nature of the anode material has been examined. Some further experiments on the electrolysis of aqueous solutions with a smooth platinum anode are also described.

Electrolysis of Potassium Acetate in Non-Aqueous Solvents.

When solutions of potassium acetate in methyl alcohol, in ethyl alcohol and in acetic acid are electrolysed at ordinary current densities the current efficiency for the Kolbe reaction by which ethane is formed may become as high as 95-97 per cent.[2] Solutions of potassium acetate in these solvents were electrolysed at low current densities in order to see whether methane could be obtained under these conditions.

The electrolyses were carried out in an H-shaped glass vessel at 20° C. as before, but since organic solvents were to be used, all rubber connections and stoppers were replaced by glass joints. The solvents were purified and dried, and a 10 per cent. by weight solution of potassium acetate made up and refluxed to get rid of dissolved air. The access of

[1] *Trans. Far. Soc.*, **27**, 35 and 722, 1931; referred to as Parts I. and II.
[2] Salauze, *Bull. Soc. Chim.*, **37**, 522, 1925.

air to the solution during the electrolysis was prevented as far as possible. The anode was a smooth platinum wire of 1·38 sq. cm. surface area, and the cathode a smooth platinum foil. Collection of the anode gases was started when the current had reached a steady value, and the mixture was analysed as described previously. A series of electrolyses of a 10 per cent. aqueous solution of potassium acetate (containing an equivalent amount of added acetic acid) were carried out in the same vessel, and under similar conditions in order to provide more comparable data.

The results are given in Table I. in the last column of which the values of the ratio CH_4/C_2H_6 are shown. It will be seen that in all cases considerable amounts of methane are formed at low-current densities, and that the ratio of methane to ethane decreases with increasing *C.D.* Qualitatively, and in a rough quantitative manner also, the composition of the anode gases obtained from aqueous and non-aqueous solutions is the same. In the case of acetic acid as solvent a N solution of the acetate was electrolysed at lower *C.D.*, using a large

TABLE I.

Solvent.	*C.D.* milli-amp./ cm².	Percentage Composition of Anode Gas.						Ratio CH_4/C_2H_6.
		CO_2.	O_2.	CO.	C_2H_6.	CH_4.	Residue.	
CH_3COOH	0·72	59·5	0·5	1·2	32·1	4·7	2·0	0·15
	2·17	61·0	0·7	1·1	33·2	2·6	1·4	0·08
	3·61	61·9	0·7	1·4	33·3	1·7	1·0	0·04
	5·78	59·6	0·4	1·2	35·8	1·8	1·2	0·05
	7·22	59·2	0·6	0·8	36·5	1·4	1·5	0·04
	10·82	58·9	0·7	1·0	36·5	1·6	1·3	0·04
CH_3OH	0·72	41·8	1·1	2·0	31·1	14·3	9·7	0·46
	2·17	57·7	1·4	1·4	35·1	2·4	2·0	0·07
	3·61	59·5	0·6	0·9	34·5	2·6	1·9	0·08
	5·78	60·4	0·4	0·9	35·4	1·7	1·2	0·05
	7·22	58·3	0·3	1·0	37·1	1·8	1·5	0·05
	10·82	57·9	0·7	1·1	37·7	0·6	2·0	0·02
C_2H_5OH	0·72	51·3	0·8	1·1	25·6	18·9	2·3	0·74
	1·80	62·6	0·8	1·0	23·8	11·0	0·8	0·46
	2·17	57·5	0·5	1·2	29·1	10·7	1·0	0·37
	3·61	55·2	0·6	1·0	31·6	10·3	1·3	0·33
	5·78	54·8	0·8	1·1	35·6	6·1	1·3	0·17
	7·22	54·4	0·7	1·0	35·9	6·5	1·5	0·18
	10·82	56·6	1·4	1·4	34·4	4·2	2·0	0·12
H_2O	0·72	54·0	38·8	2·1	0	0	5·1	—
	1·08	52·4	43·3	2·9	0	0	1·4	—
	1·26	65·6	2·9	2·1	11·8	15·8	1·8	1·35
	1·30	71·5	1·2	1·9	12·2	12·5	0·5	1·03
	1·44	71·1	1·1	1·3	19·1	7·1	0·2	0·37
	2·17	70·0	0·7	1·0	23·7	4·3	0·3	0·18
	3·61	66·9	0·5	1·1	27·5	3·4	0·6	0·14
	5·78	66·6	0·6	1·1	28·5	2·5	0·7	0·09
	7·22	64·9	0·8	1·0	30·5	2·2	0·6	0·07
	10·82	57·3	0·7	0·9	38·0	2·0	1·1	0·05

foil anode (14 sq. cm. surface area), and the following values of the CH_4/C_2H_6 ratio were obtained :—

C.D.	0·036	0·071	0·19	0·36
CH_4/C_2H_6	3·33	1·43	0·84	0·69

These values are of the same order as those obtained with aqueous solutions.

In the case of the aqueous solutions the CH_4/C_2H_6 ratio affords a convenient measure of the extent to which these two hydrocarbons are formed under specified conditions, but in the non-aqueous solvents the composition of the anode gas will undoubtedly be affected by the increased solubility of methane and of ethane. Moreover, in the alcohols ethane is about five times more soluble than methane. In these cases, therefore, too much importance must not be attached to the actual values of the CH_4/C_2H_6 ratio.

It is of interest also to compare the current efficiency for the formation of methane with different solvents. In the following table the values of the CH_4/H_2 ratio, *i.e.*, the ratio of the volume of methane evolved at the anode to the volume of hydrogen evolved at the cathode, are compared for the region of *C.D.* in which the CH_4/C_2H_6 ratio varies rapidly during the electrolysis of 10 per cent. solutions of potassium acetate in (*a*) water, and (*b*) acetic acid. The corresponding values of the C_2H_6/H_2 ratio are also shown. The decrease in the CH_4/C_2H_6 ratio with increasing *C.D.* is due mainly to the increasing current efficiency for ethane formation.

TABLE II.

Solvent.	*C.D.* Milliamps./sq. cm.	CH_4/C_2H_6.	C_2H_6/H_2.	CH_4/H_2.
Water	1·26	1·35	0·068	0·092
	1·81	0·29	0·32	0·090
	3·61	0·13	0·60	0·075
Acetic acid	0·11	0·91	0·18	0·17
	0·21	0·52	0·37	0·19
	0·36	0·34	0·57	0·19
	0·71	0·27	0·23	0·061

Nature of the Anode Material.

The electrosynthesis of ethane from acetate in aqueous solution is dependent on the nature of the anode material. For example, ethane formation occurs readily at smooth platinum, iridium, and graphite electrodes, whereas at platinised platinum and gold anodes the gas evolved consists mainly of oxygen and carbon dioxide. In the non-aqueous solvents considered in the preceding section, however, the nature of the anode, provided it is not attacked, has much less influence than in aqueous solution,[3] *e.g.*, synthesis takes place readily at a gold anode in glacial acetic acid solution.

In the following experiments aqueous solutions of potassium acetate were electrolysed at 20° C. with anodes of iridium, graphite, and gold of surface area 1·38, 7·0, and 1·38 sq. cm., respectively. A 3·5 *N* solution was used, since with this solution the largest CH_4/C_2H_6 ratios were obtained with the smooth platinum anode.

With the gold anode no hydrocarbons were formed at any *C.D.* within the range employed, *viz.*, 0·72-700 milliamps/sq. cm. The anode gas consisted of oxygen with 20-40 per cent. of carbon dioxide. The anode is attacked, especially at the higher *C.D.* and the solution becomes dark-coloured by the dispersed gold.

[3] Fairweather and Walker, *J.C.S.*, 3118, 1926.

With the iridium and graphite anodes, however, the composition of the gas evolved is very similar to that obtained with a smooth platinum

TABLE III.

Current Density Milliamps./sq. cm.	Percentage Composition of Anode Gases.						Ratio. CH_4/C_2H_6.
	CO_2.	O_2.	CO.	C_2H_6.	CH_4.	Residue.	
Graphite anode							
0·71	78·0	0·5	1·4	5·4	13·9	0·8	2·57
1·43	77·1	0·6	1·0	5·3	15·4	0·6	2·89
2·14	73·7	0·5	0·9	6·2	18·5	0·2	2·97
3·57	69·1	0·4	0·7	9·2	20·6	0	2·23
5·71	68·5	0·4	0·9	11·4	18·5	0·3	1·63
7·14	65·5	0·5	1·3	18·7	13·8	0·2	0·74
17·9	70·0	0·5	1·7	23·8	3·5	0·5	0·15
Iridium anode							
0·65	35·5	1·2	1·5	35·5	24·3	2·0	0·68
0·72	53·5	0·8	1·3	32·2	11·5	0·7	0·36
1·44	60·5	0·5	1·0	32·5	4·6	0·7	0·14
2·16	60·7	0·5	0·9	33·7	3·4	0·8	0·10
3·61	59·6	0·5	1·1	35·7	2·2	0·9	0·06
7·22	61·3	0·3	0·9	35·3	1·5	0·7	0·04

anode, and at low *C.D.*'s quite appreciable amounts of methane are formed. The results of the gas analyses are given in Table III. By comparing these results with the corresponding data for a smooth platinum anode in Part II. (Table III.), it is seen that qualitatively all three electrodes behave in a similar manner. A quantitative comparison of the specific effect of different anodes on the methane reaction cannot be obtained simply from an inspection of the values of the CH_4/C_2H_6 ratio, since this ratio is dependent on the effect of the anode material on the ethane synthesis also. This can be done, however, by comparing the values of the CH_4/H_2 ratio, which affords a measure of the current efficiency for the formation of methane. In the following table the data for the electrolysis of the 3·5 *N* solution with platinum and iridium anodes are compared for the range of *C.D.* 0·72-7·2 milliamps./sq. cm.

TABLE IV.

C.D.	CH_4/H_2, Platinum.	CH_4/H_2, Iridium.
0·72	0·21	0·10
2·17	0·14	0·067
3·61	0·12	0·044
7·22	0·053	0·032

Within this range of *C.D.* the current efficiency for the formation of methane at a platinum anode is approximately double that at an iridium anode. In both cases, however, the amount of methane formed decreases with increasing *C.D.*

Variation of the Concentration of Free Acetic Acid.

In examining the effect of the concentration of acetate on the formation of methane during the electrolysis of aqueous solutions, an equivalent amount of acetic acid was added to the solution in order to keep it acid. The effect of varying the acidity of the solution by adding varying amounts of acetic acid or of potassium hydroxide to a solution which was kept 1·0 *N* throughout with respect to potassium acetate can be seen from the following table, in which the values of the CH_4/C_2H_6 ratio at approximately 2·1 and 3·6 milliamps./sq. cm. are compared :—

TABLE V.

Electrolyte.	CH_4/C_2H_6.	
	2·1 milliamps./sq. cm.	3·6 milliamps./sq. cm.
1·0 *N* CH_3COOK + 3·5 *N* CH_3COOH	0·21	0·11
,, + 1·0 *N* ,,	0·37	0·15
,, + 0·5 *N* ,,	0·34	0·14
,, + 0 ,,	0·49	0·18
,, + 0·1 *N* KOH	0·63	0·21
,, + 0·5 *N* ,,	—	—

The variation of the acetic acid concentration has only a small effect compared with that of varying the acetate concentration. The CH_4/C_2H_6 ratio tends to increase with decreasing acidity of the solution. If the latter is made not too strongly alkaline the ratio is still further increased, due to the Hofer and Moest reaction having commenced at the expense of the ethane synthesis. With 0·5 *N* KOH, however, no hydrocarbons are evolved.

Mechanism of Methane Formation.

It has been shown in this paper and the two preceding papers that methane may be formed at the anode during the electrolysis of potassium acetate solutions under very varying conditions when the anodic current density is low. The question naturally arises, What is the nature of the reaction by which this hydrocarbon is formed? It must be admitted that the experiments described so far do not provide any definite answer. Before a more detailed study has been made of the anode processes under the conditions most favourable for the formation of methane any suggestions regarding the mechanism of its formation must be somewhat speculative, and we do not propose, therefore, to enter into a detailed discussion of the possible reactions at this stage. There is, however, one possibility which deserves being mentioned, and which may form the basis of further investigation.

In the first place, it is necessary to emphasise again the almost general occurrence of methane as a decomposition product of acetic acid or of its salts and derivatives. In particular, mention must be made of two reactions in which both methane and ethane are formed, the proportions of the two hydrocarbons depending on the experimental conditions. Baur and Rebmann [4] showed that in the photolysis of acetic acid in

[4] *Helv. Chim. Act.*, **5**, 221, 1922.

presence of uranyl salts two distinct processes take place, *viz.*, (1) a photocatalytic decomposition of acetic acid into methane and carbon dioxide

$$CH_3COOH = CH_4 + CO_2 \quad . \quad . \quad . \quad . \quad (1)$$

and (2) an oxidation of the acetate ion into ethane and carbon dioxide. Gordon [5] found that when a solution containing sodium persulphate and acetic acid or sodium acetate is heated, a mixture of gases is evolved, consisting of carbon dioxide, methane and ethane, and that the formation of methane is favoured by a high concentration of sodium acetate. He also assumed a catalytic decomposition of acetic acid according to (1), accompanied by an oxidation to ethane and carbon dioxide. The catalytic decomposition of acetic acid into methane and carbon dioxide can also occur in other ways, *e.g.*, when acetic acid is passed over reduced nickel at 210°,[6] or over silica gel at 430-460°.[7] It is possible, therefore, that a reaction of this kind is taking place at the anode during the electrolysis of the acetate, *e.g.*, by the action of an acetate radical on a molecule of acetic acid, as follows

$$\overbrace{CH_3COOH + CH_3COO} = CH_3COO + CH_4 + CO_2.$$

The net result of this reaction is a decomposition of acetic acid as in (1). With increasing *C.D.* and consequent increase in the concentration of acetate radicals at the anode surface, the tendency for the reaction

$$2CH_3COO = C_2H_6 + 2CO_2$$

to occur increases, and therefore the ratio of methane to ethane decreases. At any rate, it does seem probable that methane is being formed by a very similar process in the electrolytic reaction and in the reactions described by Baur and by Gordon.

Summary

(1) Methane is formed at the anode during the electrolysis at low current densities of solutions of potassium acetate in acetic acid, in methyl alcohol, and in ethyl alcohol.

(2) In aqueous solution methane is also formed at anodes of iridium and of graphite.

In conclusion, one of us (S. N. S.) wishes to thank the Government of the United Provinces of Agra and Oudh, India, for a research scholarship during the tenure of which the work described in this and the two preceding papers has been done.

[5] *J. Physical Chem.*, **18**, 55, 1914.
[6] Sabatier and Senderens, *Ann. Chim.* [8], **4**, 476.
[7] Mitchell and Reid, *J. Amer. Chem. Soc.*, **53**, 338, 1931.

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A.7.

THE DECOMPOSITION OF ACETYL PEROXIDE

BY

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AND

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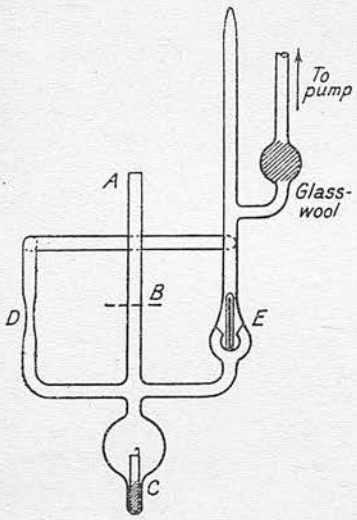
47. *The Decomposition of Acetyl Peroxide.*

By O. J. Walker and G. L. E. Wild.

In the discussion of the anode reactions taking place during the electrolysis of organic acids or their salts, the theory of the intermediate formation of peroxides and per-acids has played a prominent part, largely due to the work of Fichter and his co-workers. This theory (known as the " peroxide theory ") is based mainly on the qualitative similarity

between the products formed at the anode during the electrolysis of any given acid and the products of the thermal decomposition of the corresponding acyl peroxide or peracid. In many cases, however, the quantitative composition of the products is very different in the two processes. In particular, it has been shown (Walker, J., 1928, 2042) that the thermal decomposition of acetyl peroxide, both in the pure state and in solution, does not consist mainly of a reaction according to the simple equation $(CH_3{\cdot}CO{\cdot}O)_2 = 2CO_2 + C_2H_6$ (1); methane is always formed, and the only circumstances in which the peroxide breaks up with any approach to the stoicheiometric proportions of equation (1) appears to be when it is exposed at the ordinary temperature to ultra-violet light; *e.g.*, in one such experiment a $CO_2 : C_2H_6$ ratio of 2·9 : 1 was obtained (Walker, *loc. cit.*, p. 2044). A more detailed investigation of this reaction is being undertaken.

As regards the thermal decomposition, however, it still seems to be assumed by supporters of the peroxide theory that if acetyl peroxide could be made to decompose at a sufficiently low temperature it would break up more nearly in accord with equation (1). On the other hand, comparison of the results of the explosive decomposition (Fichter and Krummenacher, *Helv. Chim. Acta*, 1918, **1**, 152) with those of the above-mentioned experiments, which were carried out at about 80°, suggested that less ethane would be formed at even lower temperatures. Since no experimental evidence was available, the nature of the gaseous products obtained by heating liquid acetyl peroxide at temperatures between 30° and 90° was investigated, and the above deduction confirmed.



Experimental.

The white crystalline peroxide, prepared by Gambarjan's method (*Ber.*, 1909, **42**, 4010), was recrystallised from ether. As the peroxide vapour readily attacks rubber and mercury, an all-glass apparatus was used (see fig.). After the peroxide, contained in a small glass tube, had been introduced through *A*, the apparatus was sealed off at *B*, evacuated through the Töpler pump, and the constriction *D* sealed, the bulb containing the peroxide being cooled with solid carbon dioxide during these operations.

The surrounding thermostat (not shown) was then slowly brought to the required temperature and maintained thereat (± 1·0°) until a sufficient quantity of gas (at least 10 c.c. measured at ordinary temperature and pressure) had been formed. The average rate of evolution of gas, in c.c. per hour, decreased rapidly at first, and then very slowly from about 14·0 at 90° to 0·2 at 30°. The bulb *C* was then cooled and, after the septum at *E* had been broken with the usual magnetic arrangement, the whole of the gas was collected through the Töpler pump. A portion of it was then transferred to a Bone and Wheeler apparatus, in which the carbon dioxide, oxygen, ethylene, and carbon monoxide were determined by absorption in the usual manner. The methane and ethane were determined by the fractional condensation method using liquid air (Walker and Shukla, J., 1931, 368) in order to confirm the presence of these two hydrocarbons independently of one another. The separated portions of the hydrocarbon residue gave *C*/*A* ratios on explosion very close to 2·00 and 1·25, *i.e.*, the theoretical values for these two gases respectively.

Results.—The composition of the gaseous products (in % by vol.) is shown in Table I. It will be seen that the amount of ethane becomes less with decreasing temperature, until it is only about 2% of the volume of methane formed.

Table I.

Temp.	30°.	45°.	55°.	70°.	80°.	90°.
CO_2, % by vol.	59·5	64·0	55·5	58·4	62·2	62·0
O_2 ,, ...	1·9	1·3	0·8	0·9	0·7	1·1
C_2H_4 ,, ...	0·5	0·4	0·3	0·1	0·7	0·1
CO ,, ...	1·9	1·1	1·6	1·0	1·0	0·8
C_2H_6 ,, ...	0·7	0·7	1·4	3·7	3·0	8·8
CH_4 ,, ...	35·4	32·3	40·0	35·9	32·2	27·1

A decomposition of the peroxide according to equation (1) is therefore not favoured by allowing the reaction to take place as slowly and at as low a temperature as possible. The results described in this and in the previous paper show that when acetyl peroxide is heated under a wide variety of conditions, both alone and in solution, methane and carbon dioxide are the main gaseous products. The formation, in the absence of solvent, of a considerable amount of a gum-like residue suggests a rather complex decomposition process in which polymerisation of simpler primary products occurs. In a few experiments upon the residue from the incompletely decomposed peroxide, no evidence was found for the formation of formaldehyde, peracetic acid, or acetic acid, which might accompany the methane according to Fichter and Panizzon's suggestion (*Helv. Chim. Acta*, 1932, **15**, 1007). Since, however, we have been concerned mainly with determining the effect of lower temperatures upon the formation of ethane, we have not attempted a complete investigation of the residue.

Discussion.—If acetyl peroxide is formed at the anode during the electrolysis of acetate solutions, then the conditions must be particularly favourable to the decomposition into $C_2H_6 + 2CO_2$, for in this case appreciable amounts of methane are formed only under very limited conditions of low current density and high concentration of acetate (cf. Shukla and Walker, *Trans. Faraday Soc.*, 1932, **28**, 457; also Fichter and Panizzon, *loc. cit.*). It does not appear likely that this is due to catalytic influence of the electrode surface, because Wieland and Pascual-Vila (*Annalen*, 1926, **446**, 60) found that the decomposition of acetyl peroxide in the presence of platinum under various conditions does not give ethane and carbon dioxide.

Finally, it is of interest to compare the gaseous products of the decomposition of acetyl peroxide with those of two other reactions in which the intermediate formation of this peroxide has been assumed, *viz.*, (i) the action of barium peroxide on acetic anhydride, and (ii) the oxidation of acetic acid with persulphates.

(i) This reaction was that actually used by Brodie (*Phil. Trans.*, 1863, **153**, 413) in his original preparation of acetyl peroxide, and for this purpose the temperature must be kept low. At higher temperatures a vigorous reaction takes place, and Schützenberger (*Compt. rend.*, 1868, **61**, 487) stated that a gas composed exactly of two volumes of carbon dioxide and one volume of a hydrocarbon having the character and composition of $2CH_3$ was evolved. This result has apparently never been confirmed, though often quoted as a method of preparing ethane (cf. Armstrong, *Nature*, 1934, **133**, 379). On the contrary the work of Darling (J., 1868, **21**, 500), of Fichter (*Z. Elektrochem.*, 1914, **20**, 473), and of Glasstone and Hickling (*Chem. and Ind.*, 1934, 512), in which barium peroxide and acetic anhydride were heated together under a variety of conditions, with and without the addition of water, shows that in every case little ethane and considerable quantities of methane are obtained. A comparison of the data of these investigators with the composition of the gas obtained by heating the peroxide alone (this paper and Walker, *loc. cit.*) shows that there is very close qualitative, and in some cases quantitative, resemblance in the gaseous products. To make the results more comparable, the gas compositions given in Table II are referred in each case to 100 vols. of methane, since in some cases the carbon dioxide was not determined and in others no ethane was found.

TABLE II.

Reaction.	Observers.	Composition (by vol.) of gaseous products ($CH_4 = 100$).		
		CH_4.	C_2H_6.	CO_2.
Decomp. of $(AcO)_2$:				
(*a*) liquid	W. & W.	100	2·0—32·5	139—229
(*b*) in aq. soln.	W.	100	5·8—14·4	360—475
	D.	100	24·3	Not measured
BaO_2 and Ac_2O	F.	100	16·5	255
	G. & H.	100	50·8	549
	G.	100	0—30·5	Not measured
AcOH and $Na_2S_2O_8$	F. & P.	100	0	489

W. & W. = Walker and Wild; W. = Walker; S. = Darling; F. = Fichter; G. & H. = Glasstone and Hickling; G. = Gordon; F. & P. = Fichter and Panizzon.

(ii) The reaction between acetic acid and sodium persulphate in aqueous solution has been investigated by Gordon (*J. Physical Chem.*, 1914, **18**, 55) and by Fichter and

Panizzon (*loc. cit.*, p. 996). The latter authors consider the first step in the reaction to be the oxidation of acetic acid to acetyl peroxide, and they attribute the fact that more methane than ethane is formed (see Table II) to hydrolysis of the peroxide to peracetic acid, since they assume that acetyl peroxide itself does not give methane as one of its primary decomposition products. In the light of the evidence now put forward, however, the products obtained in the oxidation of acetic acid appear to be such as are normally obtained from the decomposition of acetyl peroxide.

We conclude, therefore, that the reaction (1) is not the main process taking place when the peroxide is decomposed either directly or in reactions in which its intermediate formation appears likely.

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A.8.

THE INFLUENCE OF THE ELECTRODE SURFACE ON ANODIC PROCESSES

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THE INFLUENCE OF THE ELECTRODE SURFACE ON ANODIC PROCESSES.

By O. J. Walker and J. Weiss.

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Two types of anodic process have been largely investigated in electrolytic reactions, *viz.* (1) the evolution of oxygen (which involves the phenomenon of oxygen overvoltage), and (2) the oxidation of various inorganic and organic ions and molecules. In general, both types of reaction may occur at the anode during the electrolysis of any given aqueous solution. Such processes have been investigated both experimentally and theoretically in great detail.[1] More recently, the mechanism of electrode processes has been discussed from the points of view of statistical and of quantum mechanics.[2] Further reference to this will be made later on.

In a recent series of studies on electrolytic oxidations Glasstone and Hickling [3] have proposed a new general theory for the mechanism of anodic oxidation, which contradicts the views of Foerster and his school [1] and the similar views maintained by one of us [4] in some recent papers. Since many of their assumptions are open to criticism, it seems necessary to reconsider the question of electrolytic oxidation.

We can first deal briefly, however, with the main arguments of Glasstone and Hickling's theory. They state that H_2O_2 is formed as the primary reaction product by the combination of hydroxyl radicals on the surface of the anode. From the purely experimental standpoint this view is highly improbable, since the anodic formation of H_2O_2 has never been detected even in traces.[5] In the homogeneous gaseous system and in solution there is no direct evidence for the recombination reaction $2OH = H_2O_2$. In the presence of a surface, however, it is known with certainty, as was first shown by Bonhoeffer and Pearson [6] and confirmed by Rodebush and Wahl,[7] that this recombination never takes place, but rather the reaction $2OH \rightarrow H_2O + O$. The formation of H_2O_2 in the glow discharge electrolysis may occur somewhere in the gas phase or at the liquid surface, as has been shown by Haber and Klemenc [8], Rodebush and Wahl [7] and others.[9] It is by no means certain that the H_2O_2 formed in this case is always due to the recombination of OH radicals, but even so it is not permissible to compare the conditions in a glow discharge (at 500-1000 volts) with those prevailing at a metal anode dipping into an aqueous solution.

[1] *Cf.* Foerster, *Elektrochemie d. wässerigen Lösungen.*

[2] J. A. V. Butler, *Trans. Faraday Soc.*, 1924, **19**, 734; R. W. Gurney, *Proc. Roy. Soc.*, 1931, **134A**, 137.

[3] Glasstone and Hickling, Part VI., *J.C.S.*, 1934, 1878.

[4] S. N. Shukla and O. J. Walker, *Trans. Faraday Soc.*, 1931, **27**, 35, 722.

[5] Except under unusual conditions of low temperature, *e.g.*, at $-40°$ C., *cf.* Riesenfeld and Reinhold, *Ber.*, 1909, **42**, 2977.

[6] Bonhoeffer and Pearson, *Z. physikal Chem.*, 1931, **14B**, 1.

[7] Rodebush and Wahl, *J. Chem. Physics*, 1933, **1**, 696.

[8] Haber and Klemenc, *Z. Elektrochem.*, 1914, **20**, 485.

[9] W. R. Cousins, *Z. physik. Chem.*, 1929, **4B**, 440.

The only experimental evidence put forward by Glasstone and Hickling for the intermediate formation of H_2O_2 in such varied processes as the anodic oxidation of thiosulphates, of sulphites, and of acetates, is that the addition of salts of Pb, Ag, Mn, Co, etc., brings about a marked change in the anode process. This is attributed by them to a catalytic decomposition of the H_2O_2, for which these salts are known to act as catalysts. As, however, H_2O_2 is certainly not formed (under the conditions of their experiments), it is necessary to account in some other way for the experimental results obtained on adding the above-mentioned metallic salts.

Many examples are known where, in the electrolysis of solutions containing these metal salts, layers of metal oxides are formed at the anode, the surface of which is thereby completely changed.[1] It seemed very likely, therefore, that in the experiments of Glasstone and Hickling the change in the electrode process was connected with the change of the anode surface. Accordingly some of their experiments were repeated to demonstrate that also under their experimental conditions oxide layers are formed on the anode.

Experimental.

For this purpose we selected the electrolysis of potassium acetate solutions described in Glasstone and Hickling's most recent paper.[3] In this reaction the effect of the added salts in changing the anode process is very marked. Their experimental conditions were reproduced in all essential points. Solutions of potassium acetate, containing free acetic acid, to which other metallic acetates had been added, were electrolysed at room temperature in a glass vessel with a smooth platinum wire cathode and a smooth platinum foil anode (1 × 1 cm.). The cathode and anode compartments were separated by a thick plug of glass wool, and the solution in the anode compartment was stirred rapidly. Previous to use, the anodes were cleaned with hot HCl, HNO_3, water, and then heated to redness. The electrolysis was allowed to proceed (as in the experiments of Glasstone and Hickling) in each case for 15 minutes at 0·5 amps, corresponding to a total passage of 450 coulombs at a C.D. of 0·25 amps per sq. cm.

The results are summarised in the following table :—

TABLE I.

No. of Expt.	Concn. of CH_3COOK gm. mols./litre.	Concn. of CH_3COOH gm. mols./litre.	Nature and Concn. of Added Acetate gm. mols./litre.	Condition of Platinum Anode (Initially Bright and Smooth) at End of Electrolysis.
1	1·0	1·0	None	Bright and smooth
2	1·0	1·0	$(CH_3COO)_2Pb$ 0·01 *M*	Thick deposit of chocolate brown PbO_2
3	1·0	1·0	$(CH_3COO)_2Mn$ 0·1 *M*	Marked brown deposit of manganese oxide
4	1·0	1·0	CH_3COOAg 0·013 *M*	Black deposit
5	1·0	1·0	$(CH_3COO)_2Co$ 0·1 *M*	No visible deposit. Electrolyte changed from pink colour to brown

In experiments 2-4, an obvious darkening of the bright anode surface commenced soon after starting the electrolysis, and a considerable deposit

was left on the anode at the end of the experiment. It is clear, therefore, that a marked change occurs in the nature of the anode surface on the addition of Pb, Mn, and Ag acetates in the electrolysis. Even in the case of cobalt a very thin film of oxide is most probably formed, and its formation is made more likely by the fact that considerable oxidation of the cobaltous salt took place, as shown by the darkening of the electrolyte.

Discussion of Experiments.

These results show that under the experimental conditions used by Glasstone and Hickling a definite change in the anode surface takes place through the formation of oxide layers.

It is well known that the nature of the surface is an important factor in influencing the reactions which may occur at an electrode. For example, Regelsberger [10] found that chromium salts, which are not oxidised at platinum anodes, are readily oxidised on the addition of small amounts of lead salts, which form a PbO_2 layer on the anode. Platinum electrodes with (electrolytically formed) cobalt, nickel and iron oxides, show a quite different behaviour to platinum itself in anodic oxidations. Müller and Spitzer [11] found the same kind of behaviour even in cases where the oxide layers are not visible to the eye. These observations are supported by some experiments of Tafel,[12] who showed that in general even monomolecular layers can change the nature of an electrode.

Theoretical Discussion.

We shall now discuss in more detail the two types of reaction referred to above, *viz.* (1) the liberation of oxygen at the anode, and (2) anodic oxidation processes.

In general there exists a potential barrier between the metal surface (of the anode) and the ions in the adsorbed layer. According to the Pauli-Sommerfeld theory we have in a metal quasi-free electrons which obey the Fermi-Dirac statistics. Electron transfer can take place into the metal from the adsorbed negative ions (or molecules) on the surface of the anode through the potential barrier. According to quantum mechanics this electron transfer takes place mainly between electron levels of the same energy. Therefore the following relation must hold :—

$$\Phi + V_a > E_{\text{ion}} + H_{\text{ion}}.$$

In this expression

Φ = work function of the metal electrode.
V_a = applied positive potential which increases the work function to $\sim (\Phi + V_a)$.
E_{ion} = electron affinity of the adsorbed negative ion which is transferring its electron to the metal.
H_{ion} = hydration energy of the negative ion.

This is similar to the expression developed in more detail by Gurney [2] who, however, did not take into account that the reacting ions are in the adsorbed state. Topley and Eyring [13] have recently pointed out that in

[10] Regelsberger, *Z. Elektrochem.*, 1899, **6**, 308.
[11] Müller and Spitzer, *Z. Elektrochem.*, 1905, **11**, 917.
[12] Tafel, *Z. physikal Chem.*, 1900, **34**, 193.
[13] Topley and Eyring, *Nature*, 1934, **133**, 292.

the case of the discharge of hydrogen ions on a metallic cathode the adsorption energies must be involved. Therefore we have

$$\Phi + V_a > E_{\text{ion}} + H_{\text{ion}} - \Delta A \quad . \quad . \quad . \quad (1)$$

where $\Delta A = A_R - A_I$, A_I being the adsorption energy of the ion and A_R the adsorption energy of the radical formed by its discharge. In general, ΔA will always be positive as $A_R > A_I$.

From expression (1) the well-known influence of the electrode surface, which we have emphasised above, can easily be seen. Two material constants of the metal are involved, one being the work-function Φ of the metal surface (under the given conditions), and the other the term ΔA, which not only differs for different metals, but also may be different for different surfaces of one and the same metal. It is difficult to discuss the influence of ΔA alone, as both ΔA and Φ are dependent in a similar way on the properties of the surface.

Oxygen Evolution at the Anode.

In the case of oxygen liberation we have to consider the discharge of OH^- ions at the surface, according to

$$(a)\ OH^- = OH + \epsilon\ (\text{metal}).$$

The direct decomposition of water on the anode may also become important (particularly in the case of low OH′ ion concentration) according to [15]

$$(a')\ H_2O \rightarrow OH + H^+ + \epsilon\ (\text{metal}).$$

These reactions are most probably followed by

$$(b)\ OH + OH = H_2O + O,$$

and finally,

$$(c)\ O + O + (M) = O_2 + (M).$$

The rate determining reaction is in general reaction (a) or (a'). Reference has already been made to the fact that reaction (b) takes place (on the metal surface). Further evidence for the formation of oxygen atoms by this process is obtained from the experiments of Tanatar,[16] confirmed by one of us,[17] on the catalytic decomposition of H_2O_2 on an anode, according to

$$(d)\ H_2O_2 + O = H_2O + O_2.$$

Furthermore, Butler and Armstrong [18] were able to show that in the case of noble metals, such as gold and platinum, a monomolecular layer of oxygen atoms is present on the metallic surface during anodic polarisation.

We can see from expression (1) that in order that electron transfer may occur (and an appreciable current flow) we must increase the work function by increasing the applied positive potential V_a. This additional

[15] In this case expression (1) takes the form :

$$\Phi + V_a > D_{H_2O} + I_H - \Delta A$$

where $(\Phi + V_a)$ has the same meaning as above.

D_{H_2O} = dissociation energy of H_2O into an H atom and an OH radical.
I_H = ionisation potential of the H atom.
$\Delta A \sim A_{OH}$ (adsorption energy of the OH radical).

[16] Tanatar, *Ber.*, 1903, **36**, 199. [17] Weiss, *in preparation.*
[18] Butler and Armstrong, *Proc. Roy. Soc.*, 1932, **137A**, 604.

positive potential, which is really the overvoltage, will be different for different metals and various surfaces, as we have pointed out above. We may refer here to the measurements of Coehn and Osaka,[19] and of Foerster and Piguet [20] on oxygen overvoltage at different anode surfaces, and to the paper of Müller and Spitzer (*loc. cit.*), who showed that the oxides of Fe, Co, and Ni have low overvoltages of about the same value as those of the metals themselves.

According to the previous considerations, one should expect the overvoltage to decrease with increasing work function of the (metal) electrode and with increasing adsorption power for the OH radical. As oxide layers in some form are always present on the surface, the work functions of the metals under electrode conditions must not be compared with those of the pure metals, but will in general be modified. It is well known [21] that the work function is influenced by gases adsorbed on the metal surface. Adsorbed oxygen usually increases the work function and the overvoltage is thereby decreased. On the other hand, the rough or spongy surface with the higher adsorption power for the OH radical (ΔA very large) should have the lower overvoltage, in agreement with experiment.

Anodic Oxidation Processes.

We shall now consider the case where we have oxidation of anions taking place as well as oxygen evolution. In this case we must compare the expression for the discharge of OH^- ion with that for the discharge of another anion (A^-) present in the electrolyte.

$$\left.\begin{matrix}\Phi + V_a \\ \Phi\end{matrix}\right\} > \begin{matrix}E_{OH^-} + H_{OH^-} - \Delta A_{OH} \\ E_{A^-} + H_{A^-} - \Delta A_A.\end{matrix}$$

Φ may differ for the two expressions. If one can assume this difference to be small, then, in general, conditions will be more favourable for the discharge of any anion present than for OH^- ion, as the electron affinity of the latter exceeds the electron affinities of other anions ($E_{OH} > E_A$). Also,[22] for the common anions $H_{A^-} < H_{OH^-}$. The primary discharge of OH^- will be possible only when ΔA_{OH} is relatively large ($\Delta A_{OH} > \Delta A_A$).

A distinction should therefore be made between (*a*) electrodes with high overvoltage, and (*b*) electrodes with low overvoltage. So that we should expect anodes of high oxygen overvoltage (*e.g.* smooth platinum) to favour the primary discharge of any anion, whereas on anodes of low overvoltage (*e.g.* platinised platinum and metallic oxides) the OH^- ion will be discharged in preference. The resulting OH radicals may then take part in chemical oxidations on the electrode.

For instance, in the case of the anodic oxidation of acetates we have to expect the following processes. On smooth platinum there will occur mainly the direct discharge of acetate ions according to

$$(e)\quad CH_3COO^- \rightarrow CH_3COO + \epsilon\ (\text{metal}).$$

[19] Coehn and Osaka, *Z. anorg. Chem.*, 1903, **34**, 86.
[20] Foerster and Piguet, *Z. Elektrochem.*, 1904, **10**, 714.
[21] Cf. Hughes and Du Bridge, *Photoelectric Phenomena*, 1933.
[22] K. F. Herzfeld, *Kinetische Theorie der Wärme* (Vieweg, 1926).

If there are no other reactive molecules present the free radicals then react

$$(f)\quad 2CH_3COO \rightarrow C_2H_6 + 2CO_2,$$

giving mainly ethane and carbon dioxide (Kolbe reaction). Practically no oxygen is evolved under these conditions.

In the case of surfaces of low overvoltage, however, such as platinised platinum, cobalt, nickel, iron, PbO_2, MnO_2, Ag_2O, we get mainly primary discharge of OH^- ions. The resulting reactive OH radicals are able even at low concentrations (*i.e.* at potentials lower than that at which appreciable oxygen evolution occurs) to react chemically with the electrolyte according to

$$(g)\quad CH_3COO^- + OH = CH_3COO + OH^-.$$
$$(h)\quad CH_3COO + OH = CH_3OH + CO_2.$$

It is clear that at an anode of low overvoltage, the OH^- ion is easily discharged and reactions (*g*) and (*h*) take place (along with some oxygen liberation).

On the other hand, if the electrode is sufficiently "poisoned," *e.g.* by $Hg(CN)_2$, KCN, brucine, etc.,[3] the overvoltage for the discharge of OH^- rises and the Kolbe reaction becomes prominent again.

The oxidation of the acetate to give CH_3OH and CO_2 in processes (*g*) and (*h*) (Hofer-Moest reaction) takes place (on electrodes of low overvoltage) at a considerably lower potential than the Kolbe reaction (on electrons of high overvoltage). This can be well understood as in reactions (*g*) and (*h*) there is a depolarising influence due to the electrolyte, which lowers the potential.[23] It therefore follows that under the conditions in question the Kolbe and Hofer-Moest reactions are taking place on electrode surfaces of different behaviour.

The same distinction between anodes of high and low oxygen overvoltage is apparent in all other anodic processes.[24]

The considerations which we have dealt with in the case of acetates hold similarly in the case of the other reactions investigated by Glasstone and Hickling. For instance, the $S_2O_3^=$ ion is either discharged directly giving $S_4O_6^=$ or else is oxidised to sulphate.

Also, in the electrolysis of sulphite solutions the effect of anodic prepolarisation in favouring [25] the formation of $S_2O_6^=$ (by the combination of directly discharged $SO_3^=$ ions) is readily explained by the well-known increased overvoltage on pre-polarised platinum anodes.[1]

The effect of the addition of the metallic salts is the same for all these anodic oxidations studied by Glasstone and Hickling. The effect decreases in the order Pb, Ag > Mn > Cu, Co, Fe. This is the same

[23] This depolarising influence on the oxygen potential is always to be expected if substances are added which are able to react quickly with the OH radical. This is indicated by the experiments of Haber, and of Haber and Grinberg, who have shown that H_2O_2 when added to the anode electrolyte lowers the anodic potential very markedly (*Z. anorg. Chem.*, 1898, **18**, 37; 1906, **51**, 361) by acting as a strong depolariser. The H_2O_2 then reacts either according to reaction (*d*) or directly with the OH radicals

$$H_2O_2 + OH \rightarrow HO_2 + H_2O$$

as in the catalytic decomposition of H_2O_2 investigated by Haber and Weiss (*Proc. Roy. Soc.*, 1934, **147**, 332).

[24] Foerster, *loc. cit.*

[25] Glasstone and Hickling, *J. Chem. Soc.*, 1932, 2345, 2800.

order as the case of formation of oxide layers found in our experiments, which all have a low overvoltage for discharge of OH^-.

Summary.

(1) The two types of anodic process, *viz.* (1) the evolution of oxygen (which involves the phenomenon of oxygen overvoltage) and (2) oxidation of various inorganic and organic ions and molecules, have been discussed.

(2) The influence of the addition of metallic salts (*e.g.*, of Pb, Mn, Ag, Co) to the electrolyte to be oxidised has been studied with reference to the work of Glasstone and Hickling.

(3) The conditions for the discharge of anions and the breaking up of molecules at the anode have been considered, and the electron transfer to the metal anode has been discussed.

In conclusion, we wish to thank Mr. B. Topley for valuable discussions.

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A.9.

THE THERMAL AND PHOTOCHEMICAL DECOMPOSITION OF ACETYL PEROXIDE

BY

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238. *The Thermal and Photochemical Decomposition of Acetyl Peroxide.*

By O. J. Walker and G. L. E. Wild.

In recent years the thermal decomposition of a number of acyl peroxides of the type $(R{\cdot}CO{\cdot}O)_2$ (R = alkyl or aryl radical) has been investigated (Wieland and co-workers, *Annalen*, 1930, **480**, 157; 1934, **513**, 93; Fichter and Buess, *Helv. Chim. Acta*, 1935, **18**, 445; Erlenmeyer and Schoenauer, *ibid.*, 1936, **19**, 338). When peroxides of this class are heated, either in the pure state or in solution, decomposition takes place according to the scheme (I). This process is in general accompanied by reactions of types (2*a*) and

$$(R{\cdot}CO{\cdot}O)_2 \longrightarrow R_2 + CO_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; (1)$$

$$(R{\cdot}CO{\cdot}O)_2 + R'H \begin{cases} \longrightarrow R{\cdot}CO{\cdot}OR' + RH + CO_2 \quad . \; . \; . \; . \; (2a) \\ \longrightarrow R{\cdot}CO{\cdot}OH + R'R + CO_2 \quad . \; . \; . \; . \; (2b) \end{cases}$$

(2*b*), where R'H may be a molecule of solvent, of peroxide, or of one of the decomposition products (cf. Gelissen and Hermans, *Ber.*, 1926, **59**, 662; this so-called RH scheme has been somewhat modified by Boeseken and Hermans, *Annalen*, 1935, **519**, 133; also Hermans, *Rec. trav. chim.*, 1935, **54**, 760). The whole decomposition process may, therefore, be very complex, and very little of the hydrocarbon R_2, which results from reaction (1), may appear amongst the final products.

The thermal decomposition of any particular acyl peroxide has usually been carried out in one of three ways: (*a*) Explosive decomposition, brought about by heating the peroxide in a steel bomb; (*b*) controlled decomposition, by gentle heating of the peroxide either alone or diluted with an inert material such as sand; (*c*) controlled decomposition of the peroxide in solution. Although a considerable amount of data has been accumulated regarding the nature of the products resulting from the thermal decomposition by these means of various acyl peroxides, very little is known about the mechanism of the decomposition process. The RH scheme (above) summarises in a convenient and comprehensive manner the different kinds of end-product of the thermal decomposition, but does not purport to represent the actual mechanism of the process. It has been applied almost entirely in discussing the behaviour of benzoyl and other aromatic peroxides. According to Hermans (*loc. cit.*, p. 767), aliphatic acyl peroxides decompose mainly according to reaction (1) but there does not exist much experimental evidence on the controlled decomposition of such peroxides (cf. Fichter, *Bull. Soc. chim.*, 1934, **1**, 1588).

Recently, we described some experiments on the decomposition of acetyl peroxide, $(CH_3{\cdot}CO{\cdot}O)_2$ (J., 1935, 207; cf. also Walker, J., 1928, 2040). It was originally considered that the results might have some bearing on the mechanism of the Kolbe electrosynthesis of ethane from acetates, since there is a possibility of the formation and decomposition of acetyl peroxide in this process, but it is doubtful whether definite conclusions can be obtained in this direction (see later). The study of the decomposition of acetyl peroxide is of more direct interest in the general problem of the thermal decomposition of acyl peroxides, especially of aliphatic peroxides, for which the validity of the RH scheme is not certain. We hoped that conditions might be found under which the decomposition of acetyl peroxide could be controlled so as to approximate as nearly as possible to reactions of type (1) or (2) alone. In this paper some experiments on the thermal decomposition of acetyl peroxide in the vapour state and in solution are described. No data are on record regarding the decomposition of any acyl peroxides in the vapour state.

In the case of a few peroxides the photodecomposition produced by their exposure to ultra-violet light at the ordinary temperature has been investigated, and it appears that the products correspond more closely to a reaction of type (1) (cf. Walker, *loc. cit.*, p. 2044; Fichter and Schnider, *Helv. Chim. Acta*, 1930, **13**, 1428). The earlier experiments

with acetyl peroxide were performed on the solid substance. The results of irradiating the peroxide in the liquid and the dissolved state are now reported.

Experimental.

1. *Thermal Decomposition of Acetyl Peroxide Vapour.*—The preparation of acetyl peroxide and the analysis of the gaseous products were carried out as previously described.

The decomposition of the peroxide vapour at 100° was performed in an all-glass apparatus (see Fig. 1). The solid peroxide, contained in a small tube, was introduced through *A* to the position shown at *C*, and surrounded by a freezing mixture. After being sealed off at *B*, the

Fig. 1.

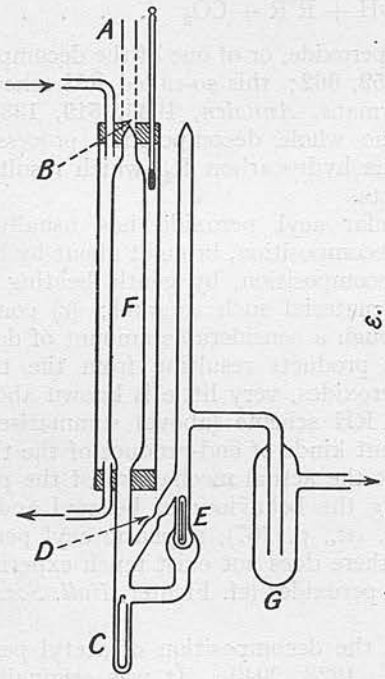
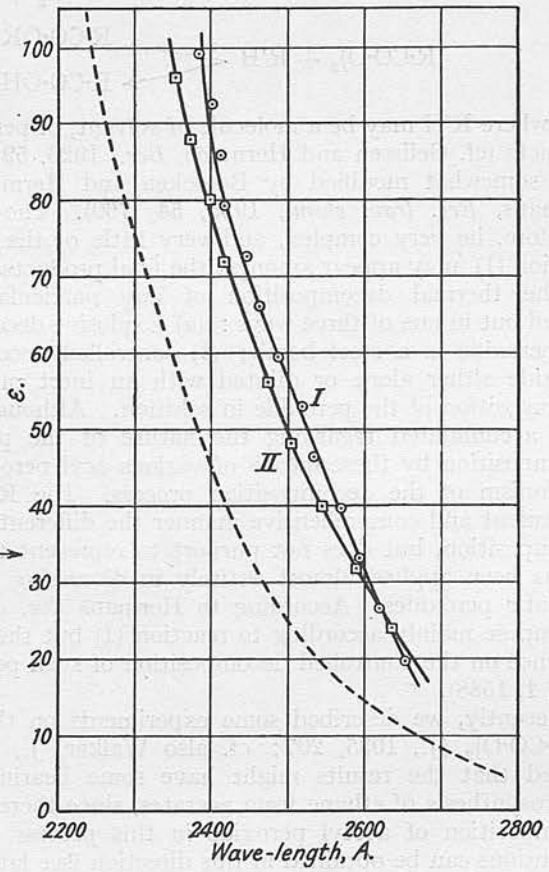


Fig. 2.

Absorption of acetyl peroxide in cyclo*hexane* (I) *and in alcohol* (II).



whole apparatus was evacuated and then isolated from the pump by sealing at *D*. The peroxide in *C* was surrounded with a water-bath at 35°, and steam then passed through the jacket of the tube *F* containing peroxide vapour. The vapour pressure of liquid acetyl peroxide at 35° is of the order of a few mm. (owing to the slow decomposition of the liquid peroxide at this temperature, reliable measurements of the vapour pressure could not be made).

After sufficient time had elapsed, the heating was stopped, the tube *C* cooled with a freezing mixture, and the seal *E* broken with an electromagnet. The gaseous decomposition products were collected by means of a Töpler pump, the trap *G*, which was immersed in carbon dioxide–ether, preventing undecomposed peroxide vapour from entering the pump. In 6 hours 7·7 c.c. of gas (converted to N.T.P.) were collected. Similar results were obtained when the acetyl peroxide in *C* was kept solid at 18°, but owing to the lower vapour pressure of the solid, only 5·0 c.c. of gas were produced in $8\frac{1}{2}$ hours.

The results of the gas analysis were as follows :—

Decomposition of acetyl peroxide vapour at 100° from	Composition of gas, % by vol.							
	CO_2.	O_2.	Unsat.	CO.	C_2H_6.	CH_4.	C_2H_6/CH_4.	CO_2/C_2H_6.
(*a*) Liquid at 35°	64·7	0·9	1·4	2·4	24·9	5·3	4·7 : 1	2·4 : 1
(*b*) Solid at 18°	66·0	0·8	1·2	3·2	24·4	4·4	5·5 : 1	2·5 : 1

The thermal decomposition of acetyl peroxide vapour at 100° takes place very largely according to equation (1) (R = CH_3). The C_2H_6/CH_4 ratio is about 5 : 1, and may be compared with the value of 0·3 : 1, found in the decomposition of the pure liquid peroxide at 90°, which was the highest value obtained previously from the thermal decomposition under any conditions.

The ratio of CO_2/C_2H_6 approaches the value of 2 : 1 required stoicheiometrically (the values given in the last column of the table have been calculated on the assumption that 1 vol. of carbon dioxide is formed for 1 vol. of methane, which seems probable). The small amount of methane produced indicates that reactions of type (2*a*) occur to a slight extent even in the vapour phase.

2. *Thermal Decomposition of Acetyl Peroxide in Solution.*—With aromatic acyl peroxides it has been well established that the solvent almost invariably takes part in the decomposition process in solution (cf. Hermans, *loc. cit.*, p. 760). The previous work on acetyl peroxide showed that decomposition in presence of a solvent always gave very much more methane than ethane in the gaseous products. This suggests, on the basis of the RH scheme, that appreciable reaction of the type (2*a*) (R = CH_3) occurs. The whole reaction process in solution is, however, undoubtedly complex, and without a more complete investigation and identification of all the reaction products formed with any given solvent, it is not possible to discuss the detailed application of the RH scheme to the case of acetyl peroxide solutions. In spite of the complexity of the decomposition process, it is possible to determine the order of the reaction in solution with respect to the acetyl peroxide decomposed. If the RH scheme applies, one would expect the rate of decomposition of the peroxide in presence of a large excess of solvent to appear unimolecular, and this was found to be the case.

Experiments were made in which the amount of peroxide left in the solution after definite time intervals was determined by titration. Toluene was chosen as solvent, since it has a sufficiently high b.p., and the thermal decomposition of acetyl peroxide in this solvent gives practically no reaction of type (1). The volume composition of the gaseous products obtained when a solution of 0·5 g. of acetyl peroxide in 100 c.c. of toluene is heated at 80° is : CO_2, 44·6; O_2, 1·4; CO, 2·0; CH_4, 50·7; C_2H_6, 1·4%; *i.e.*, almost entirely methane and carbon dioxide. At the ordinary temperature the solution of acetyl peroxide in toluene is quite stable. At 50° the rate of decomposition is too slow to allow of accurate measurements, but above 70° the decomposition becomes quite rapid, and the rate of reaction was measured at 80·0° and 87·3° ± 0·1°. Solutions of 1·25 g. of peroxide in 200 c.c. of toluene were used. The peroxide, dissolved in a small amount of toluene, was added to the main bulk of the solvent after it had attained the desired temperature. Portions of the solutions were removed at suitable intervals into cooled flasks, and the peroxide determined by titration of the iodine liberated from excess of potassium iodide with sodium thiosulphate solution in the usual manner. The results show that the reaction is of the first order with respect to the acetyl peroxide. In the following table the values of the percentage decomposition and of the unimolecular constant, k, at the different time intervals are recorded :

Temp.								
80·0°	t (mins.)	26	84	144	234	309	369	
	Decomp., %	8·8	30·6	46·7	65·3	75·2	79·0	
	$k \times 10^4$	(36·6)	43	44	45	45	42	Mean = 44
87·3	t (mins.)	29	59	95	144	203	256	
	Decomp., %	24·2	47·6	65·5	80·1	88·6	92·3	
	$k \times 10^4$	(96)	110	112	112	107	100	Mean = 108

The temperature coefficient of k is 3·3 for a rise of 10°, and the activation energy is 31 kg.-cals./mol.

3. *Photochemical Decomposition of Acetyl Peroxide.*—All the photodecomposition experiments were performed in a flat quartz cell fitted with a glass capillary delivery tube leading to a gas-collecting tube over mercury. The flat surface of the quartz cell (area about 12 cm.^{2}) was exposed at 3—4 inches distance to the full light of a mercury vapour lamp of the horizontal

type, using a constant current of 2 amps. The cell was cooled by a jet of water flowing over it, the temperature being controlled to keep the peroxide solid or liquid as desired.

(a) *Solid acetyl peroxide.* In order to obtain data on the photodecomposition of the solid under conditions of exposure comparable with those for the decomposition of the liquid and dissolved peroxide, a few experiments were made in which the solid substance was irradiated at room temperature. About 30—40 c.c. of gas could be collected in ½ hour. The mean composition of the gas from several experiments is given in the following table, and confirms the earlier results in which the percentages of ethane and methane had been determined by explosion of the total hydrocarbon residue. In the present experiments the presence of these two hydrocarbons was checked more directly by the method of fractional condensation and separate explosion.

After removal of the undecomposed peroxide by means of dilute acetic acid solution, an insoluble gum was left which smelt strongly of esters. It was not analysed further.

Composition of the Gaseous Products from the Photodecomposition of Acetyl Peroxide.

		Composition, % by vol.						
State of peroxide.	Temp.	CO_2.	O_2.	Unsat.	CO.	C_2H_6.	CH_4.	C_2H_6/CH_4.
Solid	16—18°	67·4	0·4	1·0	1·3	25·0	5·1	4·9
Liquid	30	61·5	—	—	1·8	17·5	19·5	0·90
Solution in *cyclo*hexane	16—18	59·7	0·9	0·9	1·3	8·4	28·9	0·29
Solution in alcohol	16—18	43·8	0·5	0·7	1·6	4·6	48·6	0·09

(b) *Liquid acetyl peroxide.* The peroxide in the quartz cell was kept liquid by running a stream of water at 30° over the outside of the cell. When the mercury lamp was switched on, sufficient gas was evolved in 1 hour. The mean composition is given in the table. Although less ethane is evolved than from the solid peroxide, the C_2H_6/CH_4 ratio is 45 times greater than in the thermal decomposition of the liquid peroxide at the same temperature, for which the ratio is about 0·02 (Walker and Wild, *loc. cit.*, p. 208).

(c) *Acetyl peroxide in* cyclo*hexane.* Approximately 1% solutions of acetyl peroxide in pure *cyclo*hexane were irradiated in the water-cooled quartz cell at the ordinary temperature. A short induction period of about 2 minutes was always observed before gas evolution commenced, and slight gas evolution occurred after the lamp was switched off. Only the gas evolved during irradiation was collected. For every 0·1 g. of peroxide decomposed, about 38 c.c. of gaseous products were collected during 2 hours, the composition being shown in the table. Much less ethane is obtained than from the photodecomposition of the peroxide in the solid or the liquid state.

(d) *Acetyl peroxide in ethyl alcohol.* Absolute alcohol, redistilled over lime, was used. The evolution of gaseous products due to photodecomposition of the alcohol (cf. Berthelot and Gaudechon, *Compt. rend.*, 1911, **153**, 383) was negligible under the conditions of our experiments. With the solutions of the peroxide it was found that, after the light source was switched off, there was a considerable evolution of gas, which continued until all the peroxide had decomposed. In one case nearly a third of the total gas was obtained from this " dark " reaction. The composition of the main portion of the gas from a typical experiment is compared in the following table with that from the thermal decomposition of acetyl peroxide dissolved in alcohol (cf. Walker, *loc. cit.*, p. 2043) :

	Composition, % by vol.		
	CO_2.	C_2H_6.	CH_4.
During irradiation	46·2	5·1	45·4
" Dark " reaction	45·3	5·0	46·8
Thermal reaction	50·7	1·6	45·7

For comparison with the other data, the mean composition of the gas evolved during the irradiation in several experiments is included in the previous table. In this case, also, the amount of ethane formed is very small.

(e) *Absorption spectrum of acetyl peroxide in solution.* The absorption spectrum of acetyl peroxide dissolved in *cyclo*hexane and in ethyl alcohol was measured by means of a Hilger rotating-sector photometer and medium quartz spectrograph, with a tungsten-steel spark as light source. In Fig. 2 the wave-length (in A.) is plotted against the molecular extinction coefficient ε, defined by $\varepsilon cd = \log I_0/I$ (d = 0·99 cm., c is in g.-mols./litre, and I_0 and I are the intensities of the incident and the transmitted light, respectively). The solutions used contained about 0·015 g.-mol. of peroxide per litre. A cell containing pure solvent was placed in the variable light beam of the photometer.

Acetyl peroxide has a continuous absorption band which commences at about 2800 A. and does not reach a maximum at the lowest wave-length investigated. As will be seen from Fig. 2, the absorption is very similar to that of hydrogen peroxide (broken curve, taken from Fergusson, Slotin, and Style, *Trans. Faraday Soc.*, 1936, **32**, 960). Both these substances contain the $-O-O-$ link, and one may attribute the ultra-violet band of acetyl peroxide to this part of the molecule (cf. also Lederle and Rieche, *Ber.*, 1929, **62**, 2578).

There is the possibility that in the photochemical decomposition of acetyl peroxide the primary process consists of a dissociation $(CH_3{\cdot}CO{\cdot}O)_2 + h\nu \longrightarrow 2CH_3{\cdot}CO{\cdot}O{\cdot}$, followed by a further fission of the acetate radicals into carbon dioxide and methyl radicals, which could combine together to form ethane or react with surrounding solvent molecules to give methane as one of the products. Further discussion of these suggestions would be too speculative, however, at this stage, since the experimental work has, so far, been concerned mainly with exploring the conditions of decomposition.

Conclusion and Summary.

Acetyl peroxide is readily decomposed under a variety of conditions either by heating to temperatures up to 100° or by exposure to ultra-violet light. Comparison of the gaseous products obtained by both methods shows that they are qualitatively similar but quantitatively different. In general, ethane is formed more readily in the photochemical decomposition, but even in this process more methane than ethane is usually produced. The whole process in either case is rather involved, and it is probable that in both types of decomposition at least two simultaneous or consecutive reactions are taking place.

Reference may be made to the question whether acetyl peroxide is formed and then decomposed at the anode in the electrolysis of acetate solutions (cf. Glasstone and Hickling, J., 1936, 826; Fichter, *loc. cit.*; Höleman and Clusius, *Z. physikal. Chem.*, 1937, *B*, **35**, 261). The fact that acetyl peroxide can be made to decompose in a variety of ways to give a complex mixture of products makes it doubtful whether the results of such experiments have any direct bearing on the mechanism of the anodic process. It is uncertain whether any of the conditions of decomposition which we have described are at all comparable with the conditions existing at the surface of the anode during electrolysis. The observed similarity between the electrolytic products and those obtained from the decomposition of the peroxide under certain particular, but not necessarily comparable, conditions cannot, therefore, be used as evidence for the peroxide mechanism in the electrolytic oxidation, further discussion of which is beyond the scope of this paper.

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B. 1.

ABSORPTION SPECTRA OF IODINE SOLUTIONS AND THE INFLUENCE OF THE SOLVENT

BY

O. J. WALKER

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ABSORPTION SPECTRA OF IODINE SOLUTIONS AND THE INFLUENCE OF THE SOLVENT

ABSORPTION SPECTRA OF IODINE SOLUTIONS AND THE INFLUENCE OF THE SOLVENT.

By O. J. Walker.

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Introduction.

The broad classification of I_2 solutions into two groups according to their colour is confirmed by the absorption spectrum measurements of Groh,[1] and of Getman.[2] They showed that the wave-length of maximum absorption, λ_{max}, of the I_2 band in the visible region is, in the brown solutions, displaced about 70 mμ towards the U.V. relative to its value of about 520 mμ in the violet solutions. [Recently it has been shown [3] that the substances ICl and IBr exhibit a similar type of dichroism in the same two classes of solvent, the displacement of λ_{max} being about 100 mμ in both cases.] The difference in the absorption spectra of violet and brown solutions of I_2 is thus well-marked, and can be

[1] Groh, *Z. anorg. Chem.*, 1927, **162**, 287.
[2] Getman, *J. Amer. Chem. Soc.*, 1928, **50**, 2883.
[3] Gillam and Morton, *Proc. Roy. Soc.*, 1929, **124A**, 604 ; Gillam, *Trans. Farad. Soc.*, 1933, **29**, 1132.

ascribed to the chemical formation of solvates in the brown solutions, evidence for which is obtained by an examination of other properties of such solutions.[4] The brown solutions, except when freshly prepared, usually also contain HI_3 (or I_3' ions) as a result of substitution reactions between the I_2 and solvent molecules.[5]

Uncertainty still exists, however, as to the existence and magnitude of any solvent effect in many " violet " or " red " solutions of I_2. For example, solutions in C_6H_6 are usually classified in the violet group, although they have a definite reddish tinge, and the absorption spectrum shows that λ_{max} is displaced about 10-20 mμ towards the U.V. as compared with its value for a solution in CCl_4, which gives truly violet solutions. Some kind of interaction between the I_2 and C_6H_6 molecules is indicated. Further evidence for this was obtained from the work of Williams [6] and of Müller and Sack,[7] who found a value of about $1{\cdot}0 - 1{\cdot}2 \times 10^{-18}$ e.s.u. for the dipole moment of I_2 dissolved in C_6H_6, but their work has been criticised recently by Wassiliew and co-workers,[8] who showed that I_2 has no measurable dipole moment in this solvent. Hildebrand and Jenks,[9] found that solutions of I_2 in C_6H_6 are abnormal in respect to their solubility-temperature relationship compared with other violet solutions. From similar considerations,[10] it has been suggested that in solutions of I_2 in ethylene dibromide, in spite of their violet colour, there is also some approach to solvation. In the case of solutions in $C_2H_4Br_2$ the solvation may be attributed to the polar nature of the solvent ($\mu = 1{\cdot}4 \times 10^{-18}$ e.s.u.). Benzene, on the other hand, is a solvent which has no resultant dipole moment. It seemed of interest, therefore, to examine further by means of absorption spectrum measurements the influence of the polar nature of the solvent molecules on the solvation of I_2 in different solvents. The effect of the polarity of the solvent in producing displacements of absorption bands of solutions has been studied by Scheibe [11] and others. In the case of violet solutions of I_2 it is not possible to draw any conclusions from the existing absorption spectrum data, because the measurements of different investigators do not extend over a large enough number of chemically similar solvents and frequently do not agree sufficiently for any one solvent. Absorption measurements have, therefore, been made of I_2 dissolved in a number of chloro-paraffins, since these solvents provide a fairly wide range of polarity and give solutions which show quite marked differences in colour.[12] During the course of this work a paper appeared by Chatelet [13] on the absorption spectra of fairly concentrated solutions of I_2 in many of these solvents. In the present work very dilute solutions were used in order to minimise any effects due to interaction between the I_2 molecules themselves (*cf.* ref. 19). The solvents used were carbon tetrachloride, chloroform, methylene chloride, ethylene dichloride, *n*-propryl chloride, *n*-butyl chloride and *cis*- and *trans*-dichloroethylenes.

[4] Gmelin-Kraut, *Handb. anorg. Chemie*, 8 Aufl., 1931, Jod, p. 125.
[5] *Cf.* Batley, *Trans. Farad. Soc.*, 1928, **24**, 438.
[6] Williams, *Physikal. Z.*, 1928, **29**, 174.
[7] Müller and Sack, *Physikal. Z.*, 1930, **31**, 821.
[8] Wassiliew, Syrkin and Kenez, *Nature*, 1935, **135**, 71.
[9] Hildebrand and Jenks, *J. Amer. Chem. Soc.*, 1920, **42**, 2180.
[10] Negishi, Donnally and Hildebrand, *J. Amer. Chem. Soc.*, 1933, **55**, 4799.
[11] Scheibe, *Ber.*, 1925, **58**, 586 ; 1926, **59**, 2617.
[12] Kaufmann and Levite, *Ber.*, 1919, **52**, 619.
[13] Chatelet, *Ann. Chim.*, 1934 (11), **2**, 5.

Experimental.

Materials.

Iodine.—A.R. I_2, containing no Cl, CN, etc., kept dry over $CaCl_2$.

Solvents.—In most cases the purest B.D.H. product was further treated with H_2SO_4, NaOH solution, H_2O, dried over $CaCl_2$ or P_2O_5 and distilled, neglecting the first and last fractions.[14] The *cis*- and *trans*-isomers of $C_2H_2Cl_2$ were obtained by fractionation of the purified mixed product, using an efficient fractionating column. The fractions distilling between the limits given were used. The b.p. of the solvents, which agree well with those given in the literature, are as follows, with the corresponding barometer readings (in mm.): CCl_4 76·8° (762), $CHCl_3$ 61·1-61·4 (762), CH_2Cl_2 40·1-40·3 (769), $C_2H_4Cl_2$ 83·2-83·3 (760), *n*-C_3H_7Cl 46·5-47·0 (775), *n*-C_4H_9Cl 77·9-78·3 (774), *cis*-$C_2H_2Cl_2$ 59·9-60·1 (760), *trans*-$C_2H_2Cl_2$ 48·4-49·4 (741).

The concentration of the solutions was 0·001 gm. mols./litre in every case. Three or more freshly prepared solutions were used for each solvent.

Absorption Measurements.

These were made by means of a Hilger-Nutting Spectrophotometer and Hilger wave-length spectrometer. The drum of the spectrometer was set at wave-lengths of 10 mμ intervals between 440-620 mμ, and the photometer adjusted to equal intensities. The results were corrected for the zero of the instrument, which was checked at intervals. A 100 C.P. pointolite lamp was used as the source, and the solutions were placed in stoppered quartz cells, for which d (internal thickness) = 0·99 cm., a similar cell containing pure solvent being placed in the comparison beam. The room temperature during the measurements varied between 16° and 22°.

In this paper the molecular extinction coefficient (ϵ) is defined in the usual way by the expression

$$\epsilon cd = \log_{10} I_0/I$$

where I_0 = intensity of incident light.
I = ,, ,, transmitted light.
c = concentration of I_2 in gm.-mols./litre (0·001 M).
d = length of absorbing layer of solution (0·99 cm.).

As a check on the absolute values of the extinction coefficients the absorption curve of I_2 in CCl_4 was also determined, using a Hilger rotating sector photometer and photographic technique, and results in good agreement with those of the above method were obtained.

Results.

All the absorption bands are of the form shown in Fig. 1, in which only the curve for the solution in CCl_4 is reproduced, as the curves are too crowded together in a small scale diagram. The curves for the other solvents are all (except with *trans*-$C_2H_2Cl_2$) more or less displaced towards the violet end, but the intensity and width of the bands are constant within the limits of experimental error (except with the two $C_2H_2Cl_2$ isomers). This is brought out clearly by Table I., in which the three quantities characteristic of a simple absorption band are tabulated, *viz.*, λ_{max}, the wave-length of maximum absorption, ϵ_{max}, the extinction coefficient at this wave-length, and δ, the width of the band, defined as the difference in wave-length of the two points on the curve for which $\epsilon = \frac{1}{2}\epsilon_{max}$. The b.p. and dipole moments, μ, of the solvents are also given. The latter are mean values taken from a recent table of dipole moments.[15]

[14] *Cf.* Baskerville and Hamor, *Ind. Eng. Chem.*, 1912, **4**, 571.
[15] Sidgwick, *Trans. Farad. Soc.*, 1934, **30**, Table of Dipole Moments.

TABLE I.

Solvent.	B.P.	μ.	$\lambda_{max.}$ $m\mu$.	$\epsilon_{max.}$	δ. $m\mu$.
1. CCl_4	76·8	0	516	890	88
2. $CHCl_3$	61·2	1·1	511	880	90
3. $CH_2Cl_2+CCl_4$	—	—	507	840	87
4. CH_2Cl_2	40·2	1·6	502	840	85
5. $C_2H_4Cl_2$	83·2	1·3-1·6	500	870	87
6. *n*-C_3H_7Cl	46·7	2·0	495	865	90
7. *n*-C_4H_9Cl	78·1	2·0	495	840	83
8. *trans*-$C_2H_2Cl_2$	49·0	0	518	680	81
9. *cis*-$C_2H_2Cl_2$	60·0	1·8	510	760	79

Discussion.

(*a*) Solutions of I_2 in CCl_4.

It seems generally accepted that in CCl_4, the molecules of which are symmetrical and have no resultant dipole moment, there is no solvation

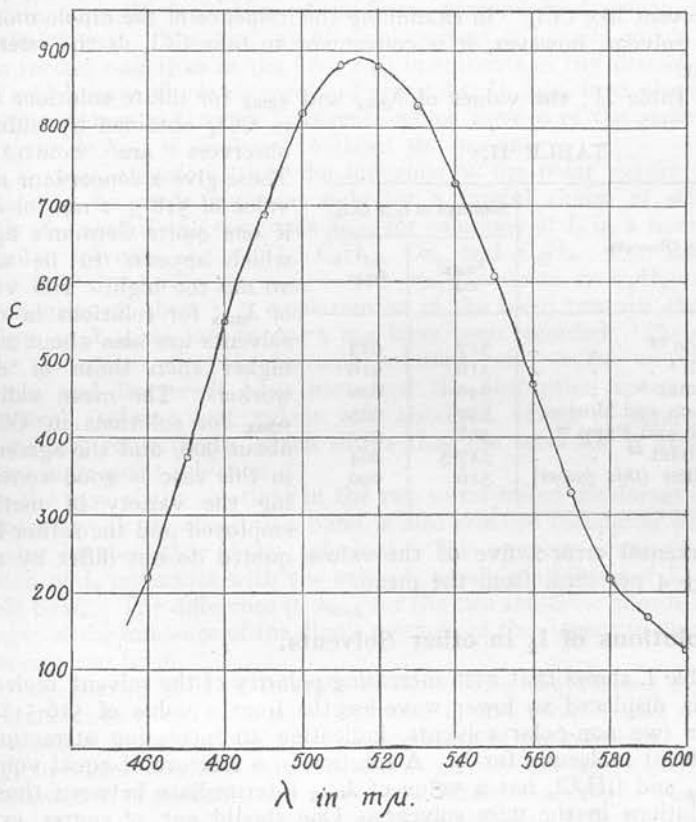


FIG. 1.—I_2 in CCl_4.

of the I_2 molecules. The inertness of this solvent is supported by the work of Chatelet [13] who found Beer's Law valid for solutions of I_2 in

CCl_4 over a wide range of concentration. In the course of this work it was found that the absorption curve of a solution which had been kept in the dark for three months, was unchanged.

Some interaction due to van der Waals forces between I_2 and solvent molecules is to be expected even in the case of solutions in CCl_4. It would be of interest to compare the values of λ_{max} and ϵ_{max} for the solution with those for I_2 vapour. The only extinction measurements available for the vapour are those of Vogt and Königsberger.[16] From their data one can calculate, for the region of low pressures in which they found Beer's Law valid, a mean value of ϵ_{max} of 850 (for temperatures of 48-56°), in good agreement with the values for violet solutions (*cf.* Table I.). For I_2 pressures corresponding to a concentration of 0·001M, however, the values of ϵ_{max} are much lower. Vogt and Königsberger found λ_{max} for the vapour to be about 506 mμ, but this result is questioned by Kuhn,[17] who states that it should be about 400 Å, on the U.V. side of the convergence limit at 4995 Å, *i.e.*, at about 460 mμ. This statement is based only on analogy with the corresponding values for Br_2 and Cl_2. In the absence of reliable extinction coefficient data for I_2 vapour, therefore, it is not possible from absorption measurements to ascertain the existence or magnitude of any solvation effect for I_2 in a solvent like CCl_4. In examining the influence of the dipole moment of the solvent, however, it is convenient to take CCl_4 as the reference solvent.

In Table II., the values of λ_{max} and ϵ_{max} for dilute solutions of I_2 in CCl_4 obtained by different observers are compared. These give a concordant mean value of 518 ± 2 mμ for λ_{max}, if one omits Getman's figure, which appears to be about 20 mμ too high. His values of λ_{max} for solutions in other solvents are also about 20 mμ higher than those of other workers. The mean value of ϵ_{max} for solutions in CCl_4 is about 900, and the agreement in this case is good considering the variety of methods employed and the rather large experimental error: five of the values quoted do not differ by more than ± 4 per cent. from the mean.

TABLE II.

Observer.	Solutions of I_2 in CCl_4.	
	$\lambda_{max.}$ mμ.	$\epsilon_{max.}$
1. Brode [18]	517	913
2. Groh [1]	518	918
3. Getman [2]	540	820
4. Gillam and Morton [3]	520	985
5. Groh and Papp [19]	518	922
6. Chatelet [13]	517·5	864
7. Walker (*this paper*)	516	890

(*b*) Solutions of I_2 in other Solvents.

Table I. shows that with increasing polarity of the solvent molecules λ_{max} is displaced to lower wave-lengths from a value of 516-518 mμ for the two non-polar solvents, indicating an increasing attraction of the solvent molecules for I_2. A solution in a mixture of equal volumes of CCl_4 and CH_2Cl_2 has a value of λ_{max} intermediate between those of the solutions in the pure solvents. One should not, of course, expect

[16] Vogt and Königsberger, *Z. Physik*, 1923, **13**, 292.
[17] Kuhn, *Z. Physik*, 1926, **39**, 87.
[18] Brode, *J. Amer. Chem. Soc.*, 1926, **48**, 1877.

the amount of displacement to be related in a simple way to the dipole moment of the solvent (measured for the gaseous state, or in dilute solution), since other factors will obviously have to be taken into account, *e.g.*, the dipole moment and the polarisability of the individual links of the molecule, and stereo-chemical effects which may hinder the approach of I_2 and solvent molecules. Scheibe [11] has shown from absorption spectrum measurements of ketones and other substances, that the influence of the solvent on the absorption of radiation by a molecule in solution may be manifested in two ways, *viz.*, by a shift of the whole band to longer or shorter wave-lengths, with a corresponding change in λ_{max}, and secondly, by a change in the height or intensity of the absorption band. A third type of change may occur when a definite chemical reaction takes place between the solvent and the dissolved molecules with the production of one or more new molecular species, in which case the character of the absorption curve may be entirely changed.

A shift of the absorption band to lower wave-lengths indicates an increased stability of the molecule or part of the molecule responsible for the particular band. It appears that in the case of I_2 solutions such a displacement occurs mainly as a result of two processes, *viz.*, (*a*) polarisation of the I_2 molecule by the electrical field of the polar solvent molecule, and (*b*) formation of addition compounds between the I_2 and the solvent. The amount of displacement is usually much larger in the second case than in the first, *e.g.*, in solvents of the alcohol series, all of which have dipole moments of about 2·0 D, λ_{max} is at about 440-450 mμ, whereas in " violet " solvents which have μ of the same order of magnitude λ_{max} is displaced to about 500 mμ only.

It is clear, therefore, that the influence of the polar nature of the solvent can be made apparent only by a careful choice of solvents. This is also seen if one compares λ_{max} for solutions of I_2 in a number of non-polar solvents, *e.g.*, CCl_4, C_6H_{14}, CS_2 and C_6H_6. For solutions in the first three solvents $\lambda_{max} = 518$ mμ,[19] whereas in C_6H_6, as has been mentioned, there is a displacement of the band towards the U.V. —values of λ_{max} as low as 494·5 mμ have been recorded. The nature of the solvation effect in benzene solutions still seems uncertain.[20] Ornstein and Burgers [21] have measured the absorption spectra of I_2 in benzene, toluene and xylene and obtained values of $\lambda_{max} = 497$, 488 and 463 respectively, which shows that the solvation is greater in the two more polar solvents.

In the case of the solutions in the two unsaturated dichloroethylenes the intensity of the absorption band is also reduced compared with the intensity in the other violet solutions. This suggests some chemical reaction of I_2 molecules with the solvent, possibly addition of I_2 at the double bond. The difference in λ_{max} for the two solutions affords a good example of the influence of the dipole moment of the solvent in displacing the absorption band.

In conclusion, it is of interest to summarise the various types of interaction which can take place between I_2 and solvent, and the corresponding changes in the absorption spectrum of the solutions.

(1) In violet solutions in inert, non-polar solvents (*e.g.*, C_6H_{14}, CCl_4) the interaction is probably due to van der Waals forces only. λ_{max} is at about 516-518 mμ and the colour of these solutions is very similar to

[19] Groh and Papp, *Z. physik. Chem.*, 1930, **149**, 153.
[20] *Cf.* also Müller, *Physik. Z.*, 1933, **34**, 703.
[21] Ornstein and Burgers, *Akad. Amst. Verh.*, 1920, **29**, 573.

that of the vapour, for which λ_{max} is uncertain. Benzene, although it is a non-polar solvent, is exceptional.

(2) In polar solvents (*i.e.*, those having a resultant dipole moment) which do not have much chemical attraction for the I_2 molecules (*e.g.*, the halogeno-paraffins) there is an attractive force due to polarisation of the I_2 molecules by the electrical field of the solvent molecules. λ_{max} may be displaced to 490-500 mμ and the solutions are violet-red in colour. The magnitude of the displacement (up to about 20 mμ) is of the order to be expected from an attractive force of the van der Waals type.

(3) In solvents of the class described by Lachmann [22] as "unsaturated" (*e.g.*, alcohols, ethers, nitriles, etc.), chemical valency forces result in the formation of molecular addition compounds between I_2 and solvent molecules. λ_{max} is displaced to about 440 mμ and the solutions are red-brown in colour.

(4) With many of the solvents of class (3) further chemical reaction occurs in which I atoms replace H atoms in the solvent molecule, with the formation firstly of HI, and then, as a secondary reaction, of HI_3. This is accompanied by a gradual disappearance of the brown colour and by the appearance in the absorption spectrum of the more intense bands at 350 and 290 mμ characteristic of HI_3.

These remarks apply to dilute solutions of I_2. In more concentrated solutions there may also be interaction of I_2 molecules with one another (*cf.* Groh and Papp [19]). In some cases, particularly in the brown solutions, colloidal complexes may be formed.[23]

I should like to thank Dr. W. R. Angus, Dr. E. Teller and Dr. J. Weiss for helpful discussion.

Summary.

(1) Measurements have been made of the molecular extinction coefficient, ϵ, between 440 and 600 mμ for violet solutions of I_2 in the following solvents:

(1) CCl_4, (2) $CHCl_3$, (3) CH_2Cl_2, (4) $C_2H_4Cl_2$, (5) *n*-C_3H_7Cl, (6) *n*-C_4H_9Cl, (7) *cis*- and (8) *trans*-$C_2H_2Cl_2$.

(2) For solutions in the two non-polar solvents (1) and (8) λ_{max} is at 516-518 mμ. For solutions in the other solvents λ_{max} is displaced towards the U.V., the displacement increasing roughly with the dipole moment of the solvent. The height and width of the absorption band in solutions 1-6 are approx. constant.

(3) The various types of interaction between I_2 and solvent are discussed with regard to their influence on the absorption spectrum of I_2.

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[22] Lachmann, *J. Amer. Chem. Soc.*, 1903, **25**, 50.
[23] Chirnoaga and Chirnoaga, *Z. anorg. Chem.*, 1934, **218**, 273.

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B.2.

ELECTRON AFFINITY SPECTRUM OF FERROUS ION IN AQUEOUS SOLUTION

By

R. H. Potterill, O. J. Walker, and J. Weiss

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Electron Affinity Spectrum of Ferrous Ion in Aqueous Solution

By R. H. Potterill, O. J. Walker, and J. Weiss (The Sir William Ramsay Laboratories of Inorganic and Physical Chemistry, University College)

(*Communicated by F. G. Donnan, F.R.S.—Received* 1 *April*, 1936)

I—Introduction

The study of the absorption spectra of ions in aqueous solution, in relation to the photochemical processes taking place, has up to the present been concerned mainly with anions. The spectra of some of these have been interpreted as electron affinity spectra, according to the views of Franck and Haber.* For example, for the I^- ion the elementary process, corresponding to the long wave-length limit of the continuous absorption spectrum in aqueous solution, is represented as

$$I^- HOH + h\nu \rightarrow I + H + OH^-.$$

An electron is transferred from the negative ion to one of the water molecules in its hydration shell.

It is not possible to predict on theoretical grounds alone whether a similar process may also occur in the case of cations. In a recent note,† however, one of us has shown that by irradiating a solution of $FeSO_4$ with ultra-violet radiation an appreciable amount of gaseous hydrogen is evolved, with the simultaneous formation of Fe^{+++} ion. This was explained by assuming that a primary process analogous to that of the electron affinity spectrum occurs, viz.,

$$Fe^{++} HOH + h\nu = Fe^{+++} + H + OH^-.$$

This paper is concerned with a more detailed discussion, from this point of view, of the absorption spectrum and photochemical behaviour of the ferrous ion in aqueous solution.

II—Absorption Spectrum of Ferrous Salts in the Ultra-Violet Region

No quantitative data are available in the literature regarding the absorption of aqueous solutions of ferrous salts in the ultra-violet region.

* ' S.B. preuss. Akad. Wiss.,' p. 250 (1931).

† Weiss, ' Nature,' vol. 136, p. 794 (1935).

From the few investigations which have been made on the absorption of these solutions even the limits of absorption are not certain. Byk and Jaffe,* who measured the absorption limits of 0·01 to 0·2 M solutions of $FeSO_4$ and of $FeCl_2$, state that absorption commences only below 3000 A. Anderson† measured the extinction coefficients of solutions of the same two salts in the infra-red and visible regions down to about 4000 A, and his curves indicate that these solutions have an absorption band extending from about 4000 A towards the ultra-violet.

Measurements have, therefore, been made of the extinction coefficients of solutions of ferrous chloride and of ferrous sulphate for wave-lengths down to about 2200 A. The very strong absorption of ferric salts below 4000 A, to which we shall refer later, makes it necessary to use solutions of ferrous salts which are as free as possible from ferric ions. In order to be able to estimate small concentrations or establish complete absence of ferric ion, extinction measurements have also been made of solutions of ferric salts as no such data have been previously recorded for wave-lengths below 4000 A.

1—Experimental

Absorption Measurements—These were made, using two different types of technique, viz., (*a*) a Hilger rotating sector photometer in conjunction with a Hilger medium quartz spectrograph and a tungsten-steel spark as light source, and (*b*) a small Hilger quartz spectrograph combined with a rotating sector and a hydrogen discharge-tube as light source. Good agreement between the two methods was obtained. The solvent and solutions were contained in 1 cm quartz cells and the measurements were made with the freshly prepared solutions. In the curves of figs. 1 and 2 the values of log ε are plotted against corresponding wave-lengths in A units. The molecular extinction coefficient ε is defined by the expression $\varepsilon = \frac{1}{cd} \log \frac{I_0}{I}$, where c is the concentration of Fe^{++} or Fe^{+++} in gram atoms of Fe per litre, and d is the length of the absorption cell in cm.

Preparation of Solutions—Pure $FeCl_2$, $4H_2O$, or $FeSO_4$, $7H_2O$, were dissolved in about 100 cc of an approximate 0·1 M solution of the corresponding acid, which had previously been boiled for an hour in an atmosphere of oxygen-free nitrogen. Some spirals of pure iron wire were placed in the ferrous salt solution, which was then boiled for an hour or two, allowed to cool, and a portion of it transferred to the absorption cell,

* 'Z. phys. Chem.,' vol. 68, p. 339 (1910).

† 'Proc. Roy. Soc., Edin.,' vol. 33, p. 35 (1913).

the whole operation being performed in an atmosphere of nitrogen. A separate portion of the solution was titrated with standard $KMnO_4$ solution. The concentrations of the ferrous salt solutions used varied from about 0·04 to 0·7 M.

For the measurements of the absorption due to the Fe^{+++} ion, solutions of ferric alum and of ferric chloride (obtained by the oxidation of ferrous chloride solutions) were used. The concentration varied from about 4×10^{-3} to 4×10^{-5} gm atoms Fe per litre, and measurements were made with 0·1 and 1·0 cm absorption cells. The solutions all contained an excess of free acid to prevent hydrolysis.

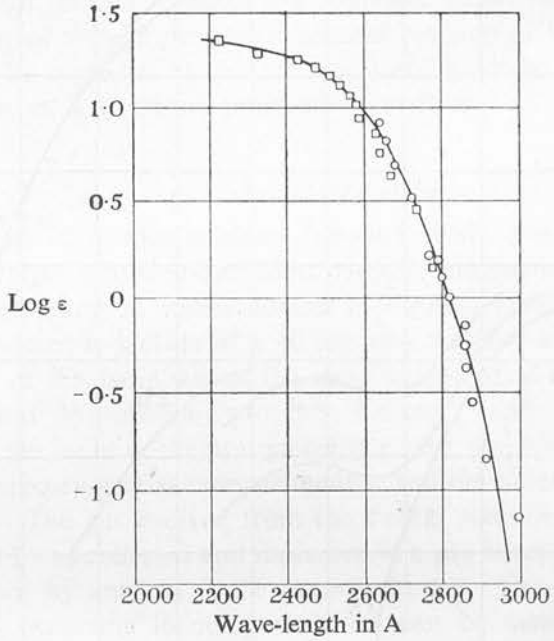


FIG. 1—Absorption spectrum of ferrous ion in aqueous solution. □ $FeSO_4$; ○ $FeCl_2$.

2—RESULTS

The values of log ε obtained with the pure solutions of $FeCl_2$ and of $FeSO_4$, when plotted against the wave-length, all lie on a single smooth curve (fig. 1), which is independent of the acid concentration and of the nature of the anion. This curve can therefore be regarded as the characteristic absorption curve of the ferrous ion in aqueous solution. No appreciable absorption occurs above 2900 A, in agreement with the qualitative observations of Byk and Jaffe.*

* 'Z. phys. Chem.,' vol. 68, p. 339 (1910).

If, however, precautions have not been taken during the preparation of the ferrous salt solution to reduce any Fe^{+++} ion present, marked absorption above 3000 A occurs, as shown in curves 2, 2*a*, and 2*b* (fig. 2). Curve 2 was obtained with solutions of $FeSO_4 . 7H_2O$ (0·11 and 0·04 M) in dilute H_2SO_4, immediately after making up the solution in an atmosphere of hydrogen, and curves 2*a* and 2*b* with the same two solutions after

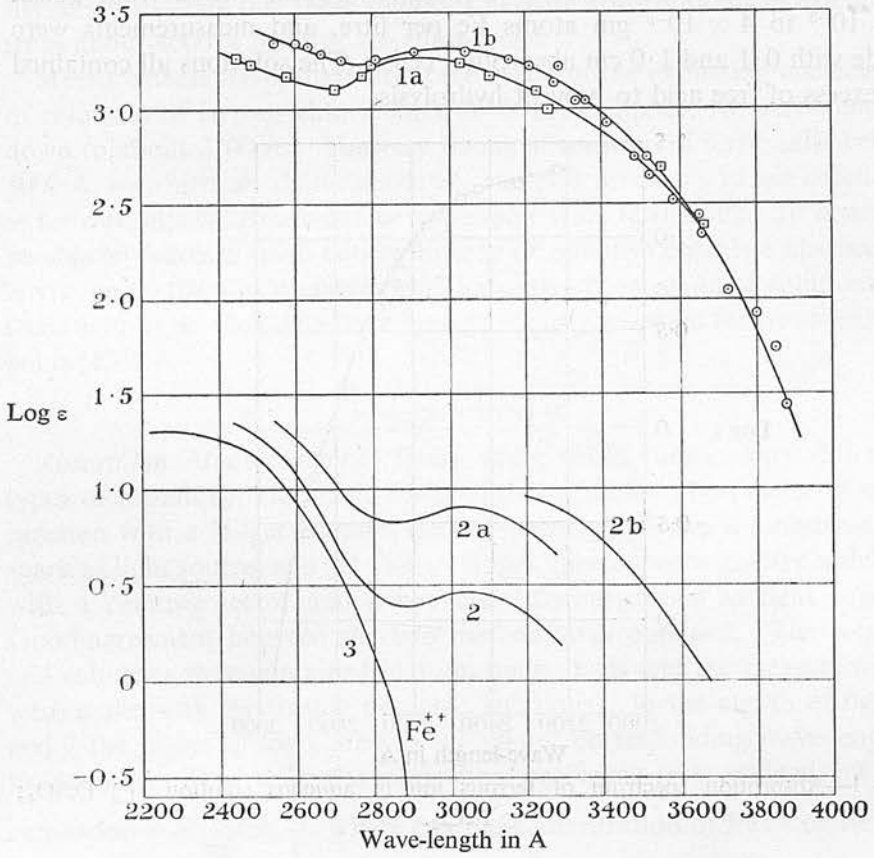


FIG. 2—Absorption spectrum of ferric sulphate (1*a*) and ferric chloride (1*b*) in aqueous solution.

standing for a short time. The additional absorption with a maximum at about 3000 A is due to the presence of Fe^{+++} ion, as will be seen by comparison with curves 1*a* and 1*b*. These are the absorption curves obtained with the solutions of ferric sulphate and chloride, respectively, and consist of a very intense absorption band with a maximum at about 3000 A, which can be attributed to the Fe^{+++} ion. By means of curves 1*a* and 1*b*, it can be calculated that the concentration of Fe^{+++} in the ferrous

solution which gave curves 2–2*b* was of the order of 10^{-3} × concentration of Fe^{++} ion. The absorption band commencing at 4000 A indicated by Anderson's results* is undoubtedly due to the presence of Fe^{+++} ion in his solutions.

III—Photochemical Behaviour of Ferrous Ion in the Ultra-Violet Region

In the preliminary note by one of us on this subject (*loc. cit.*), the photochemical formation of molecular hydrogen and of Fe^{+++} ions from solutions of ferrous sulphate was reported. That no previous observations exist of this simple photochemical reaction of the Fe^{++} ion may probably be attributed to the fact that it can be observed only in solutions of ferrous salts which are practically free from Fe^{+++} ion.

1—*Experimental*

Solutions of ferrous sulphate (about 0·5 M), prepared by dissolving $FeSO_4 . 7H_2O$ in boiled-out dilute H_2SO_4 solution in an atmosphere of oxygen-free nitrogen were irradiated in a quartz vessel, which formed one of the concentric jackets of a 40-cm long mercury arc lamp. The construction of this lamp was of the same water-cooled type as that used by Haber and Wansborough-Jones,† Farkas,‡ and others.§ We shall describe the inner concentric jacket (*i.e.*, the one which is nearer to the central mercury arc) as compartment I, and the outer jacket as compartment II. The gas evolved from the $FeSO_4$ solution contained in compartment I was collected and measured in a gas-burette over mercury, and was shown by analysis to be pure hydrogen. Quantum efficiencies of reactions occurring in compartment I can be measured by placing a standard substance in compartment II. For the present purpose, monochloracetic acid which absorbs in about the same region as the Fe^{++} ion, was used. This substance, in the spectral region below 2800 A, is decomposed with a quantum efficiency of about 0·9–1·0, according to the reaction‖

$$ClCH_2 . COOH + H_2O + h\nu = HO . CH_2 . COOH + H^+ + Cl^-.$$

* ' Proc. Roy. Soc. Edin.,' vol. 33, p. 35 (1913).

† ' Z. phys. Chem.,' B, vol. 18, p. 103 (1932).

‡ ' Z. phys. Chem.,' B, vol. 23, p. 89 (1933).

§ Frankenburger and Klinkhardt, ' Z. phys. Chem.,' B , vol. 15, p. 421 (1932).

‖ Rudberg, ' Z. Physik,' vol. 24, p. 247 (1924); L. Farkas, ' Z. phys. Chem.,' B, vol. 23, p. 89 (1933).

b 2

* Section III is not included in the work submitted in the thesis.

O.J.W

The amount of photo-decomposition is measured by titration of the Cl^- produced. From the difference in the quantities of $ClCH_2 . COOH$ decomposed under comparable conditions using (*a*) $FeSO_4$ solution, and (*b*) H_2O in compartment I, it is possible to calculate the quantum efficiency, ϕ, for the formation of molecular hydrogen from the $FeSO_4$ solution.

In determining the quantum efficiency by this method the following conditions must be fulfilled. Firstly, the standard substance in compartment II must, in every case, absorb completely the light transmitted through compartment I, which can be achieved by using a sufficiently high concentration (about 1 M) of monochloracetic acid. Secondly, with non-homogeneous light, which was actually used, the absorption region of the standard substance must overlap that of the substance under investigation. The absorption data show that the absorption of $FeSO_4$ extends to slightly longer wave-lengths than that of the monochloracetic acid. It was shown, however, that this would introduce an error of not more than 10%, by performing a control experiment in which a $FeSO_4$ solution was irradiated with light which had been filtered through a solution of 1·0 M monochloracetic acid (*see* experiment 7, Table I).

2—*Results*

The values of ϕ under different conditions are summarized in Table I.

IV—Discussion

The observed photochemical reaction of ferrous sulphate solutions in the region of absorption due to the Fe^{++} ion can be attributed to the primary process

$$Fe^{++} HOH + h\nu \rightarrow Fe^{+++} + H + OH^-. \qquad (1)$$

The energy required for the transfer of an electron to a water molecule in the hydration layer of the Fe^{++} ion is given by the following expression

$$h\nu = D_{H_2O} + I_{Fe^{++}} - E_{OH^-} - X,$$

where

D_{H_2O} = energy required to dissociate an H_2O molecule into H and OH (= 115 kcal/gm mol).

$I_{Fe^{++}}$ = ionization potential of Fe^{++} ion.

E_{OH^-} = electron affinity of OH radical.

X = difference in potential energy before and after electron transfer.

TABLE I

No. of experiment	Time of exposure in secs t	Liquid in compartment I (vol 200 cc)	Vol. of H_2 in cc (at N.T.P.) in t secs from compartment I	Vol. of H_2 in cc (at N.T.P.) in t secs from compartment II	Mols $H_2 \times 10^5$ formed per sec during reaction in I	Mols $H_2 \times 10^5$ formed per sec during reaction in II	Liquid in compartment II (vol 375 cc)	Mols $Cl^- \times 10^5$ formed per sec in II	Quantum efficiency ϕ
1	1800	H_2O	—	—	—	—	1·0 M Cl . CH_2COOH	0·75	0·030
	1800	0·5 M $FeSO_4$ + 0·1 M H_2SO_4	9·2	—	0·0228	—	1·0 M Cl . CH_2COOH	—	
2	2100	H_2O	—	—	—	—	1·0 M Cl . CH_2COOH	1·11	0·020
	2100	0·5 M $FeSO_4$ + 0·25 M H_2SO_4	10·5	—	0·0222	—	1·0 M Cl . CH_2COOH	—	
3	1800	H_2O	—	—	—	—	1·0 M Cl . CH_2COOH	1·00	0·033
	1800	0·4 M $FeSO_4$ + 0·25 M H_2SO_4	13·3	—	0·0330	—	1·0 M Cl . CH_2COOH	—	
4	1800	H_2O	—	—	—	—	1·0 M Cl . CH_2COOH	0·95	0·047
	1800	0·5 M $FeSO_4$ + 0·25 M H_2SO_4	18·2	—	0·045	—	1·0 M Cl . CH_2COOH	—	
5	2000	H_2O	—	16·6	—	0·037	0·5 M $FeSO_4$ + 0·25 M H_2SO_4	—	—
6	2000	2·0 M H_2SO_4	—	15·7	—	0·035	0·5 M $FeSO_4$ + 0·25 M H_2SO_4	—	—
7	2000	1·0 M $ClCH_2COOH$	—	1·8	—	0·004	0·5 M $FeSO_4$ + 0·25 M H_2SO_4	—	—

According to the Franck-Condon principle, the hydration energy of the OH^- ion does not enter into the expression, as the H_2O dipoles cannot adjust themselves during the rapid electron transfer process. Therefore, X consists mainly of the difference in hydration energies of the Fe^{++} and Fe^{+++} ions, since the water dipoles are already oriented round the Fe^{++} ions, and by the electron transfer process are merely subjected to an increased field and thus increase their energy without moving.*

In spite of the high ionization energy of ferrous ion *in vacuo*, the energy required for the electron transfer process in solution is considerably smaller ($\sim 4{\cdot}5$ electron volts), and consequently the effect due to X must be large. The fact that the work function of metals is considerably decreased in media of high dielectric constant† can be regarded as a similar phenomenon.

Reaction (1) is followed by a combination of the H atoms to give molecular hydrogen

$$H + H \rightarrow H_2. \qquad (2)$$

If the Einstein equivalence law were to hold exactly, the maximum quantum efficiency, ϕ, for the formation of H_2 should be equal to $\frac{1}{2}$. As will be seen from Table I, however, ϕ is always considerably less than this, viz., about 1/50–1/20.‡ This can be explained by a reverse reaction, which competes for the H atoms, as follows

$$Fe^{+++} + H \rightarrow Fe^{++} + H^+. \qquad (3)$$

This view is supported by the experimental observation that when a sufficient concentration of Fe^{+++} ions are present initially in the solution, the evolution of gaseous hydrogen may be completely suppressed. For example, a concentration of Fe^{+++} greater than $10^{-3} \times [Fe^{++}]$, which may easily be produced by atmospheric oxidation before irradiation, is sufficient to reduce ϕ to practically zero.§

For the photostationary state we have the condition

$$\frac{d[H]}{dt} = k_1 I_{abs} - k_3 [H] [Fe^{+++}] - 2k_2 [H]^2 = 0,$$

where I_{abs} = absorbed light intensity per second, and k_2 and k_3 are the

* We are indebted to Professor N. F. Mott for this suggestion.

† Groschew, ' Phys. Z. Sowjet,' vol. 7, p. 617 (1935).

‡ In the preliminary note (Weiss, *loc. cit.*) ϕ referred to gram-atoms of hydrogen formed and not, as in this paper, to gram-mols.

§ The absorption of the Fe^{+++} present acting as " inner filter " does not, under the conditions of the experiment, exceed 10% of the total light absorbed.

velocity constants for reactions (2) and (3), respectively. From this relationship it can be shown that the quantum efficiency is given by

$$\phi = \frac{k_2}{2k_2 + k_3 \dfrac{[Fe^{+++}]}{[H]}}. \qquad (4)$$

If $k_2 \gg k_3 \cdot \dfrac{[Fe^{+++}]}{[H]}$, then $\phi = \frac{1}{2}$, which is the value to be expected if Einstein's Law holds exactly.

For the actual experimental conditions where $\phi = 1/20$, one can use expression (4) to estimate the magnitude of k_3. From the absorption measurements $[Fe^{+++}]$ can be estimated to be about 5×10^{-4} mols/litre. The hydrogen atom concentration cannot differ greatly from the stationary H atom concentration measured by Geib and Harteck* (*i.e.*, 10^{-5} mm Hg, equivalent to 5×10^{-10} mols/litre). We then obtain $k_3 \sim k_2 \times 10^{-5}$. Since every binary collision between H atoms in solution (where a third body is practically always present) can be assumed to be effective, one can conclude that in reaction (3) one in every 10^5 collisions is effective. This means that the energy of activation of the electron transfer process (3) is about 7 k cals.

In conclusion, we should like to express our sincere thanks to Professor F. G. Donnan, F.R.S., for his great interest and encouragement.

V—Summary

The extinction coefficients of solutions of ferrous and ferric sulphates and chlorides have been measured for wave-lengths down to 2200 A. The Fe^{++} ion in solution has in this region a continuous absorption with a long wave-length limit of about 2900 A.

On the irradiation of $FeSO_4$ solutions below 2900 A, gaseous hydrogen is evolved, with the simultaneous formation of ferric ion. The quantum efficiency for the formation of molecular hydrogen has been measured and found to have a value of about 1/20.

The observed photochemical reaction is attributed to a primary process analogous to that of the electron affinity spectrum, viz.,

$$Fe^{++}\ HOH + h\nu \rightarrow Fe^{+++} + H + OH^-, \qquad (1)$$

followed by the combination reaction of the hydrogen atoms formed

$$H + H \rightarrow H_2, \qquad (2)$$

* 'Z. phys. Chem.,' B, vol. 15, p. 116 (1931).

which competes with the reverse reaction

$$Fe^{+++} + H \rightarrow Fe^{++} + H^{+}. \qquad (3)$$

The experimental observations lead to the conclusion that the energy or activation of the simple electron transfer process (3) in the forward direction is about 7 k cals.

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B. 3.

THE ULTRA-VIOLET ABSORPTION SPECTRA OF IODOFORM AND OF OTHER TRI-IODIDES IN SOLUTION

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THE ULTRA-VIOLET ABSORPTION SPECTRA OF IODOFORM AND OF OTHER TRI-IODIDES IN SOLUTION.

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Received 11th December, 1936.

The apparent similarity of the absorption spectra of iodoform and of potassium tri-iodide was first noted by Crymble, Stewart and Wright in 1910.[1] Later quantitative measurements of the absorption spectra were made by Lowry and Sass.[2] According to them, both iodoform and potassium tri-iodide give two bands with maxima at about 2900 and 3500 Å., and the shape of the whole absorption curve is very similar in the two cases. In a further paper on this subject, Gilbert, Goldstein and Lowry,[3] showed that the absorption spectrum of potassium tri-iodide is really characteristic of the I_3^- ion, since the position of the two bands is independent of the cation present in the solution (K^+, Cs^+ or quaternary ammonium ion). Dissociation into $I_2 + I^-$, which is especially marked in aqueous solution, diminishes the intensity of the two bands but does not change the form of the absorption curves, as neither of the dissociation products has any appreciable absorption in the region in which the I_3^- ion absorbs strongly.

Lowry and Sass considered that the similarity in the absorption spectra of iodoform and of the I_3^- ion amounted almost to an identity of the two curves, and that therefore some definite similarity of structure between the two compounds was indicated. Since the ordinary formulæ do not point to any similarity in structure, they suggested that the reason might be found in the presence in both compounds of three contiguous atoms of iodine in the space model " from which all traces of the bonds between the atoms have been erased." This picture is admittedly unconventional, and no definite structural formulæ were put forward. The available evidence on the spatial arrangements of the iodine atoms in the two compounds is opposed to any real similarity of structure. Whereas in iodoform the three iodine atoms form a pyramidal structure

[1] Crymble, Stewart and Wright, *Ber.*, 1910, **43**, 1183.
[2] Lowry and Sass, *J.C.S.*, 1926, 622.
[3] Gilbert, Goldstein and Lowry, *J.C.S.*, 1931, 1092.

with the carbon atom to which they are directly linked, it appears from X-ray measurements that in the I_3^- ion there is, in the crystalline state at any rate, a very nearly linear arrangement of the tri-iodide group.[4] In this complex group two iodine atoms are probably co-ordinated with the third central atom, which has two of its valency group of ten electrons present as an " inert pair." [5]

The experimental observation, therefore, that iodoform and the I_3^- ion give very similar absorption spectra in solution, is not easy to explain theoretically, and it seemed more probable that the absorption curve of iodoform found by Lowry and Sass is not really characteristic of that molecule, but is complicated by the occurrence of reactions in the solution which form I_3^- or HI_3. It is well known [6],[7] that solutions of iodoform in alcohol are readily decomposed photochemically with the production of I_2, and in alcoholic solution this would inevitably [8] produce I_3^- or HI_3. Furthermore, Scheibe [9] measured the absorption of iodoform in alcohol and obtained results differing somewhat from those of Lowry and Sass. He also found that the absorption curve in hexane differed slightly from that in alcohol.

It seemed worth while to investigate further the absorption spectrum of iodoform to see to what extent the two so-called iodoform absorption bands are (*a*) really characteristic of the iodoform molecule, and (*b*) occur also in the absorption spectra of other normal tri-iodide molecules of the iodoform type, *i.e.* in which three iodine atoms are covalently linked to some central atom.

For this purpose, measurements of the absorption spectrum of iodoform in alcohol and in cyclohexane have been made, and also of methyl iodoform, for which no previous absorption data exist. The absorption spectra of phosphorus, arsenic and antimony tri-iodides have also been measured. These substances, when dissolved in non-ionising solvents, are largely in the covalent state, there being a gradual increase in the dipole moment of the molecule in passing from phosphorus tri-iodide ($\mu = 0$) to antimony tri-iodide ($\mu = 1{\cdot}58$).[10] Practically no data were available on the absorption of these substances, but since the commencement of this work a paper appeared by Kato and Someno [11] on the absorption spectra of the tri-halides of the phosphorus family in the vapour state and dissolved in ether. These results, which are of a semi-quantitative nature, will be referred to later.

Experimental.

Absorption Measurements.

These were made by using a Hilger rotating sector photometer in conjunction with a tungsten-steel spark as light source and a Hilger medium quartz spectrograph, the spectra being recorded on Wellington Ortho Process plates. The solvents and solutions were contained in 1 cm. quartz cells. In the curves, values of log ϵ are plotted against the corresponding wave-length in A units. The molecular extinction coefficient ϵ is defined

[4] Mooney, *Z. Krist.*, 1935, **90**, 143.
[5] Sidgwick, *Ann. Reports*, 1933, **30**, 126.
[6] Dubrisay and Emschwiller, *Bull. Soc. Chim.*, 1935, **2**, 127.
[7] Gibson and Iredale, *Trans. Faraday Soc.*, 1936, **32**, 571.
[8] Batley, *ibid.*, 1928, **24**, 438.
[9] Scheibe, *Ber.*, 1925, **58**, 586.
[10] Malone and Ferguson, *J. Chem. Physics*, 1934, **2**, 99.
[11] Kato and Someno, *Inst. Phys. Chem. Res. Tokio*, 1935, **28**, 95.

by the expression $\epsilon = \frac{1}{cd} . \log \frac{I_0}{I}$, where c is the concentration of the solute in gm. mols./litre, d the length of the absorption cell in cm., and I_0 and I the intensities of the incident and transmitted light, respectively.

Solvents.

Ethyl alcohol : Absolute alcohol was dried over CaO and redistilled.
Cyclohexane : The " specially purified for spectroscopy " B.D.H. Product.
Benzene : A.R. benzene, redistilled.

Preparation of Iodides.

Iodoform : B.D.H. product recrystallised from absolute alcohol, m.p. 118·5° — 119·5° C.
Methyl iodoform : Prepared according to the method given by Boissieu.[12] The preparation was found to be more successful by diluting the methyl chloroform with CS_2 and adding it very slowly to the aluminium iodide solution. The final product was recrystallised from absolute alcohol, and the whole preparation was carried out in the dark. Yellow crystals m.p. 93° C.
Phosphorus tri-iodide : The preparation given by Traxler [7] and Germann,[13] involving the direct combination of the elements in carbon disulphide solution was used. The solvent was removed in a current of dry CO_2, by warming on a water bath. M.p. 57°-61° C.
Arsenic and Antimony tri-iodides : The purest B.D.H. products were recrystallised from " analar " benzene, m.p. 146° C. and 168° C. respectively.

Absorption Spectrum of Iodoform and Methyl Iodoform.

(a) Iodoform in Ethyl Alcohol.—Preliminary measurements, in which the solutions were examined soon after being prepared, but were not protected from exposure to light during the preparation, gave an absorption curve (*cf.* curve 2, Fig. 1) in which the height and position of the two maxima agree fairly well with those of Lowry and Sass.[2] The following experiments show, however, that in such solutions an appreciable amount of photo-decomposition of the iodoform has occurred. Iodoform, which had been recrystallised four times from alcohol, was dissolved in alcohol to a known concentration, the crystallisation and preparation of the solution being performed in the dark. Absorption measurements were then made in which the solution was exposed only to the light of the spark source and, in order to reduce to a minimum the photo-decomposition during this operation, the solution in the cell was renewed after every minute of total exposure to the spark. The absorption curve obtained in this way is shown in curve 1, Fig. 1, and the values of λ_{max} and log ϵ_{max} are tabulated in Table I. The results agree very well with those of Scheibe,[6] who also took precautions to reduce the photo-decomposition of the iodoform during the absorption measurements. The effect of a small amount of decomposition of the iodoform on the absorption curve is illustrated by curves 3 and 4 in Fig. 1. These were obtained with the same solution that gave curve 1, but which had been exposed to ordinary daylight for five and ten minutes respectively, before carrying out the absorption measurements. The result of even these short exposures is that the absorption maxima increase in intensity and at the same time approach the wave-lengths of 2900 and 3600 Å., which are the values of λ_{max} characteristic of the two I_3^- bands (*cf.* Table I.). Since the latter are about 15-20 times more intense than the iodoform bands, the height of the absorption curve of iodoform may

[12] Boissieu, *Bull. Soc. Chim.*, 1888 (2), **49**, 16.
[13] Traxler and Germann, *J. Amer. Chem. Soc.*, 1927, **49**, 307.

be appreciably increased by even a small amount of decomposition, and this appears to have occurred under the conditions used by Lowry and Sass, since their absorption curve lies between curves 3 and 4 of Fig. 1.

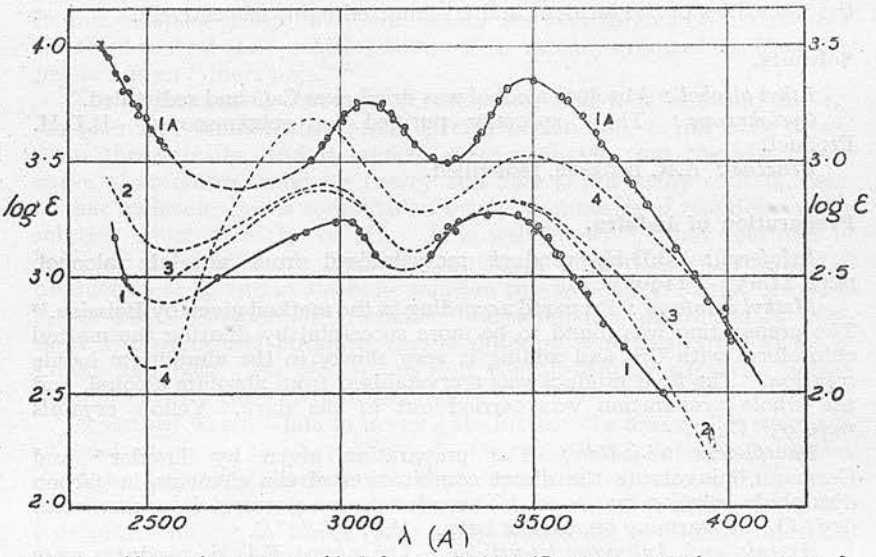


FIG. 1.—Absorption curves of iodoform solutions (C. = $1{\cdot}2 \times 10^{-4} - 2{\cdot}5 \times 10^{-3}$ gm. mols/litre) in alcohol (curve 1), and in cyclohexane (curve 1A). Log ϵ: left hand scale curves, 1-4; right-hand curve 1A.

TABLE I.

Solvent.	1st Maximum.		2nd Maximum.		Reference.
	$\lambda_{max.}$	$\log \varepsilon_{max.}$	$\lambda_{max.}$	$\log \varepsilon_{max.}$	
(a) Iodoform.					
Alcohol . .	3010	3·25	3410	3·30	Curve 1, Fig. 1.
,,	3010	3·25	3410	3·35	Scheibe.[9]
Alcohol . .	2960	3·41	3440	3·32	Curve 3, Fig. 1.
,,	2940	3·5	3450	3·45	Lowry and Sass.[2]
,,	2920	3·7	3500	3·53	Curve 4, Fig. 1.
Cyclohexane .	3070	3·27	3490	3·35	Curve 1A, Fig. 1.
Hexane . .	3070	3·26	3480	3·35	Scheibe.[9]
(b) Methyl Iodoform.					
Alcohol . .	3065	3·26	3400	3·18	Curve 1, Fig. 2.
Cyclohexane .	3110	3·21	3440	3·20	Curve 2, Fig. 2.
(c) Caesium Tri-iodide.					
Alcohol . .	2900	4·60	3600	4·46	Gilbert, Goldstein and Lowry.[3]

(b) Iodoform in Cyclohexane.—Solutions of iodoform in cyclohexane are also sensitive to light and slowly turn violet-pink due to the liberation of free iodine. Since iodine dissolved in cyclohexane has only a

weak absorption in the region where iodoform absorbs strongly, we should expect the absorption curve of iodoform in this solvent to be less influenced by the photo-decomposition than that obtained with the alcoholic solution.*

The absorption curve of iodoform in cyclohexane is given in Fig. 1 (curve 1A). The data in Table I. show that the position and height of the maxima agree well with those found by Scheibe using hexane as solvent.† The measurements were reproducible even when the iodoform solution had become faintly pink after exposure to daylight for half-an-hour. The whole absorption curve of iodoform in cyclohexane is shifted about 60-80 A. towards the visible region compared with the curve in alcohol, but otherwise the absorption is very similar in the two solvents (it should be noted that curve 1A in Fig. 1 is plotted with a different ordinate scale).

(c) Absorption Spectrum of Methyl Iodoform.—Solutions of methyl iodoform are more readily decomposed on exposure to light than solutions of iodoform. By using the procedure described in the case of iodoform it was found possible, however, to prepare colourless solutions

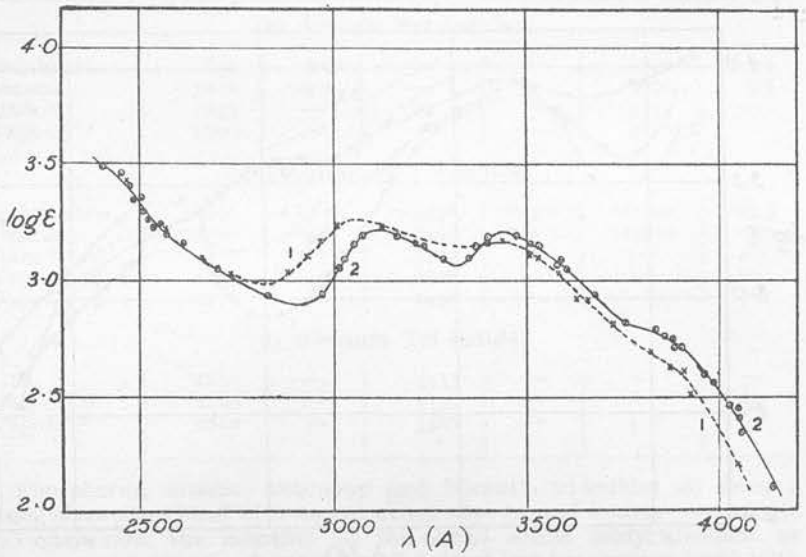


FIG. 2.—Absorption curves of methyl iodoform solutions (C. = $5 \times 10^{-5} - 1{\cdot}2 \times 10^{-3}$ gm. mols/litre) in alcohol (curve 1), and in cyclohexane (curve 2).

of methyl iodoform in alcohol and in cyclohexane and to measure their absorption spectra before any appreciable decomposition took place. The absorption curves are shown in Fig. 2, and the characteristic data are compared in Table I. with the data for iodoform. The absorption curves of the two substances are very similar, but in both the methyl iodoform curves the existence of a third less intense band at about 3800 A. is indicated. On continued exposure of the solution of methyl iodoform in alcohol to light, the two bands became more pronounced, and the values

* Although the formation of I_3^- cannot take place in a solvent like cyclohexane, there is a possibility that HI_3 may be formed. Absorption measurements were made of solutions in cyclohexane of (*a*) I_2, (*b*) HI, and (*c*) I_2 + HI. There was no increased absorption with (*c*) such as would be expected if HI_3 were formed (*cf.* also, Tinkler, *J.C.S.*, 1907, **91**, 996; Warburg and Rump, *Z. Physik*, 1928, **47**, 305).

† The extinction curve of iodoform in hexane has recently been measured by Hunter, Qureishy and Samuel (*J.C.S.*, 1936, 1576), who find $\lambda_{max} = 3075$ and 3490 A. Their values of log K_{max} are only about 2·4, but it is not certain whether their K is really the same as ϵ.

of λ_{max} approached those characteristic of the I_3^- ion, exactly as in the case of iodoform. In cyclohexane it was more easy to obtain reproducible results.

The results which have been described for iodoform and methyl iodoform show that the two " iodoform " bands are characteristic of this type of molecule. They are, however, much less intense than those which are characteristic of I_3^-, and the maxima occur at different wave-lengths. While there is a qualitative similarity between the absorption of the two types of molecule, the quantitative data show that it does not amount to identity of the absorption curves.

Absorption Spectra of the Tri-iodides of the Phosphorus Group.

The chief difficulties in attempting to measure the absorption curves of solutions of the tri-iodides of this group are due to (*a*) the limited solubility of some of these substances in suitable solvents, and (*b*) the instability

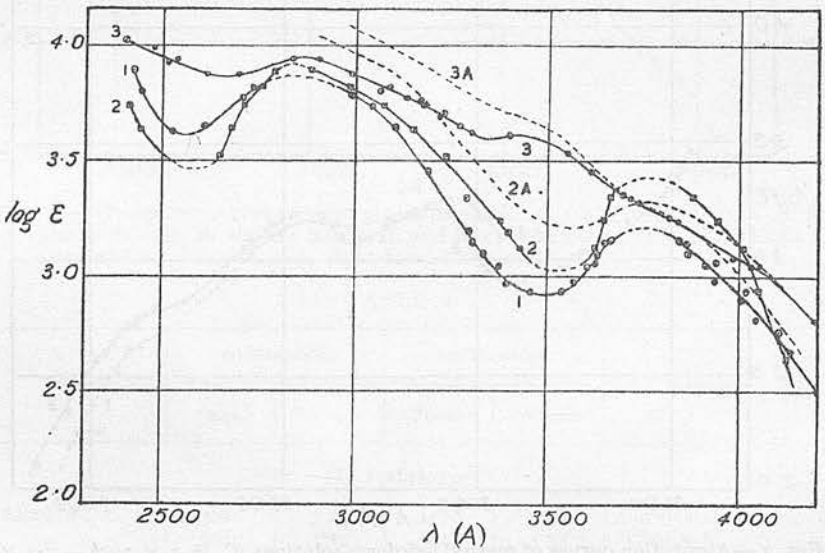


FIG. 3.—Absorption curves of solutions in cyclohexane of PI_3 (curve 1), AsI_3 (curve 2), and SbI_3 (curve 3), and of solutions in benzene of AsI_3 (curve 2A), and SbI_3 (curve 3A).

of many of the solutions and the consequent uncertainty whether the absorption observed is really due to the molecular species originally dissolved. For the latter reason (*e.g.*, formation of I_3^-) reliable results could not be obtained with alcohol as solvent.

In the case of phosphorus, arsenic, and antimony tri-iodides, it was possible to measure the absorption curves of the solutions in cyclohexane. With the arsenic and antimony compounds measurements were also made in benzene solution over a more restricted wave-length range. The solutions of these substances in cyclohexane or in benzene are colourless or pale yellow when freshly prepared, but turn pink more or less rapidly due to liberation of iodine. As in the case of iodoform, however, a small amount of decomposition does not appreciably affect the absorption curve in this type of solvent.

The absorption curves of the three tri-iodides are shown in Fig. 3. These curves were obtained with solutions varying in concentration from $0{\cdot}7\text{-}7{\cdot}0 \times 10^{-4}$ gm. mols/litre. In the case of SbI_3 it was found that below

this concentration range Beer's Law is not strictly obeyed—there is a gradual displacement of the whole curve to higher values of log ϵ with increased dilution. Owing to the small solubility of AsI_3 in cyclohexane the practically saturated solution had to be used for the absorption measurements. The characteristics of the absorption curves in cyclohexane are summarised in Table II., and compared with the other data available in the literature regarding the absorption of these tri-iodides in the vapour state and in solution.

TABLE II.

Solvent.	$\lambda_{max.}$	log $\epsilon_{max.}$	$\lambda_{max.}$	log $\epsilon_{max.}$	$\lambda_{max.}$	log $\epsilon_{max.}$
(a) Phosphorus Tri-iodide.						
Cyclohexane .	2850	3·82	—	—	3750	3·2
(b) Arsenic Tri-iodide.						
Cyclohexane .	2840	3·90	—	—	3770	3·4
Benzene .	<3000	~4·0	—	—	3770	3·3
Ether [11] .	2853	—	—	—	3773	—
(Vapour) [14] .	2840	—	—	—	3860	—
(c) Antimony Tri-iodide.						
Cyclohexane .	2860	3·95	~3450	~3·6	~3800	~3·3
Benzene .	<3000	~4·0	~3450	~3·7	~3800	~3·3
Ether [11] .	2875	—	3440	—	—	—
(Vapour) [11] .	2893	—	3500	—	—	—
(Vapour) [14] .	2770	—	3430	—	—	—
(d) Bismuth Tri-iodide.						
Ether [11] .	2830	—	3333	—	—	—
(Vapour) [11] .	2830	—	3350	—	—	—
(Vapour)[14] .	2810	—	3386	—	—	—

Phosphorus, arsenic, antimony and bismuth tri-iodides all have a strong absorption band with λ_{max} at about 2850 A., and from measurements in cyclohexane the intensity of this band seems fairly constant at log $\epsilon_{max} = 3{\cdot}8$ to $4{\cdot}0$. A second well-defined but less intense band with λ_{max} at about 3800 A. occurs in the curves of phosphorus and arsenic tri-iodides, but with antimony iodide its existence is marked by the increased absorption due to a third band at about 3400 A. For bismuth iodide no quantitative data could be obtained, since it is practically insoluble in cyclohexane. The data of Kato and Someno,[11] and of Butkow,[14] however, indicate that the absorption of bismuth iodide is similar to that of the antimony compound.

Comparison of the absorption curves of these tri-iodides in cyclohexane, especially those of phosphorus and of arsenic with the absorption curves of iodoform and of methyl iodoform in the same solvent, shows that all these substances have two absorption bands in the near ultra-violet region with maxima at 2800-3100 and 3400-3800 A. Apart from this general similarity, however, the following differences in the absorption curves of the iodoform and phosphorus tri-iodide groups should be noted :.

(*a*) In the PI_3 group the maxima are at about 2850 and 3800 A., whereas the " iodoform " bands are much closer together at about 3100 and 3500 A.

(*b*) The " iodoform ". bands are very nearly equal in intensity (log $\epsilon_{max} \sim 3{\cdot}3$), but in the PI_3 group the shorter wave-length band

[14] Butkow, *Z. Physik*, 1934, **90**, 810.

($\log \epsilon_{max} \sim 4$) is about five times more intense than the longer wave-length band ($\log \epsilon_{max} \sim 3{\cdot}3$).

(*c*) With SbI_3 and BiI_3 the existence of a third band between the two above-mentioned maxima is indicated.

It is seen, therefore, that in all these normal tri-iodides definite differences in the absorption curve can occur, in spite of the general similarity of structure.

Comparison of the Absorption Spectra of Iodides Containing One or More Iodine Atoms.

In conclusion, it is of interest to see how the region of maximum absorption varies in the ultra-violet absorption spectra of covalent iodides as the number of iodine atoms attached to one common atom increases. With iodides in the gaseous, liquid or dissolved states, the continuous absorption spectrum may show either one or two maxima, the positions of which appear to depend mainly on the number of iodine atoms which are linked to one common atom in the molecule.[15] As the number of iodine atoms is increased, there is a gradual displacement of the region of maximum absorption to higher wave-lengths. This is particularly well shown in the series methyl iodide, methylene iodide, and iodoform,[2,16] and corresponds to a progressive loosening of the whole molecule in this series.*

From the results described in this paper, along with previously recorded data, it can be stated that practically all molecules containing either three or four iodine atoms linked to one central atom have two absorption bands in the near ultra-violet region 2800 to 4000 Å. The maxima of these bands do not correspond exactly to those given by iodoform, but vary according to the nature of the central atom. The positions of the two maxima for many such molecules (*cf. e.g.* PI_3 and AsI_3) are fairly constant, however, at about 2800-2900 and 3700-3800 A., respectively, and only slightly influenced by the nature of the atom to which the iodine atoms are bound. The bands occur, for example, in neutral molecules such as phosphorus tri-iodide or stannic iodide [17,18] or even in complex ions of the TlI_3^{--} or PbI_4^{--} type.[19]

As regards the primary light absorption process, there is a considerable amount of spectrographic and photo-chemical evidence that with non-ionised iodides, the light absorption in the region 2000 to 4000 Å. results in a dissociation of the molecule with the production of free iodine atoms.

The alkali iodide vapours, for example, show two absorption maxima at 3240 and 2580 Å., which can be attributed to dissociation giving iodine atoms in the normal ($^2P_{3/2}$) and first excited ($^2P_{1/2}$) states, respectively. The frequency difference of the two maxima ($\Delta\nu = 8000$ cm.$^{-1}$) corresponds very closely with the energy of excitation of the iodine atom $^2P_{1/2} - {}^2P_{3/2} = 7600$ cm.$^{-1}$). With the alkyl iodides on the other hand,[21]

[15] Butkow, *Acta Physicochim. U.R.S.S.*, 1935, **3**, 205.

[16] Henrici, *Z. Physik*, 1932, **77**, 35.

* The preparation of CI_4 and the measurement of its absorption spectrum were attempted, but it is too unstable in solution to give reliable results ; *cf.* also Lowry and Sass (*loc. cit.*,[2] p. 628).

[17] Grant, *Trans. Faraday Soc.*, 1935, **31**, 433.

[18] Banov, *Acta Physicochim., U.R.S.S.*, 1935, **2**, 733.

[19] Fromherz and Kun Hou-Lih, *Z. physikal. Chem., A*, 1931, **153**, 321.

[20] Schmidt-Ott, *Z. Physik*, 1931, **69**, 724.

[21] Herzberg and Scheibe, *Z. physikal. Chem., B*, 1930, **7**, 390.

only the maximum at about 2600 Å. occurs, both for the gaseous state and in solution, and can be attributed to a dissociation giving $^2P_{1/2}$ iodine atoms.

In the case of tri-iodides the frequency differences of the two bands is always about 5600 (*e.g.* CHI_3) to 8700 cm.$^{-1}$ (*e.g.* PI_3). Although this frequency difference does not correspond exactly in every case with the energy of excitation of the iodine atom, it is reasonable, as has been suggested elsewhere [7,15] to relate the two maxima to dissociation giving $^2P_{3/2}$ and $^2P_{1/2}$ iodine atoms (with molecules like SnI_4 and BiI_3 illuminated by ultra-violet light of shorter wave-length (about 2500-2100 Å.) a dissociation in which an activated I_2 molecule is eliminated in one act is possible).[22] For covalent iodides containing two iodine atoms bound to a common atom, fewer absorption spectrum data are available, but it seems that in general only one maximum exists in the region under discussion. This maximum occurs in the wave-length range 2600 to 3000 A.,* *i.e.* intermediate between the maxima for mono- and tri-iodides, respectively, which correspond to dissociation giving exited $^2P_{1/2}$ iodine atoms.

Note *added in proof* (10*th February*, 1937): A paper has just been published by C. B. Allsopp on the absorption spectra of tri-iodides (*Proc. Roy. Soc.*, 1937, **158**, 167). His conclusions regarding the primary processes associated with the two absorption bands of tri-iodides containing covalently bound iodine are essentially the same as those in our paper. It is doubtful, however, whether the intensities of the two bands of the tri-iodides of As, Sb, and Bi shown in Fig. 1 ($\log \epsilon_{max} \sim 4$) are really characteristic of these molecules.

Summary.

(1) The absorption spectra of iodoform and of methyl iodoform in alcohol and in cyclohexane have been measured for the wave-length range 2000-4000 A.

(2) The absorption curves of both substances are very similar to one another and differ from the curve characteristic of I_3^-.

(3) The absorption spectra of PI_3, AsI_3 and SbI_3 in cyclohexane have been measured and compared with that of iodoform.

(4) The results are discussed in relation to the absorption of iodides in general.

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[22] Terenin, *Compt. Rend. Acad. Sci. U.R.S.S.*, 1935, **1**, 482.

* *E.g.* mercuric [15] iodide 2700, methylene [2] iodide 2960.

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B 4

THE CONTINUOUS ABSORPTION SPECTRUM OF BROMINE IN SOLUTION

BY

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By C. L. Child and O. J. Walker.

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The nature of the electronic transition involved in the primary light absorption process can be interpreted from direct observations of the absorption spectrum only in the case of dilute gaseous systems, and particularly where the absorption spectrum is of the discontinuous type showing regions of band structure. In more condensed systems, and especially in solutions, there is usually a smoothing out of any fine structure found when the absorbing molecules are in the dilute gaseous state, and the absorption spectra of such systems are generally completely continuous with only comparatively broad bands.

It is customary, therefore, in considering the primary process of light absorption in solutions to make use of information obtained with gaseous systems. If there is a close similarity between the absorption of a substance in the gaseous and dissolved states, and in particular if there is no appreciable difference in the wavelength of maximum absorption of an electronic band in the two states, it is usually considered reasonable to assume that the absorption process is accompanied by the same electronic transition in both cases. Most investigations concerning the influence of a solvent on light absorption have dealt with the effect of the solvent on the wavelength of maximum absorption. A better comparison of the absorption of a substance in the gaseous and dissolved states can be obtained from the complete extinction coefficient curves in the two cases, yet in the voluminous literature recording absorption measurements there are very few data from which a reliable comparison of such a kind can be made.

Examples of fairly simple molecules for which extinction coefficient curves are available both for the gas and for solutions are: halogens, H_2S, H_2O_2, $(CH_3)_2CO$, alkyl halides.

From such data the conclusion can be drawn that in the absence of marked solvent effects the absorption in the two states is very similar.[1] Differences do occur, however, and it is of interest to consider in more detail such differences between the absorption of a simple molecule in the gaseous and dissolved states. For this purpose the halogen molecules are very suitable, especially as they have frequently been used in the study of photochemical reactions, and the theoretical interpretation of their absorption spectra in the gaseous form is reasonably complete. When, however, one attempts to make a detailed comparison of this kind from the literature on the absorption of the halogens, the paucity of extinction data for the gases and the disagreement between the extinction coefficient data of different observers for solutions are very apparent.

The extinction coefficient curve of iodine vapour has only recently been accurately determined by Rabinowitsch and Wood.[2] The previous

[1] Bonhoeffer and Harteck, *Grundlagen der Photochemie*, 1933, p. 83.
[2] Rabinowitsch and Wood, *Trans. Faraday Soc.*, 1936, **32**, 540.

erroneous data of Vogt and Koenigsberger,[3] combined with inaccurate absorption curves of iodine solutions, indicated an absorption for the latter considerably greater than for the vapour, whereas it now seems established that for inert solvents like carbon tetrachloride the extinction coefficient curve of iodine in solution is only slightly higher than that of the vapour. For solutions in non-inert solvents, solvation effects or chemical changes may occur, so that the " gaseous " absorption curve may be considerably modified. In the case of bromine the data quoted by Rabinowitsch and Wood show that the maximum extinction coefficient is increased by about 30 per cent. in going from the vapour to a solution in carbon tetrachloride. If, however, the data of Acton, Aickin and Bayliss [4] for bromine vapour are compared with those of Bovis [5] for bromine dissolved in carbon tetrachloride, it is found that over a wide region the extinction coefficient curves are almost identical. For chlorine, the data quoted by Rabinowitsch and Wood indicate a 50 per cent. greater absorption in solution than in the gas, whereas Barratt and Stein's [6] value of the maximum extinction coefficient for a solution in carbon tetrachloride is more than double that obtained for the gas by Gibson and Bayliss.[7]

The influence of the solvent on the absorption curves of the three halogens has been discussed by Rabinowitsch and Wood.[2] Further reference to their interpretation of the solvent effects will be made later. The brief reference made above to the literature on the extinction coefficient curves of the halogens shows that there is some doubt as to whether the increased absorption discussed by Rabinowitsch and Wood really does exist. It seemed desirable, therefore, to obtain further experimental evidence. Bromine was chosen in the first place, since for this molecule the maximum absorption is in the continuous region and the absorption curves available for the vapour seem reliable and concordant.* The discrepancies referred to above can probably be attributed to the uncertainty of the solution data, caused by the difficulty of avoiding reaction of the bromine with many of the solvents. In the case of bromine the absorption curve of the pure liquid has been measured by Porret,[8] so that a comparison can be made of the extinction curves for the range of state gas → solution → liquid.

Experimental.

Materials.

Bromine : Analar Br_2, containing not more than 0·0005 per cent. I_2.

Solvents : (1) CCl_4. The 99·9 per cent. product was thoroughly washed with conc. H_2SO_4, dilute NaOH, H_2O, dried and distilled over P_2O_5, first and last fractions being neglected. (2) $CHCl_3$. The anæsthetic product was treated as above. (3) $C_6H_5NO_2$, Analar, redistilled over P_2O_5. (4) CH_3COOH, Analar. (5) CS_2 Analar. (6) H_2O, good conductivity water. (7) EtOH, absolute. (8) C_6H_6, Analar purified for M.W. determinations.

[3] Vogt and Koenigsberger, *Z. Physik*, 1923, **13**, 292.
[4] Acton, Aickin and Bayliss, *J.Chem. Physics*, 1936, **4**, 474.
[5] Bovis, *J. Phys. Rad.*, 1929, **10**, 267.
[6] Barratt and Stein, *Proc. Roy. Soc.*, 1929, **122**, 582.
[7] Gibson and Bayliss, *Physical Review*, 1933, **44**, 188.
* See refs. 4 and 10. Recalculation of Ribaud's absorption coefficients, χ in terms of ϵ, gives a value of $\lambda_{max.} = 4150$ A., as compared with the value 4210 A. which corresponds to $\chi_{max.}$
[8] Porret, *Proc. Roy. Soc.*, 1937, **162**, 414.

Measurements.

In most cases the concentration of the bromine solution was determined by titration of a stock solution against standard $Na_2S_2O_3$ solution after the addition of excess KI. Other solutions were made up by accurate dilution of the stock solution. The range of concentrations used is shown in Table I.

TABLE I.

Solvent.	Concentration Range Used.	$\lambda_{max.}$	$\epsilon_{max.}$	δ.
CCl_4	M./50—M./500	4170 A.	242	1230 A.
$CHCl_3$	M./50—M./200	4130 A.	212	1170 A.
CS_2	M./220—M./440	4195 A.	441	950 A.
C_6H_6	M./200—M./500	4140 A.	334	915 A.
$C_6H_5NO_2$*	M./225—M /450	—	—	—
$CH_3 . CO . OH$	M./90—M./450	4070 A.	220	1330 A.
H_2O	M./50—M./420	3980 A.	226	1180 A.
EtOH	M./170—M./315	3710 A.	235	1280 A.

* Owing to the absorption of the solvent only the portion of the absorption curve shown in Fig. 2 could be obtained.

A Hilger Spekker photometer, in conjunction with a Hilger E3 quartz spectrograph and a tungsten steel spark as light source, was used for the extinction measurements. With the CCl_4 solutions some measurements were also made as a check with (*a*) a rotating sector photometer, and (*b*) a Hilger-Nutting photometer along with a Hilger V_2 glass spectrograph and a Pointolite lamp as light source. Good agreement between the three methods was obtained. In all the measurements Hilger 1 cm. adhesed quartz cells were used to contain the solutions and solvents.

The molecular extinction coefficient, ϵ, is defined in the usual way by the expression

$$\log \frac{I_0}{I} = \epsilon cl$$

where c = concentration in gm. mols./litre, and
l = length of absorbing layer (1 cm.).

All measurements were done at room temperature, except those with the solutions in ethyl alcohol. These measurements were made at $-75°$ C. in order to prevent chemical reaction.

Low-temperature Measurements.—For the temperature control of the absorption cells the following apparatus was devised and found to be convenient and satisfactory in use.

The box A, made of $\frac{1}{8}$-in. brass sheet, was of the dimensions indicated in Fig. 1. The front and back faces are cut out as shown at (*a*) and provided with end-plates B and B′, which can be screwed on so as to cover the openings. The plate B carries two brass tubes C and D, which are soldered on, while the corresponding tubes C′ and D′ slide freely but tightly through the plate B′. The quartz cells fit closely into the screw ends of the tubes C and D, which contain slots to allow for the insertion of the necks of the cells. With the cells in position the tubes C′ and D′ can then be screwed on to C and D, respectively. The assembly is completed by screwing the end plates B and B′ on to the front and back faces, respectively, of the box, and making all the joints liquid tight with plasticine. A small amount of P_2O_5 is placed in the tubes C, C′, D, and D′, to the outer ends of which quartz windows Q are attached by means of plasticine. A current of dry air blown over the outside of these windows prevents them from becoming frosted. The box is lagged on the outside with asbestos and filled with

a solid CO_2-alcohol mixture. In this way the absorption cells can be maintained at a temperature of about $-75°$ for at least half an hour and the optical path through them kept clear. The dimensions of the apparatus are such that it can be placed directly on the bench of the Spekker photometer.

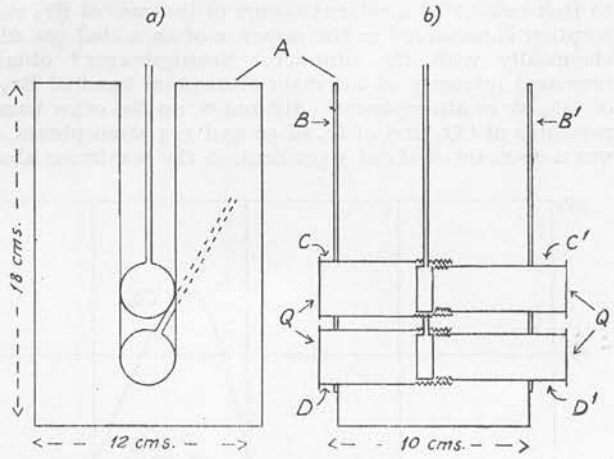


FIG. 1.

The pure solvent (ethyl alcohol) was placed in the bottom cell before assembling the apparatus. The solution of bromine was prepared by adding approximately the required amount of bromine to some alcohol cooled to $-78°$ and then transferring the cold solution quickly to the top cell which was already in the cooled box. The concentration of the cold solution was determined in the usual way by titration, allowance being made for the temperature in measuring the volume of the cold solution.

Results.

The extinction coefficient curves obtained at room temperature are reproduced in Fig. 2, together with the curve for bromine vapour obtained by Acton, Aickin and Bayliss [4] at 0° C. The corresponding values of $\lambda_{max.}$ and $\epsilon_{max.}$ are tabulated in Table I. It should be stated that in most solutions, over the concentration range used, there was a small decrease in ϵ with increasing concentration. The curves shown are the mean curves for the different concentrations. In Fig. 3 the extinction coefficient curve obtained with solutions of bromine in alcohol at $-75°$ is compared with that for bromine in carbon tetrachloride at room temperature.

The results for the main absorption band of bromine in solution can be summarised as follows :—

(1) The height of the extinction coefficient curve for the solutions is in every case greater than that of the gas and is dependent on the nature of the solvent. The ratios of $\epsilon_{max.}$ (solution) : $\epsilon_{max.}$ (gas) lie between the values 2·9 and 1·4 for the solvents investigated. Except for CS_2, the values of $\epsilon_{max.}$ of the solutions are between those of the gas and the liquid. For a given solvent, *e.g.*, CCl_4, the ratio of $\epsilon_{max.}$ (solution) : $\epsilon_{max.}$ (gas) is definitely greater for Br_2 than for I_2.

(2) The wavelength of maximum absorption in solution is unchanged or only slightly displaced towards the ultra-violet compared with that of the gas. Displacement appears to occur when the solvent is polar, but even with a solvent like water the displacement is small. With alcohol solutions, however, the displacement is comparable with that found with iodine.

(3) The shape of the absorption curve is much the same for the solutions as for the gas. The hump at 4900 A., which is quite evident in the curve for the gas, is smoothed out in the solution curves, which, however, remain

unsymmetrical about the maximum and are steeper on the short wavelength side.

It is of interest to examine whether an increase of absorption similar to that caused by a solvent occurs in the case of Br_2 vapour when the absorption is measured in the presence of an added gas which does not react chemically with the bromine. Koenigsberger [9] obtained a somewhat increased intensity of the main absorption band of Br_2 with the addition of CO_2 at 20 atmospheres. Ribaud [10], on the other hand, found that with pressures of CO_2 and of O_2 of 56 and 115 atmospheres, respectively, there was a decrease of about 5 per cent. in the maximum absorption coefficient.

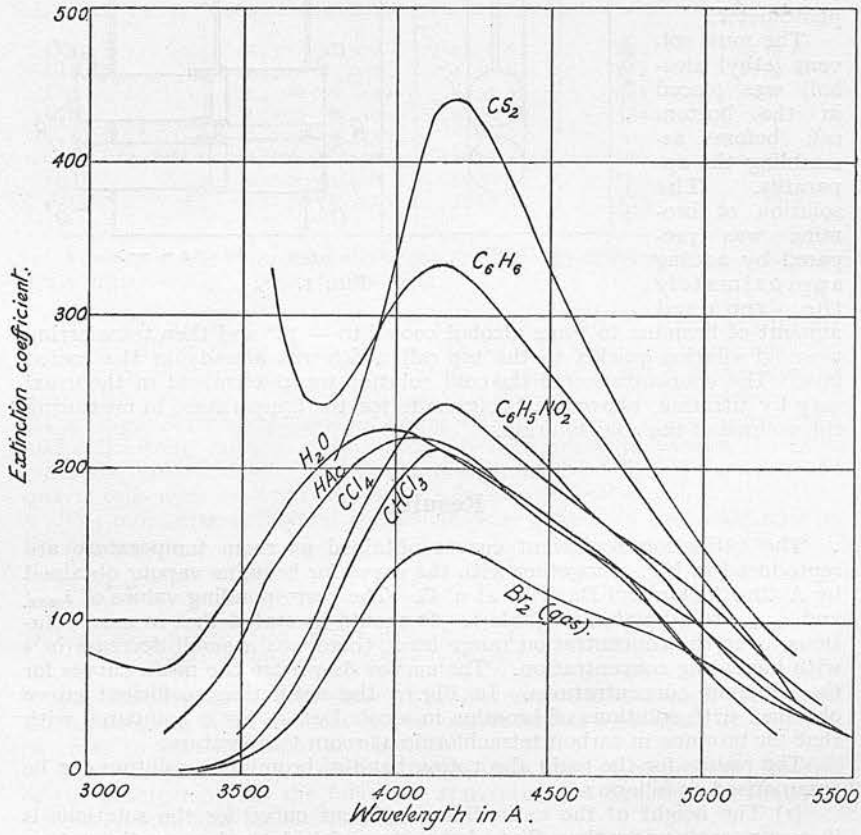


FIG. 2.—Extinction coefficient curves of bromine in various solvents at room temperature.

Shearer and Wright [11] claimed that there is a small increased absorption even when air at 1 atmosphere is added to Br_2 vapour, but their results were only qualitative.[12] We have determined the extinction coefficient curve of Br_2 vapour mixed with air at a total pressure of 1 atmosphere and obtained a curve which agrees almost exactly with that of Acton, Aickin and Bayliss.[4] There does not appear to be any case recorded in the literature where an increased absorption by Br_2 in the presence of an added

[9] Koenigsberger, *Z. Physik*, 1923, **13**, 308.
[10] Ribaud, *Ann. Physique*, 1919, **12**, 107.
[11] Shearer and Wright, *J. Chem. Soc.*, 1930, 1202.
[12] *Cf.* also Jost, *Z. physikal. Chem., A*, 1931, **153**, 148.

gas, comparable in magnitude with that found for solutions, has been observed.

If the concentration of the surrounding molecules is increased by varying the concentration of the bromine vapour itself, it appears that for low

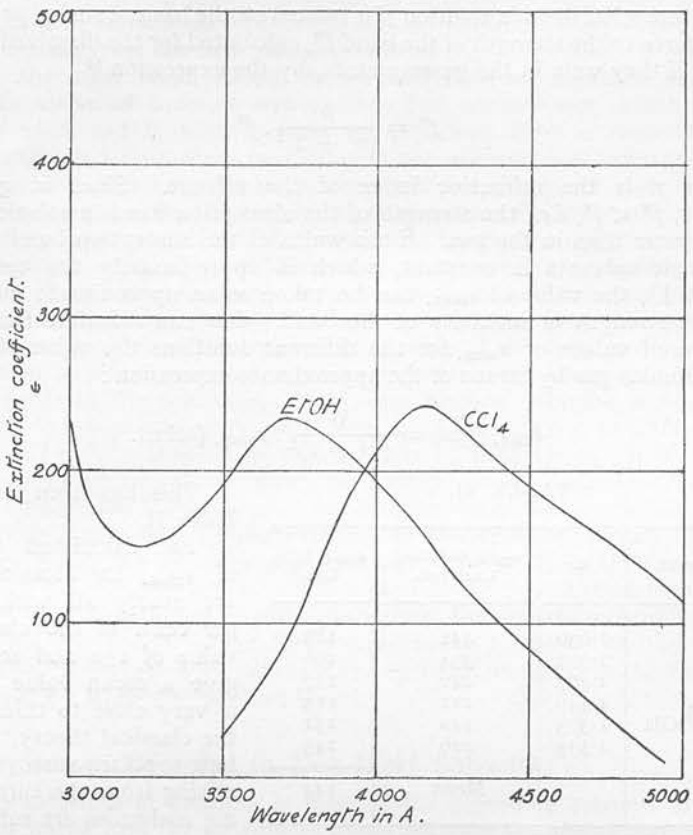


FIG. 3.—Extinction coefficient curves of bromine (*a*) in CCl_4 at room temperature and (*b*) in C_2H_5OH at — 75° C.

pressures of Br_2 the absorption is proportional to the concentration and Beer's Law is exactly obeyed.[13] This law is, however, not valid for the passage from the gaseous to the liquid state. Porret [8] has recently confirmed the observations of Bovis that $\epsilon_{max.}$ for liquid Br_2 is more than double that of the gas.

Discussion.

Absorption of Bromine in Inert Solvents.

In the continuous absorption band of bromine in the visible region the main effect of a chemically inert solvent is to increase the amount of absorption as compared with that of gaseous bromine, without causing any marked change in shape or displacement of the absorption curve.

According to both the classical and quantum theories of light absorption an increased absorption of bromine in solution compared with that in the gaseous state may be expected.

[13] Ribaud, *Ann. Physique*, 1919, **12**, 166.

Classically, the " strength " of an absorption band f, which may be taken as a measure of the intensity of the band, is influenced in the presence of a solvent by the Lorentz-Lorenz force, which arises from the polarisation of the surrounding molecules. The measured strength of the absorption band in solution f' is related on the basis of such a polarisation force to the strength of the band f'', calculated for the dissolved molecules if they were in the gaseous state, by the expression [14]

$$f'' = \frac{9}{(n^2+2)^2} \cdot f'$$

where n is the refractive index of the solvent. Since in general $n > 1$, $f'' < f'$, *i.e.*, the strength of the absorption band in solution will be greater than in the gas. If the width of the absorption band in the different solvents is constant, which is approximately the case (*cf.* Table I.), the value of $\epsilon_{max.}$ can be taken as an approximate measure of the strength or intensity of the band. One can calculate from the measured values of $\epsilon_{max.}$ for the different solutions the value of $\epsilon_{max.}$ for bromine gas by means of the approximate expression :

$$\epsilon_{max.}\,(\text{gas}) = \frac{9}{(n^2+2)^2} \cdot \epsilon_{max.}\,(\text{soln.}).$$

TABLE II.

Solvent.	n.	$\epsilon_{max.}$ (solution) Observed.	$\epsilon_{max.}$ (gas) Calc.
CS_2	1·630	441	183
C_6H_6	1·502	334	166
CCl_4	1·463	242	127
$CHCl_3$	1·446	212	114
CH_3COOH	1·373	220	131
H_2O	1·333	226	143
		Mean .	144

This has been done in Table II.

The calculated values of $\epsilon_{max.}$ for bromine gas are nearly all within 20 per cent. of the observed value of 150 and actually give a mean value which is very close to this. On the classical theory, therefore, polarisation forces arising from the surrounding molecules are sufficient to account for the increases in absorption of bromine of the order of magnitude found with inert or nearly inert solvents. There is no need to invoke the formation of complexes by association of bromine molecules with the solvent, as has been done, for example, in the case of solutions of bromine in carbon disulphide by Purkayastha and Ghosh.[15]

Rabinowitsch and Wood [2] have interpreted the influence of the polarisation of the surrounding molecules in terms of quantum theory and attribute the increased absorption of bromine in solution, for which our results provide further experimental evidence, to the nature of the electronic transition involved. Their explanation assumes that this transition is a ${}^3\Pi \leftarrow {}^1\Sigma$ one, *i.e.*, of the inter-combination type, which becomes more probable under the influence of a strong electric field.

Recent work on the absorption spectrum of bromine vapour, however, has raised further discussion of the electronic states involved in the absorption process. The extinction curve of bromine vapour shows a well-marked hump in the region of 4900 A. In the absorption curves

[14] Chako, *J. Chem. Physics*, 1934, **2**, 644.
[15] Purkayastha and Ghosh, *J. Indian Chem. Soc.*, 1927, **4**, 409.

of bromine solutions this hump is in general not so easily recognised, but the less steep slope of the curves on the long wavelength side of the maximum is quite evident. Rabinowitsch and Wood attributed the existence of this hump to the superposition on the main band series arising from the zero vibrational level of the ground electronic state of a second series coming from the first vibrational level.

On the other hand, Acton, Aickin and Bayliss [4] analysed the absorption curve of bromine vapour into two components, which they denote as A and B, with maxima at 4150 and 4950 A. respectively. They suggested that these two components are not due to transitions from the zero and first vibrational levels of the $^1\Sigma$ ground state to the vibrational levels of the $^3\Pi$ state, but to two separate electronic transitions, which they interpret as $^1\Pi \leftarrow {}^1\Sigma$ and $^3\Pi \leftarrow {}^1\Sigma$ for the A and B components, respectively. Alternative interpretations, however, are possible, and Mulliken [16] and Darbyshire [17] have shown that there are really three overlapping continua corresponding to transitions from the ground state to three different electronic states. One of the chief points under discussion in these various assignments of electronic transitions to the components of the continuous absorption band of bromine is whether the main A component of Acton, Aickin and Bayliss is due to a $^1\Pi \leftarrow {}^1\Sigma$ or to a $^3\Pi \leftarrow {}^1\Sigma$ transition or to a mixture of both types. If it arises mainly from a $^1\Pi \leftarrow {}^1\Sigma$ transition, as is suggested by Mulliken then this type of transition is not so weak in the halogens as was previously supposed. In Darbyshire's interpretation of the complex nature of the bromine band, the A component is assigned to a $^3\Pi \leftarrow {}^1\Sigma$ transition. While no definite conclusion in this direction can be obtained from the data on the absorption of bromine in solution, the results on the influence of the solvent would appear to be more easily explained on the basis of a $^3\Pi \leftarrow {}^1\Sigma$ transition for the main absorption continuum, in the manner suggested by Rabinowitsch and Wood.*

Absorption of Bromine in Non-Inert Solvents.

The solutions of bromine in most of the preceding solvents are relatively stable, and the differences found between the absorption curves of these solutions and that of bromine vapour can be ascribed mainly to the polarisation forces of the surrounding molecules. It seems unnecessary to assume the formation of solvates, and the shape of the absorption curves in solution indicates that very little chemical reaction between the bromine and the solvent takes place under the conditions of measurement.

With many solvents, however, it is more difficult or even impossible to determine the true absorption curve of bromine in solution, because of the more or less marked reactivity of the bromine with the solvent. Bromine reacts very readily with many of those organic solvents which in the case of iodine form brown solutions. It is difficult, therefore,

[16] Mulliken, *J. Chem. Physics*, 1936, **4**, 620.

[17] Darbyshire, *Proc. Roy. Soc.*, 1937, **159**, 93.

* An abstract of a paper to be published by Aickin, Bayliss and Rees (*cf. Proc. Roy. Soc.*, 1938, **167**, S. 105) on the effect of solvents on the continuous absorption spectrum of bromine provides further confirmation that non-aqueous solvents cause a marked increase in the absorption of bromine with a small or zero shift of the maximum towards the U.V. These authors, however, apparently favour the assignment of a $^1\Pi \leftarrow {}^1\Sigma$ transition to the main component of the bromine band.

to determine whether the bromine band is appreciably shifted towards the ultraviolet in such solvents, as is the corresponding band of iodine. The data for water and acetic acid, both of which are solvents in which iodine dissolves to give brown solutions, show that there is a small but definite displacement of the bromine band towards lower wavelengths as compared with its position for the vapour or for a solution in carbon tetrachloride (*cf.* Table I.). In freshly made solutions of bromine in these two solvents there is very little chemical reaction in diffuse daylight at the ordinary temperature. The hydrolytic reaction

$$Br_2 + H_2O \rightleftharpoons H^{\cdot} + Br' + HOBr,$$

with a hydrolysis constant of about $5{\cdot}8 \times 10^{-9}$,[18] does not appreciably reduce the concentration of free bromine in aqueous solution. The low values of the extinction coefficients found with many of the aqueous solutions—in some cases the values were less than the extinction coefficient of bromine vapour—are probably due to the disappearance of free bromine as a result of the hydrolysis reaction being accompanied by the photochemical process: $HOBr + h\nu \rightarrow H^{\cdot} + Br' + \frac{1}{2}O_2$ (*cf* Pagel and Carlson).[19] The position of $\lambda_{max.}$ is, however, quite reproducible in the aqueous solutions.

With a solvent like alcohol bromine reacts so rapidly at the ordinary temperature that reliable absorption measurements cannot be made. For this reason the absorption curve of bromine in ethyl alcohol was measured at about $-75°$, at which temperature the solutions appear to be relatively stable. The data given in the experimental part show that under these conditions there is a well-marked maximum in the absorption curve of bromine in alcohol at 3700 A., with $\epsilon_{max.} \sim 240$ and which shows little change in half an hour. If this corresponds to the absorption band of free bromine the displacement is about 450 A. or 2900 cm.$^{-1}$, as compared with the maximum of bromine vapour. (It is unlikely that the displacement is due to a temperature effect.[20]) The displacement for the corresponding case of iodine is about 3000 cm.$^{-1}$ The value of $\epsilon_{max.}$ for bromine dissolved in alcohol at $-75°$ C. is of the same order of magnitude as that for the solution in carbon tetrachloride at room temperature. The displacement of the absorption curve suggests that with bromine in alcohol solvation effects occur which are analogous to those responsible for the "brown" iodine solutions[21] and for the similar phenomenon which has been shown to occur with ICl and IBr.[22] In the case of bromine, however, there is no very obvious change in colour associated with these solvation effects, since the absorption of the unsolvated bromine is already near the U.V. end of the visible region. (The erroneous statement[23] is found in the literature that solutions of bromine in carbon disulphide are violet.) The difference in colour between solutions of bromine in various solvents is rather a difference in intensity.[24]

[18] *Cf.* Liebhafsky, *J. Amer. Chem. Soc.*, 1934, **56**, 1504.
[19] Pagel and Carlson, *J. Physical Chem.*, 1936, **40**, 613.
[20] Groh and Papp, *Z. physikal. Chem.*, 1930, **149**, 153.
[21] *Cf.* Walker, *Trans. Faraday Soc.*, 1935, **31**, 1432.
[22] Gillam, *Trans. Faraday Soc.*, 1933, **29**, 1132.
[23] *Cf.* Gmelin-Kraut, *Handb. anorg. Chem.*, 1931, Systemnummer 7, Brom, p. 89.
[24] *Cf.* Joseph, *J. Chem. Soc.*, 1915, **107**, 1.

Summary.

(1) The extinction coefficient curves for solutions of bromine in the following solvents have been determined : CCl_4, $CHCl_3$, CS_2, C_6H_6, $C_6H_5NO_2$, H_2O, CH_3COOH, C_2H_5OH.

(2) In inert solvents the main effect of the solvent on the bromine absorption band with $\lambda_{max.}$ 4150 A. is to increase the amount of absorption as compared with that of gaseous bromine, without causing any marked change in shape or displacement of the extinction coefficient curve.

(3) In polar solvents the wavelength of maximum absorption is more or less shifted towards the U.V. In alcohol solutions the shift is comparable in magnitude with that found for the corresponding iodine solutions.

(4) The influence of the solvent in increasing the amount of absorption is discussed.

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Appendix

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A QUARTERLY REVIEW OF THE HISTORY OF SCIENCE SINCE THE RENAISSANCE

(January, 1939)

AUGUST KEKULÉ AND THE BENZENE PROBLEM.

By

OSWALD J. WALKER, B.Sc., Ph.D.



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AUGUST KEKULÉ AND THE BENZENE PROBLEM.

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AUGUST KEKULÉ AND THE BENZENE PROBLEM.

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[PLATE I.]

AMONG the outstanding single contributions to the progress of both theoretical and applied chemistry a high place must be given to Kekulé's publication of the ring structure of benzene in 1865. Ever since that date the structure of this interesting molecule has continued to be the subject of speculation and of experimental investigation by chemists, and during the last few years there has been a considerable increase in our knowledge of it as a result of the application of modern theoretical methods and experimental technique [1]. In view of these recent advances it seems opportune to look again at some of the early developments in the understanding of the benzene problem. The discovery of many of the most important scientific truths has frequently been the result of a process of gradual evolution accompanied by occasional flashes of sudden inspiration. That this is true of the conception of the hexagonal benzene ring is illustrated by the way in which this idea was born in the mind of Kekulé. This forms one of the most interesting chapters in the history of benzene, and since many of the facts are, in general, none too familiar, a brief recapitulation of the more important stages by which Kekulé arrived at the idea of the ring structure will not be out of place.

Friedrich August Kekulé was born in Darmstadt on September 7, 1829 [2]. In the autumn of 1847, at the age of eighteen, he proceeded to the University of Giessen to take up the study of architecture, a subject which pleased him very well at first. In the summer term of 1848, however, he was prompted to attend Liebig's lectures on chemistry. Kekulé was so impressed by the personality of the master and the interest of the subject that he decided to abandon his architectural career and to devote himself to the study of chemistry, a change that evoked serious objections on the part of his relatives. After an interval of almost a year these objections were overcome, and Kekulé returned to Giessen, where he continued his general chemical studies until 1850, and then worked for a year in Liebig's private laboratory under his direct supervision. In his later life Kekulé always attached considerable importance to the

[1] Cf. *Nature*, 1938, **141**, 150.

[2] R. Anschütz, *August Kekulé*, Berlin, 1929, 1st edn., 2 vols.

influence that his early architectural studies had exerted in directing his interests towards the problem of molecular structure.

In 1851, as a result of the offer of financial assistance from his step-brother Karl, who was a corn-merchant in London, Kekulé was given the opportunity of extending his chemical experience beyond the Giessen laboratory. His own wish was to go to Berlin, but Liebig dissuaded him from this course [3]. " Go to Paris ", said Liebig, " there you will widen your outlook, there you will learn a new language and experience the life of a large city—but you will not learn any chemistry there ".

Liebig, however, proved to be wrong in the last part of his advice, for in Paris Kekulé came into contact with most of the contemporary French leaders of chemical theory, for example, Dumas, Wurtz, and Gerhardt. It is of particular interest to note that Kekulé became very friendly with Charles Gerhardt, with whom he had many long discussions about the topics that were of primary importance to chemistry, and especially organic chemistry, at that time. We know from Kekulé's own statement, to which further reference will be made later, that he obtained much first-hand knowledge about the classification of organic compounds in terms of the then much-discussed type theories, of which Gerhardt himself was one of the chief instigators and expounders. Kekulé remained over a year in Paris, and during this period his discussions with Gerhardt took place at least twice a week. He also was given the privilege of reading through the manuscript of the *Traité de Chimie Organique*, then ready for the press, in which Gerhardt developed his type theory based on the four types, hydrogen, hydrochloric acid, water, and ammonia. The teachings and influence of Gerhardt undoubtedly played a great part in directing Kekulé's interests along the lines of theoretical and structural chemistry.

In 1853 Kekulé, who had been in the meantime acting as private assistant to Baron von Planta in Switzerland, received the offer of an assistantship with John Stenhouse at St. Bartholomew's Hospital, London. He was recommended for the post by Liebig, of whom Stenhouse was an old pupil. The conditions of the appointment were to carry out qualitative and quantitative analyses between the hours of 9 a.m. and 4 p.m., excepting Sundays, and with no lecturing duties, at a salary of £60 a year [4]. Kekulé was not very attracted by this offer, for he looked on Stenhouse as a *Schmierchemiker*, and he turned to Bunsen, with whom he was friendly, for advice. Bunsen strongly recommended him to accept the post and pointed out the advantage of learning a new language, coupled with the warning that he would not learn any chemistry in London [5]. This forecast, however, was to prove just as incorrect as

[3] Speech by Kekulé at Bonn, 1892 ; *cf.* Anschütz, *op. cit.*, ii, 949.

[4] Anschütz, *op. cit.*, i, 38.

[5] *Ibid.*, ii, 950.

Liebig's had been about Paris. At any rate Kekulé accepted the appointment, arrived in London about Christmas of 1853, and remained there nearly two years.

Kekulé's work in Stenhouse's laboratory was mostly of a routine nature and had very little influence on his development as a theoretical organic chemist. His spiritual home, where he received most of his chemical teaching and inspiration during his stay in London, was without doubt University College, where he came under the influence of Williamson. There were several other young German chemists holding assistantships in various London laboratories at this period, amongst them Reinhold Hoffman, who arrived in the metropolis almost at the same time as Kekulé to be Williamson's assistant at University College. Hoffman and Kekulé were very friendly, and, indeed, shared lodgings in Clapham, and Kekulé frequently called for his friend at Gower Street at the end of the day's work in order to return home together. In this way Kekulé made the acquaintance of Williamson and soon became on terms of very intimate friendship with him. Williamson, it should be recalled, had already published his famous theory of " ætherification " three years previously.

Like most other contemporary organic chemists of note, Williamson also had been a pupil of Liebig, but it is interesting to observe that his first impression of Liebig's lectures was quite different from that obtained by Kekulé. In a letter to his father from Giessen in 1844 Williamson wrote [6] saying that he found Liebig's first lecture " rather tedious from the extreme elementary manner in which he treated it ", and that he was " not remarkably pleased with his delivery ".

There is abundant evidence that Kekulé had a very high opinion of Williamson's philosophical powers and was strongly influenced by him in the formation of his own chemical views. Kekulé himself tells us that :

> " Just as in Paris I had had the opportunity of getting to know the unpublished views of Gerhardt, so now I had the good fortune, through intimate and friendly intercourse with Williamson, of becoming familiar with the manner of thought of this philosophic spirit. Originally a pupil of Liebig, I had become a pupil of Dumas, Gerhardt, and Williamson. I no longer belonged to any school " [7].

In his short memoir on Williamson we are told by Carey Foster [8] that

> " Kekulé, Odling, and Brodie were constant visitors [at University College], and in the talk of these men in Williamson's little room at the end of the laboratory the seed was planted of much of the chemical theory of the day ".

[6] *J. C. S.*, 1905, 607.

[7] Speech by Kekulé at Berlin, 1890 ; *Ber.*, 1890, **23**, 1302 ; *cf.* Anschütz, *op. cit.*, ii, 943.

[8] *J. C. S.*, 1905, 611.

The ideas current concerning the structure of molecules when Kekulé arrived in London were limited to the recognition of certain characteristic groupings of atoms or radicals in molecules and the classification of molecular formulæ into a number of groups or " types " based on the formulæ of certain simple molecules. Considerable interest had been aroused by the publication in 1853 of Gerhardt's later type theory, to the development of which Williamson's own work had contributed no small part. Gerhardt's theory was not, however, universally accepted and alternative views were current. Kolbe, for example, had little use for the Gerhardt formulæ. But none of the formulæ of that time were really structural in the later sense, since they did not give any indication of the actual arrangement of the atoms with respect to one another in the molecule.

The advent of structural organic chemistry was dependent on the clear recognition of the combining power or valency of the elements, and this conception, often referred to at that time as the atomicity of an element, was only just being developed, chiefly by Kolbe in Germany and by Frankland in this country. The latter's famous paper in which the valency idea was put forward on the basis of his study of the organo-metallic compounds was published in 1852 [9].

Such, in brief, were the topics that were hotly debated in those meetings at University College, and here, no doubt, Kekulé, at first a firm believer in the views of Gerhardt and of Williamson, gradually became convinced that it was not sufficient to look on molecules as made up of radicals in order to represent completely the properties of compounds, but that one must actually examine the constitution of molecules in terms of the ultimate particles, namely, the atoms themselves. The discussions in Williamson's little room must be held responsible, in part at any rate, for Kekulé's own first great contribution to structural theory—the recognition of the tetravalency of carbon and of the power of carbon atoms to combine with one another by the mutual linking of some of these valencies.

Kekulé's earliest views on valency are contained in a paper, entitled " On a new series of sulfurated acids ", published in the *Proceedings of the Royal Society* for 1854 [10] and submitted to the Society by Williamson. Williamson had actually been largely responsible for the completion of the work described in this paper. When Kekulé proposed the idea of using phosphorus sulphide as a reagent for replacing oxygen by sulphur in organic acids, anhydrides, and esters, Williamson urged him repeatedly to carry out the suggestion. But Kekulé's other duties at St. Bartholomew's Hospital did not give him the necessary time, and finally

[9] *Phil. Trans.*, 1852, 417.

[10] *Proc. Roy. Soc.*, 1854, **7**, 37 ; also *Ann.*, 1854, **90**, 309.

Williamson was forced to say : " The idea must be tried—if you don't, I shall " [11]. The result was that Kekulé found time for experimental work outside his official hours and apparently to the annoyance of Stenhouse. This episode serves to show how Kekulé during his stay in London must indeed be regarded as a pupil of Williamson.

In the paper just mentioned Kekulé still adhered to the " type " formulæ of Gerhardt. His ideas on structural chemistry were, however, already forming. For in the same year, 1854, he had his well-known vision of the linking up of carbon atoms. The story of how this idea came vividly before his mind on the top of a London omnibus has been told by Kekulé himself and is worth repeating here. He says :

> " During my stay in London I lived for a long time in Clapham Road near the Common. But I often spent my evenings with my friend Hugo Müller in Islington, at the opposite end of the giant city. We talked there about all sorts of things, but mostly about our beloved chemistry. On a fine summer's evening I was travelling once again with the last omnibus through the then deserted streets of the metropolis, usually so full of life,—' outside ' on the top deck of the bus, as usual. I fell into a reverie. Then the atoms gambolled before my eyes. I had always visualised them in motion, those little beings, but I had never succeeded in discovering the nature of their motion. To-day, I saw how two small ones often joined up to form pairs, how larger ones seized two small ones, still larger ones kept hold of three or even four of the small ones, and how everything revolved in a whirling dance. I saw how larger ones formed a chain and grabbed hold of smaller ones only at the end of a chain. I saw what the old master Kopp, my highly honoured teacher and friend, presents to us in his ' Molekularwelt ' in such an attractive way ; but I saw it long before him. The conductor calling ' Clapham Road ' wakened me out of my dream, but I spent a part of the night putting sketches at least of that dream picture on paper. Thus arose the theory of structure " [12].

The accompanying illustration (Plate I, A) shows an actual " knife-board " horse-bus that ran in service in Islington in the eighteen-fifties. Perhaps, owing to its picturesque nature, undue emphasis has been given to the dream on the London bus, even by Kekulé himself—about thirty-five years after its occurrence. At any rate one must not forget that Kekulé's dream was only one incident in and probably the direct result of a period of intense mental activity devoted to the problem of valency in organic compounds.

Kekulé's sojourn in London marks not merely the beginning of his success as an explorer in the field of structural organic chemistry ; for it was at this time also that, after having considered more than one offer of an industrial position, he finally decided to aim at an academic career. The interest in chemistry first aroused in the mind of the young student

[11] Anschütz, *op. cit.*, i, 45.

[12] Berlin speech, see foot-note [7] above ; *cf.* Anschütz, *op. cit.*, ii, 941.

of architecture by Liebig's lectures at Giessen and directed towards the study of molecular structure under the influence of Gerhardt in Paris became, during his intimate association with Williamson in London, confirmed as the settled object of his life-work.

The theory of the tetravalency of carbon and of the formation of carbon chains was not published by Kekulé until 1858, by which time he had returned to Germany and set up a private laboratory at Heidelberg. The conception of the tetravalency of carbon was already contained in an earlier paper [13], entitled " On the constitution of fulminic acid " and published in 1857, and Kolbe and Frankland, as is well known, also claimed priority for the idea in a paper [14] published in the same year under Kolbe's name but in reality written jointly with Frankland. The merits of these claims have been sufficiently discussed by Japp in his Kekulé Memorial Lecture [15]. What is certain is that the first clear statement of the tetravalency of carbon is to be found in Kekulé's paper [16] of 1858, entitled " On the constitution and metamorphoses of chemical compounds, and on the chemical nature of carbon ", where he says that " the sum of the chemical units combined with one atom of carbon is 4. This leads to the view that carbon is tetratomic (or tetrabasic) ". In this paper we also find the first enunciation of the principle of the linking up of carbon atoms by means of some of their valencies to form chains. Kekulé's delay in publishing his views, which was characteristic of him, nearly made him lose his claim to the priority of the idea of carbon chains. For only a few months later Archibald Scott Couper, in a paper [17] from Wurtz's laboratory, also put forward the hypothesis of the tetravalence of carbon and of the linking up of carbon atoms. The story of how Couper, through an unfortunate delay in publication, for which Wurtz was responsible, had to give way to Kekulé has been told by Anschütz [18]. In one respect, however, Couper's paper surpasses that of Kekulé. By his method of writing formulæ with bonds (for which he used dotted lines) joining the atoms, Couper can be called the originator of graphic or structural formulæ in organic chemistry. Kekulé still used the older " type " notation, along with his own " roll " formulæ, which will be referred to later.

In 1858, therefore, with the clear recognition of the tetravalency of carbon and of the ability of carbon atoms to link up with one another, and with the birth of graphic formulæ, structural organic chemistry may

[13] *Ann.*, 1857, **101**, 200.
[14] *Ibid.*, p. 262.
[15] *J. C. S.*, 1898, **73**, 97.
[16] *Ann.*, 1858, **106**, 129.
[17] *Compt. rend.*, 1858, **46**, 1157.
[18] *Proc. Roy. Soc. Edin.*, 1909, **29**, 193.

be said to have begun. The first stage in the developments that led to the benzene ring had been reached.

The year 1858 was an important one for Kekulé in another respect; for in that year, on the recommendation of the great Belgian chemist Stas, he was called to the chair of chemistry in Ghent. The nine years that he spent there mark the next stage in the evolution of the benzene ring. While at Heidelberg he had begun to write his *Lehrbuch der Organischen Chemie*, and a year or two after his transfer to Ghent he was preparing the section on the aromatic compounds. For a long time he had been puzzled to find a key that would make it possible to include benzene and its derivatives along with the aliphatic substances in one general structural theory. Once again Kekulé had a fortunate dream, and again the story can be told in his words, taken from his speech at the celebration in 1890 of the twenty-fifth anniversary of the benzene ring [19]:

> " During my stay in Ghent in Belgium I occupied an elegant bachelor apartment in the main street. But my study looked on to a narrow lane and had no light during the day. For the chemist, spending his hours of daylight in the laboratory, this was no disadvantage. I was sitting there working at my text-book ; but I made no progress—my mind was on other things. I turned my chair to the fire and dozed off. Again the atoms gambolled before me. This time small groups remained modestly in the background. My mind's eye, sharpened by repeated visions of a similar kind, was now able to distinguish larger structures of many varied arrangements. Long rows, much more closely packed, all moving, twisting and turning like a snake. And look—what was that ? One of the snakes gripped hold of its own tail and mockingly the structure whirled around before my eyes. As if by a flash of lightning I awoke. This time also I spent the rest of the night working out the consequences of the hypothesis.
>
> " Let us learn to dream, gentlemen, then we shall perhaps find the truth, but let us take care not to publish our dreams until they have been tested by our wakened understanding ".

We can well believe that, when Kekulé was working away at his text-book on that evening in his study in Ghent, his mind wandered away from the chemistry of the aromatic compounds. For it was not long since he had suffered a great bereavement in the death of his young wife, a few days after the birth of his first-born son. Kekulé felt the loss very deeply, and was just beginning, at the time that he had his vision of the benzene ring, to try and seek distraction in the resumption of his scientific work.

In the publication of his benzene structure Kekulé followed the advice contained in the concluding sentence of his account of the second dream. He himself says [20] that " the benzene theory lay written for almost a year

[19] Berlin speech, see foot-note [7] above ; *cf.* Anschütz, *op. cit.*, ii, 942.

[20] *Ibid.* ; *cf.* Anschütz. *op. cit.*, ii, 941.

amongst my papers, until the beautiful synthesis of aromatic hydrocarbons by Fittig and Tollens induced me to publish it ". The work of these two chemists [21], it may be recalled, showed clearly that the hydrocarbons toluene, xylene, etc., which had been known for some time, were homologues of the parent substance benzene. Before describing Kekulé's publication of his benzene theory, it will be interesting to mention some amusing consequences of the dream in Ghent.

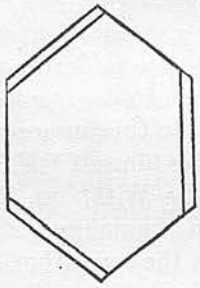
The story of this second dream has been frequently confused with that of the first, which Kekulé had ten years earlier on the top of the London bus. Furthermore, the two stories have even been combined with a later incident to produce a curious legend concerning the birth of the benzene ring. In 1886, more than twenty years after the benzene dream, Kekulé was elected President of the Deutsche Chemische Gesellschaft, and in this capacity he presided over the chemical section at the Versammlung Deutscher Naturforscher und Ärzte in Berlin. Among the lighter functions at this gathering was a *Bierabend* organized by the chemists. For this occasion a special journal was published, resembling in outward appearance and general arrangement an ordinary number of the *Berichte*, but entitled *Berichte der Durstigen Chemischen Gesellschaft—Unerhörter Jahrgang No. 20*. In this humorous production there appeared an article by an author styling himself " F. W. Findig " (who, according to Anschütz [22], was probably Witt) on the constitution of benzene, which was represented by the " monkey " structures shown in Plate I, B. This probably accounts for the unauthorized version of the benzene dream according to which Kekulé, on the top of a London omnibus, saw a cage full of monkeys, six of whom suddenly formed a ring by taking hold of one another's tails. The origin of this version, to which an appearance of verisimilitude is given in at least two publications by putting it in the form of a quotation due to Kekulé himself, has been investigated by Kekulé's son Stephan [23].

With regard to the correct snake version of the benzene dream Anschütz [24] mentions the interesting fact that the picture of a snake biting its own tail had appeared much earlier in his life to Kekulé in a more concrete form. During his later Giessen period he had assisted Liebig when the latter was called in to act as an expert witness in a murder trial. One of the most damning pieces of evidence against the accused man was a ring stolen from the murdered woman, and consisting of two interwoven rings of gold and platinum, each representing a snake biting its own tail.

[21] *Ann.*, 1864, **131**, 303.
[22] Anschütz, *op. cit.*, i, 610.
[23] *Z. angew. Chem.*, 1927, **40**, 736.
[24] Anschütz, *op. cit.*, i, 18.

Kekulé's benzene theory was first published [25] in the *Bulletin de la Société Chimique de Paris* in a paper entitled "Sur la constitution des substances aromatiques", after having been communicated to that body by Wurtz at the meeting held on January 27, 1865. A second paper [26] communicated to the Académie Royale de Belgique on May 11, 1865, completes the essential part of the original theory. Shortly afterwards these papers were republished [27] in German in the *Annalen* for 1866, and the whole theory was again given in the second volume of Kekulé's *Lehrbuch*, also published in 1866. The important features of Kekulé's original theory are familiar to every chemist and are to be found in most text-books of organic chemistry. The symbols and formulæ used by Kekulé in these first communications are not so widely known.

The familiar hexagon device with the alternate single and double bonds



first appears in a somewhat later publication [28] by Kekulé in 1869. In his papers of 1865 and 1866 Kekulé still made use of his own rather cumbersome symbolism which he had first employed in the first volume of his *Lehrbuch* published in 1861 [29]. According to this scheme the symbol used for an element was made to represent its valency. Thus hydrogen was shown as a single circle, oxygen as a fusion of two, and carbon as a fusion of four circles, as seen in the left-hand column of symbols below :

Hydrogen  

Oxygen  

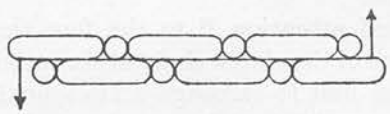
Carbon  

By 1865 Kekulé had simplified these symbols to the forms shown in the right-hand column, the length of the symbol being proportional to the

[25] *Bull. Soc. Chim.*, 1865, **3**, 98.
[26] *Bull. Acad. R. Belg.*, 1865, **19**, 551.
[27] *Ann.*, 1866, **137**, 129.
[28] *Ber.*, 1869, **2**, 362.
[29] *Lehrbuch der Organischen Chemie*, 1861, i, 159.

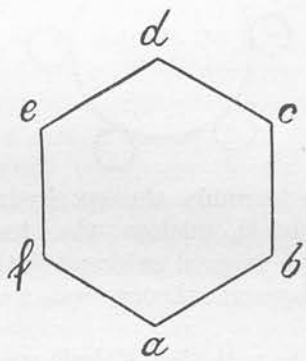
valency. These symbols are frequently referred to as Kekulé's " sausage " formulæ, and the author of this nick-name is often stated to have been Kolbe. Actually Kolbe called them [30] " roll " formulæ : " Kekulé gab den Atomen die Form von Semmeln ". Kolbe went on to speak of these formulæ, referring to the original form, as " Zwei-, Drei-, und Vierback ähnliche Gestalten, deren Wulste je eine Affinität repräsentieren ". A misreading of the word *Wulste* (=bulges) as *Wurste* probably accounts for the erroneous " sausage " appellation attributed to Kolbe.

In Kekulé's original publication of the benzene theory we find these " roll " symbols used extensively to represent benzene and its derivatives. The closed chain of carbon atoms in benzene was depicted as follows :



The arrows at the ends denote single carbon valencies saturating one another and thereby making the configuration cyclic. This formula does not indicate, however, the actual structural arrangement of the carbon atoms in the ring.

The regular hexagon formula of benzene,

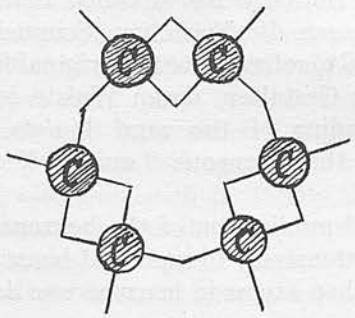


which we meet for the first time in the paper communicated to the Académie Royale de Belgique [31], was used there not to show the spatial arrangement of the carbon atoms, but simply as a convenient representation of the equivalence and symmetrical distribution of the six hydrogen atoms round the carbon nucleus. This was preferred by Kekulé to the alternative triangular distribution of the hydrogen atoms, which, he showed, led to possibilities of isomerism in derivatives not justified by the facts. The first explicit graphical representation of the symmetrical

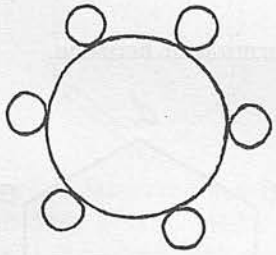
[30] *J. prakt. Chem.*, 1881, **24**, 375.

[31] *Bull. Acad. R. Belg.*, 1865, **19**, 551.

arrangement of the six carbon atoms in the nucleus is to be found in his *Lehrbuch* as shown below :—



Anschütz has called attention [32] to the fact that, although Kekulé was the first to conceive of the closed chain of six carbon atoms for benzene, strictly he was not the first to envisage a hexagonal arrangement of the six hydrogen atoms around the carbon nucleus. Loschmidt, well known for his paper on the size of air molecules, had published [33] in 1861 the following formula for benzene :



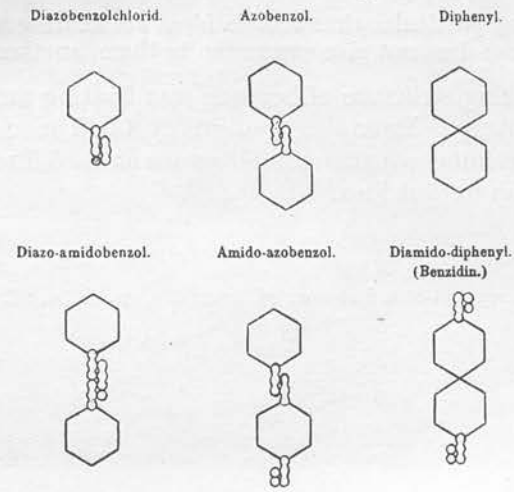
In Loschmidt's benzene formula the six hydrogen atoms are placed symmetrically around the C_6 nucleus, the structure of which he left an open question. There is good evidence [34] that Kekulé, at the time that he published his benzene theory, was aware of the existence of Loschmidt's formulæ.

It is also interesting to note that Kekulé was not the first to use the hexagonal device in chemical symbolism. The hexagon as a chemical symbol appeared for the first time in 1854 in Laurent's text-book, *Méthode de Chimie* [35], without, however, any such structural significance as was later implied.

It is not generally realized that Kekulé himself made very little use of the convenient plain hexagon symbol for benzene in his publications.

[32] *Ber.*, 1912, **45**, 539.
[33] *Cf.* Ostwald's *Klassiker*, 1913, No. 190.
[34] Anschütz, *op. cit.*, i, 305.
[35] *Méthode de Chimie*, Paris, 1854, 408.

In the parts of his *Lehrbuch* that dealt with the aromatic compounds, apart from the section where he fully described his benzene theory, we find only two pages that contain benzene rings, and here these are still used in conjunction with the earlier " roll " symbols, as follows :



After the publication of his benzene theory Kekulé wrote about thirty papers dealing with aromatic substances, in only four or so of which he used the benzene hexagon, and even in these only to a limited extent.

With organic chemists in general the benzene ring soon came into common use, although, of course, there were also criticisms of the theory. Of the correctness of Kekulé's fundamental assumptions, and in particular of the closed chain of six carbon atoms, there was almost immediate and universal agreement. Only confirmed die-hards like Kolbe continued to assert their disbelief in the benzene ring and in the whole of structural organic chemistry. Thus as late as 1881 Kolbe, who was a bitter critic of Kekulé, still wrote in the following manner :

> " If anything is fitted to show what confusion structural chemistry has caused in the minds of chemists it is van't Hoff's recent publication ' On the arrangement of atoms in space '. I should not have mentioned this book and the unbelievable chemical nonsense it contains, if it had not originated under the auspices of Kekulé " [36].

Most of the serious criticism of Kekulé's theory was concerned with his method of disposing of the six remaining valencies in the benzene ring by means of the alternate single and double bonds, and very rapidly the numerous alternative benzene structures due to Ladenburg, Claus, Koerner, Dewar and others began to appear. Kekulé himself recognized this weakness and in 1872 put forward his modified oscillation formula [37].

[36] *J. prakt. Chem.*, 1881, **24**, 418.

[37] *Ann.*, 1872, **162**, 77.

These attempts to overcome the chief difficulty in Kekulé's original theory form another very interesting chapter in the history of the benzene ring, but are outside the scope of this paper.

In an autobiographical note Kekulé once remarked [38] :

> " At any particular time certain ideas are floating around in the air. If one person does not give expression to them, another will ".

The idea of the ring structure of benzene was floating around during the sixties of last century. From this brief survey it will be seen that Kekulé's own particular training, experience, and genius marked him out as destined to give expression to that idea.

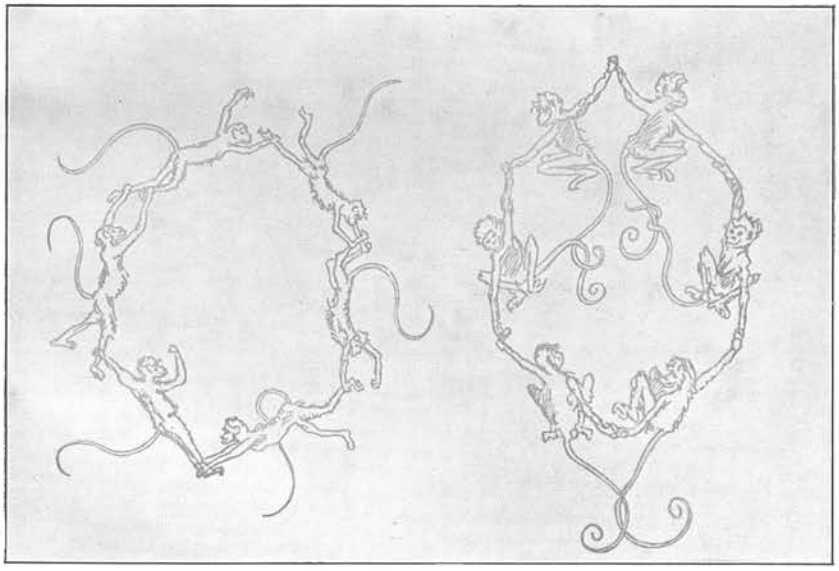
[38] Berlin speech, see foot-note [7] above ; *cf.* Anschütz, *op. cit.*, ii, 939.



A.

London horse-bus of the 1850's (see p. 38).

By courtesy of the London Passenger Transport Board.



B.

" Monkey " structures of benzene (see p. 41).