IRRADIATION OF ORGANIC SYSTEMS
WITH GAMMA RAYS

by

GEORGE HEDDLE ROBERTSON, B.Sc.

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University of Edinburgh

TO

MY WIFE AND PARENTS

CONTENTS

Page

INTRODUCTION

SECTION I:

SECTION II:

Page

SECTION III:

(1) Carbon tetrachloride-trichloroethylene:-

(2) Chloroform - trichloroethylene:-

Page

INTRODUCTION

Shortly after Roentgen's discovery of X- or Roentgen rays in 1895 Henri Becquerel noticed the penetrating effect of uranyl salts which emitted rays without exposure to sunlight. The phenomena was named radioactivity by Marie Curie in 1898. The ionising property of these rays was noted by Bequerel's gold leaf electroscope experiment. Further contributions as to the nature of radioactivity by Marie Curie and others gave indication of the nature of these particles with respect to charge and mass and the subject of atomic structure and isotopes, due in this country mainly to E. Rutherford and F. Soddy, was a rapidly developing science which culminated in the discovery of uranium fission in 1938. Two distinct branches of chemistry have developed from these researches, namely radiochemistry, which is the study of radioactive elements and their properties and radiation chemistry, which depends on the former for its source of energy, covering the chemical effects of high energy radiations.

The growth of radiation chemistry was not only allied to these radiochemical experiments but was also dependent on investigations into the nature of radiation. The advances in our understanding of the nature of light and related radiations are due to J.C. Maxwell in the late 19th century and later to Max Plank and Albert Einstein with Plank's quantum theory forming the basis of all subsequent studies.

Radiation chemistry is the study of the chemical effects of short wavelength (<100Å; energy > 10 electron-volts) electromagnetic radiation and of ionising corposcular radiations such as electrons (beta rays) neutrons, protons, deuterons, helium nuclei (alpha particles) and fast fission fragments.

Natural radioactive decay gives such emissions as alpha particles, beta and gamma rays, neutrons and fission fragments while highly accelerated protons, deuterons, helium nuclei, fast electrons and X-rays can be artificially produced.

The availability of radiation sources has greatly increased in recent years owing to the expanding nuclear reactor developments. Although the initial cost

and cost /

cost of protection are still high the negligible running costs have made radioactive sources commerciably feasible. This has been demonstrated by the Dow Chemical Company of America in the production of ethyl bromide from ethylene and hydrogen bromide in a flow system with gamma irradiation from a cobalt-60 source. Although the commercial applications of ionising radiations are more limited than the early optimistic hopes, several mechanistic polymerisation studies have been made possible by radiation initiation[1]

Varied applicationsof radiation and radioactive isotopes are found in the medical field. The selective treatment of tumours by radioactive elements such as calsium-137 and cobalt-60 is now a well developed technique. Radioactive iodine (^{131}I), a gamma ray emitter, and phosphorus (^{32}P), a beta emitter, are also extinsively used in medicine. The subjection of medical equipment to gamma irradiation gives a high degree of sterilization and the process has now been used successfully on a large scale.

Isotopes have been used very successfully in the study of chemical reaction mechanisms where the stable isotopes D, ^{18}O and the beta emitters T, ^{14}C and ^{36}Cl are widely used. Metabolic processes are studied by means of radioactive tracers such as ^{14}C, ^{32}P, ^{35}S, all beta emitters.

The biological effects of high energy radiation have received considerable attention recently owing to widespread concern about the fall-out from nuclear explosions. The common effects here are the uptake of radioactive iodine - ^{131}I - from milk, and the replacement of calcium in the bones by radioactive strontium, ^{90}-Sr. Although these are the spectacular examples, the effect of radiation on the body is a widely studied science and much work is published in this field in "Radiation Research" and other scientific journals.

Cobalt-60, the radiation source used in the work to be described in this thesis/

thesis, is one of the most frequently used radioisotopes in the study of the action of ionising radiation on chemical systems. This isotope has a half-life of 5·3 years and emits gamma rays of 1.17 and 1.33 MeV and beta rays of 0.31 MeV; the latter have little effective penetration and their effect can be neglected. The gamma rays are emitted from the nucleus and the definite nuclear transitions from upper to lower states determine their precise values. This nearly monenergetic nature of the gamma rays is an important difference from X-rays which are extranuclear in origin and the large number of electronic transitions involved give rise to a range of energies.

Cobalt-60 is produced in an atomic pile by the slow neutron bombardment of ordinary cobalt. The isotope thus produced has a higher neutron/proton ratio than is consistent with nuclear stability and to regain stability it emits a beta particle (electron) from the nucleus thus lowering the ratio of neutrons to protons. This emission now leaves an excited daughter nucleus which returns to the ground state by emission of gamma ray photons.

$$^{60}_{27}\mathrm{Co} \rightarrow {}^{60}_{28}\mathrm{Ni} + {}^{0}_{-1}\beta + 2\gamma \text{ (photons)}$$

Gamma rays are radiations of the same character as ultraviolet or visible light but of much shorter wavelengths and consequently give quanta of much greater energy. There are both similarities and differences between photochemistry and radiation chemistry: in photochemistry only certain molecules may absorb photons of a particular energy directly as the primary process, whereas high energy radiation affects all molecules. Despite this, such high energy radiations cause many specific chemical reactions since the initial energy is rapidly degraded in matter and much of the chemical change is caused by electrons of energy less than 100 eV. Furthermore the species first produced by these electrons do not give final products immediately but take part in various processes in such a way that the final molecules altered may not be those taking part in the initial process.

Again/

Again differing from the photochemical process is the distribution of reactive intermediates in the irradiated system: in photochemistry the intermediates are taken as evenly distributed throughout the system while in radiation chemistry the intermediates are more concentrated along electron tracks owing to the nature of interaction of high energy radiation with matter.

Interaction of High Energy Radiation with Matter.

There are five ways in which radiation of high energy may interact with matter.

In X-ray crystallography the phenomena of coherent scattering is important in determining crystal structure. However, for the higher energy radiation of cobalt-60 gamma rays this process is unimportant as no chemical effect is produced in the system.

Similarly of little importance to radiation chemistry is nuclear disintegration which only occurs when energies of greater than 10 MeV are used. In this process neutrons are emitted from the nucleus under the influence of these high energy photons.

The three processes which require most attention in radiation chemistry are pair production, the photoelectric effect and Compton scattering[2] with the latter playing the most important role in the case of cobalt-60 gamma rays.

Pair production. This effect does not assume any importance until the energies passing through the electric field of the nucleus are greater than the rest mass of the positron-electron pair produced; the energies thus required being ($= 2mc^2$) 1.02 MeV. The electron-positron pair lose their energy by causing excitation and ionisation and disappear by recombination giving two gamma ray photons of energy 0.51 MeV each, travelling in opposite directions. This process is of considerable importance only when energies are in the range 50-100 MeV.

The/

The photoelectric effect is of greatest importance for photon energies below 0.2 MeV or for more energetic radiation, in materials of high atomic number. Here the photon is absorbed by the atom with the ejection of a fast electron which bears the initial energy of the incident photon less the binding energy of the electron; this binding energy may either be emitted as soft X-rays or utilised to eject a further electron known as the Auger electron. This effect is of greatest importance for elements of high atomic number; thus the contribution of total energy absorption is greater for alkyl iodides than for alkyl chlorides.

Compton scattering is the most important effect for cobalt-60 gamma rays of energy 1.17 and 1.33 MeV. In this process photons in the energy range 0.5 to 10 MeV lose their energy by ejecting an electron from an atom; the deflected photons now of reduced energy lose their energy by further Compton scattering or photoelectric absorption while the ejected electrons in turn cause further excitations and ionisations. This process is the most important mode of energy absorption by systems of low atomic number and is dependent on the electron density of the medium.

It is seen that the net effect of X- or gamma ray interaction with matter whether by pair production, the photoelectric effect, or Compton scattering, is the production of fast electrons in the system. These ejected electrons have energies of up to almost the entire energy of the original photon and since the energy required to produce chemical change is only a few electron-volts per molecule, (1 electron-volt per molecule = 23.1k.cal. per gram-mole) a fast electron may alter several thousand molecules. Obviously the initial interaction of the gamma rays makes a negligible contribution to the total chemical change which is practically entirely due to those fast electrons.

The main chemical effect of these fast electrons is interaction with the outer electrons of atoms causing excitation to a higher energy level or ejection to leave a/

a positive ion. Some of these ejected electrons may have sufficient energy themselves to continue the process and as such are known as secondary electrons. However, as their kinetic energy decreases, but still remains greater than 100 eV, the electrons are known as delta rays, and when less than 100 eV but greater than the ionisation potential of the medium (ca. 10eV), the electrons cause ionisation and excitation very close to the original ion (within 10Å in condensed phases) in clusters. The greater part of the ionisation in the system is created along these delta ray tracks or in the clusters since the slow electrons cause ionisation by "knock-on" collision which is more efficient than a glancing collision in causing ionisation. As the energy of the electrons fall below the ionisation potential only excitation is possible and finally only interatomic motion. The fate of the electron finally may be to attach itself to an electronegative atom or molecule such as oxygen or undergo neutralization with a positive ion to give a highly excited molecule; this latter event is of major importance in reactions in the liquid phase.

The excited molecules produced in radiation chemistry are excited as a whole but chemical reaction may take place at some specific point within the molecule: the excited molecules may dissociate into free radicals or yield molecular products by unimolecular decomposition with the former process generally contributing the main chemical change within the system. These radicals may react with other molecules or disappear by radical - radical combinations. However, the excited molecules may meet other fates and a complete understanding of these can only be gained by a study of fluorescence, collisional deactivation and energy transfer[3].

The ions produced by high energy radiation may undergo dissociation by two general routes dependent on whether the fragment ion retains an even or an odd number of electrons. For alkane ions a carbonium ion and a neutral free radical may be formed or alternatively the products may be an olefin ion and a neutral molecule. /

molecule. The two processes are illustrated by the fragmentation of n-pentane following ionisation

$$n\text{-}C_5H_{12}^{+\cdot} \longrightarrow C_3H_7^{+} + C_2H_5^{\cdot} \qquad (a)$$

$$n\text{-}C_5H_{12}^{+\cdot} \longrightarrow C_3H_6^{+\cdot} + C_2H_6 \qquad (b)$$

The parent ions or fragment ions can undergo reaction with neutral molecules in two main ways: (a) by hydride transfer give a neutral product and another ion e.g. in the reaction of neo-pentane and the fragment ion $C_3H_5^{+}$

$$C_3H_5^{+} + \text{neo } C_5H_{12} \longrightarrow C_3H_6 + C_5H_{11}^{+}$$

or (b) by forming carbon-carbon bonds give an ionic product and a free radical as in the ethylene reaction :-

$$C_2H_4^{+\cdot} + C_2H_4 \longrightarrow C_3H_5^{+} + CH_3^{\cdot}$$

The main reaction in the gas phase is hydride ion transfer resulting in the more stable, even electron ion.

The fragmentations and ion-molecule interactions of individual ions are best studied by means of a mass spectrometer. The ion-molecule reactions are very rapid and recent publications have stressed their importance in the radiation chemistry of hydrocarbons in the liquid and gas phase.[4]

G-values.

As a standard term to express the destruction or production of some entity by radiation the G-value is quoted. This value refers to the number of atoms, radicals, or molecular products formed or destroyed per 100eV of energy absorbed by the system. The G-values are expressed thus $G_{(A)}$ or $G_{(-B)}$, indicating either the production of A in the former or the destruction of B in the latter per 100 eV absorbed. It is therefore necessary to have a measure of this energy absorption and/

and this is accomplished by use of a dosimeter.

Dosimetry.

The most useful units of energy absorption are the electron-volt or rad with respect to unit volume and time give measurements in eV/ml/min. and rad/ml/min. The roentgen is defined for gamma irradiation as the radiation unit from which one millilitre of water absorbs 0.98 rad, the rad being equivalent to the absorption of 100 ergs/gm; the roentgen thus equals 98 ergs/ml and as 1 erg = 6.24×10^{11} eV the relationship between roentgen and electron-volt is 1 roentgen = $98 \times 6.24 \times 10^{11}$ eV/ml.

The most convenient method of measuring dose rate is by means of a standardised chemical dosimeter employing a radiation induced chemical reaction whose dependence on dose has been established. The ideal system should satisfy conditions such as an energy yield independent of dose rate, total dose and type of radiation and show no post-irradiation effects. The medium should have a mean atomic number close to that of the system in which radiation effects are under investigation and the dosimeter should be easy to prepare and have an easy and accurate method of analysis. It would also be convenient for the dosimeter to be stable under storage.

The most widely used chemical dosimeter is the Fricke dosimeter which utilises the oxidation of ferrous to ferric ions in an aerated aqueous solution of $\frac{M}{100}$ ferrous sulphate, $0.5 - 1.0\bar{N}$ with respect to sulphuric acid[5, 6]. The chemical yield of this oxidation has been accurately measured by spectroscopy and the corresponding energy input by calorimetry[7, 8] and ionisation chamber method[9]. The value given to this system and used at present is 15.5 ± 0.2 ferric ions produced per 100 eV absorbed i.e. $G_{Fe^{3+}} = 15.5 \pm 0.2$.

The Fricke dosimeter has certain disadvantages in that for doses greater than 50,000 r. air saturated solutions become depleted in oxygen and the ferric yield/

yield falls; also at doses less than 2,000 r. it is not sufficiently sensitive. Care must be taken to exclude all organic impurities which even in very small amounts increase the value of $G_{Fe^{3+}}$[10] and to avoid this highly purified water is used. However it has been shown that similar results can be obtained by addition of sufficient chloride ions[10] which react with all free hydroxyl radicals, produced by irradiation, and yield an equivalent number of chlorine atoms which are much less reactive towards organic compounds, but which will oxidise an equal number of ferrous ions. This has been demonstrated by Burton[11] with benzene/aqueous ferrous sulphate solution systems.

Various other dosimeters have been reported: a modification of the Fricke dosimeter was used by Bakewell and Adams[12] in which the system contained 9.26×10^{-4}M ferrous sulphate in $1.0\bar{N}$ sulphuric acid with 1.32×10^{-3}M benzoic acid; these modifications made the system~~s~~ four times more sensitive while it was stable over a period of years, showing no change in sensitivity or linearity of response. Another chemical method of dosimetry is the measurement of acid yields from the chloroform / water system but no great accuracy is obtainable. Organic halides have been studied to some considerable extent in their application to dosimetry[13] but apart from some use in measuring low dose rates in the region 100 - 1000roentgen they have too many disadvantages to be of general use.

Physical changes may also be used to estimate dose rates and colour changes in certain glasses and rigid polyvinyl films[14] with polymethacrylate and polyethylene terephthalate[15] are useful for dose rates up to 10^{8} roentgen.

Fricke Dosimeter.

In the present work all the dose rates were determined using the Fricke dosimeter. As the energy absorption of ^{60}Co gamma rays is predominantly due to Compton scattering, this absorption for any given system will be proportional to the electron concentration, thus a correction is required for comparing the energy/

energy absorption value of the dosimeter with the system, under identical conditions.

The energy absorbed per unit volume (E erg/cm^3) is related to the radiation flux (I erg/cm^3) by the relation $E = Iu$ where u, the absorption coefficient of the material, equals $N_e\,{}_e\sigma_a$ where N_e is the number of electrons per unit volume and ${}_e\sigma_a$ is the electronic absorption cross-section for Compton scattering. This latter function being a constant for radiation of a given frequency and with the geometry of the experimental and dose rate systems identical, the ratio of electron densities gives the ratio of energy absorption by the two systems.

Therefore :-

$$\text{Energy absorbed by the organic system} = \text{energy absorbed by the ferrous solution} \times \frac{N_e\ \text{(organic system)}}{N_e\ \text{(ferrous system)}}$$

where the electron density N_e of 1 ml of liquid is given by

$N_e = \frac{d}{M} \times N \times \Sigma Z$, with d = density of the liquid,

M = Molecular weight of liquid

N = Avogadro's number

and ΣZ = sum of atomic numbers of each of the atoms in the molecule.

If a mixture of two compounds a and b are irradiated in solution, the contribution to the electron density of the solution by the solute is taken into account by the general equation.

$$N_{e\,(\text{sol}^n)} = \frac{Va}{Va + Vb} \cdot \frac{da}{(MW)_a} \cdot N\,\Sigma Z_a + \frac{Vb}{Va + Vb} \cdot \frac{db}{(MW)_b} \cdot N\,\Sigma Z_b$$

where $\frac{Va}{Va + Vb}$ represents the volume fraction of a in solution.

The electron density of the ferrous sulphate solution is obtained by treating it as pure water with a density of 1.023 gm/cc. i.e.

$$N_e = \frac{1.023}{18.02} \times N \times 10$$

$$= 0.5675\ N.$$

Experimental estimation of dose rate./

Experimental Estimation of Dose Rate.

The required reagents for the ferrous sulphate dosimeter are :-

(a) Analar Ferrous Ammonium Sulphate;

(b) Analar Sulphuric Acid;

(c) Pure water free from organic impurities or with added sodium chloride. To obtain pure water, tap water was subjected to a three stage distillation in an all Pyrex glass apparatus, the water being distilled first from acid potassium permanganate, then from potassium carbonate, and finally redistilled without any reagent.

For added sodium chloride the quantity must be sufficient to convert all diffused hydroxyl radicals to chlorine atoms; this quantity is based on the approximate dose rate and the knowledge that G(OH) = 2.92 radicals per 100 eV absorbed for cobalt-60 gamma rays for an aqueous solution $0.8\overline{N}$ with respect to sulphuric acid.

All glassware was cleaned with chromic acid, hot water and distilled water before being flame dried on a vacuum line. The ferrous sulphate irradiation vessel was identical with the vessel used for irradiation of the organic liquid and was placed in an identical position with respect to the source. Samples were then removed at intervals and the ferric ion concentration measured spectrophotometrically with a Unicam S.P.500 spectrophotometer by comparison of the transmission of the irradiated sample with that of the original solution at 304 mu. The molar extinction coefficient of the ferric ion in $0.8\overline{N}$ sulphuric acid at this wavelength is accurately known (Table 1(a)) and the concentration was calculated from the equation $\log \frac{I_o}{I} = e.c.d.$

where e = molar extinction coefficient.

d = cell thickness in centimeters.

c = concentration in moles per litre.

Figures/

Figures in Table 1(b) are those obtained in a recent dose rate determination of the ^{60}Co source and the results shown graphically in graph 1.

<u>Calculation</u> :-

$$\log \frac{Io}{I} = \text{e.c. for 1 cm. cells.}$$

$$\therefore c = \log {}^{Io}/{}_{I}/e \text{ moles per litre of ferric ions}$$

and number of ferric ions produced per ml.

$$= \frac{\log \frac{Io}{I}}{e} \times \frac{6.023 \times 10^{23}}{1000}$$

From the graph, the value of $\log \frac{Io}{I}$ per minute $= 5.7 \times 10^{-3}$ and the value of e at 21°C is 2165. In the reaction $Fe^{++} \rightsquigarrow Fe^{+++}$ $G = 15.5$ ions per 100 eV

thus :-

the energy absorbed by the ferrous system

$$= \frac{5.7 \times 10^{-3} \times 6.023 \times 10^{23} \times 10^{2}}{2165 \times 10^{3} \times 15.5} \text{ eV/ml/min.}$$

$$= 1.02 \times 10^{16} \text{ eV/ml/min.}$$

(multiplication of this above value by $1.602 \times 10^{-12}/98$ converts the dose into roentgens/ml/minute.)

If <u>S</u> molecules of an organic product are formed per ml. per minute from the irradiation of the same vessel occupying the identical position at the source then, by definition, the G-value of its production is given by

$$G(org) = \frac{S \times 100}{E(org)}$$ where E(org) is the energy absorbed by the organic system and equals

$$1.02 \times 10^{16} \times \frac{\text{Ne (organic system)}}{\text{Ne (ferrous system)}} \text{ eV/ml/min.}$$

TABLE I(a)

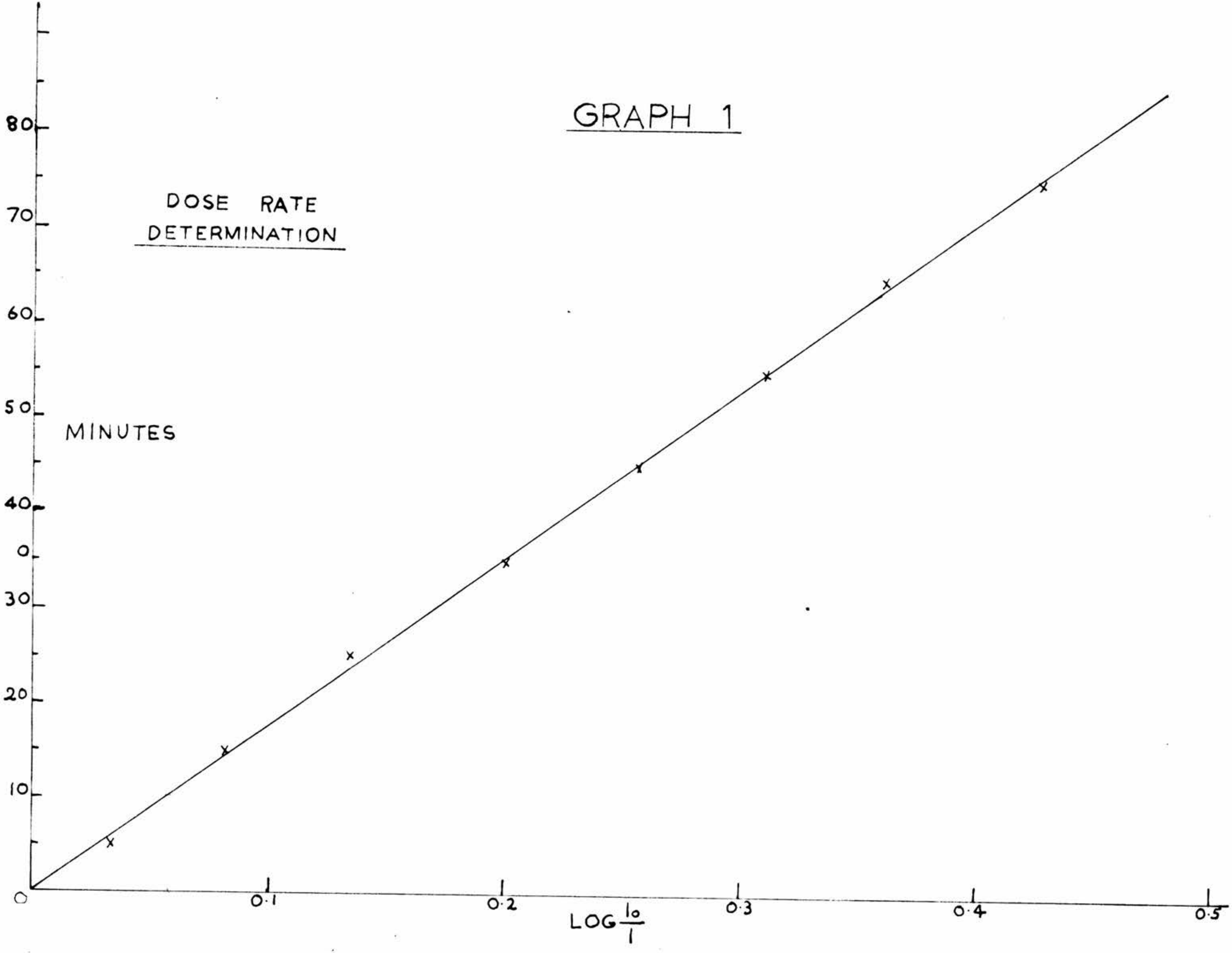
The Molar Extinction Coefficient for Ferric ions in 0.8$\overline{N}$ sulphuric acid solution at 304 mμ at a temperature T°C.

T°C	e
15	2074
16	2089
17	2104
18	2119
19	2135
20	2150
21	2165
22	2181
23	2197
24	2131
25	2229

TABLE I(b)

Dose Rate Determination

Time in mins.	$\log {}^{Io}/I$	Temperature	e
5	0.034	21	2165
15	0.082	21	2165
25	0.134	21	2165
35	0.200	21	2165
45	0.256	21	2165
55	0.310	21	2165
65	0.360	21	2165
75	0.426	21	2165



GRAPH 1

DOSE RATE
DETERMINATION
MINUTES
80
70
60
50
40
0
30
20
10
0
0·1
0·2
0·3
0·4
0·5
LOG $\frac{Io}{I}$

General Introduction

The general scope of radiation chemical studies can be divided into two main sections : (a) water and aqueous systems; (b) organic or non-aqueous systems. Although these two categories do not differ fundamentally with respect to the effect of ionising radiation, it is convenient to deal with the subject under these headings and the majority of reviews of radiation chemistry are set out in this way.

Aqueous systems

The radiolysis of pure water has been, and still is, the subject of considerable research and this system, with inorganic additives has been more thoroughly investigated than any other. The products have long been known as hydrogen and hydrogen peroxide, with hydrogen atom and hydroxyl radical being formed in the solution.

The yield of molecular products, hydrogen and hydrogen peroxide is dependent on the density of ionisation along the tracks. This absorption of energy along the particle track is measured in electron volts per micron and the linear density of events is known as the linear energy transfer (L.E.T.). Alpha particles have a high L.E.T. whereas gamma rays display a low value. The net effect of this difference is that with alpha particles the radicals are produced in such locally high concentrations that dimerisation is the main cause of radical disappearance whereas in the lower L.E.T. gamma rays the radicals may diffuse from the track and react with the solute. This difference is exhibited in the oxidation of ferrous ions in dilute aqueous solutions[16] where gamma rays give $G_{Fe^{3+}} = 15.5$ but alpha particles give a value only about a third of this . Inversely the yields of hydrogen peroxide and hydrogen are increased for the alpha particle irradiation.

The nature of the primary effect has been the source of considerable controversy. The present interpretation of the observations that indicate the production of/

of two types of reducing species (the "two types of hydrogen atom") is dependent on the identification of the solvated electron designated $e(aq)$ or H_2O^-. The nature of this entity is proved in experiments by Czapski et al[17] and Collinson et al[18]. The two reducing species present in acid solution are then connected thus:-

$$e(aq) + H_3O^+ \longrightarrow H + H_2O \qquad (1)$$

The evidence for concurrent formation of $e(aq)$ and the hydrogen atom is based on the molecular hydrogen yield from various aqueous-organic systems. The two competing reactions of the reducing species would then be hydrogen abstraction and electron transfer i.e.

$$H + RH \longrightarrow H_2 + R. \qquad (2)$$

$$e(aq) + RH \longrightarrow RH^- + H_2O \qquad (3)$$

Experiments have shown that reaction (1) is not the only source of hydrogen atoms as the addition of such electron scavengers as acetone[19], azide ion[20], and bicarbonate[21] give a molecular hydrogen yield greater than the "unscavengeable" hydrogen. Contrary to this Czapski et al[22] have shown with added hydrogen peroxide and oxygen that $e(aq)$ accounts for the total reducing species produced. Similarly Dainton et al[23] using nitrous oxide as an electron scavenger found $G_{e(aq)}$ equivalent to the total reducing species. However work by Lifschitz[24] has indicated some primary hydrogen atom production from the interpretation of results in the radiolysis of H_2O/D_2O mixtures. The "H" production may be due to a sharing of the excitation energy by several water molecules[24] and not the decomposition of one excited molecule as suggested by Allan et al[19].

Aqueous solutions of organic compounds studied from the aspect of products formed have shown the presence of hydroxyl radicals. The irradiation of dilute solutions/

solutions of chlorobenzene[25], nitrobenzene[26] and benzoic acid[27] produces all three isomers of the corresponding hydroxy compounds. This substitution, independent of the substituents in the aromatic ring, is characteristic of a free radical mechanism rather than an ionic mechanism. In benzene itself, as well as the production of phenol[28], Daniels et al[29] have observed ring opening to give mucondialdehyde via the ring hydroperoxide.

In aqueous systems containing aliphatic compounds the results are also indicative of hydrogen atoms and hydroxyl radicals. The radiolysis of aqueous solutions of methane[30] in presence of oxygen and acid gives formaldehyde, and at pH 5.5 methyl hydroperoxide is also formed.. For aqueous cyclohexane solutions, hydrogen abstraction takes place and this may be compared with the very low probability of hydrogen abstraction from benzene[31]. In deaerated aqueous solutions of ethylene[32] at one atmosphere the products are acetaldehyde, n-butyraldehyde, and hydrogen peroxide along with an oily polymer. However in oxygen saturated solutions at high pressures of ethylene, acetaldehyde, formaldehyde, glycoll aldehyde, and hydrogen peroxide have been detected with a small quantity of an organic peroxide[32]. Acetylene[33] in deaerated aqueous solution gives glyoxal as the main product with $G = 8 - 10$, dependent on the acetylene/oxygen concentration, indicating a short chain mechanism.

Halogen compounds liberate the corresponding hologen acid when irradiated in aqueous or organic solvents. Chloral hydrate[34] gives hydrogen chloride with $G = 2 - 5 \times 10^{2}$ dependent on dose, temperature and concentration. Similarly bromal hydrate[35] forms hydrogen bromide in high yield ($G = 5 - 25 \times 10^{2}$) as well as dibromoacetaldehyde and dibromoacetic acid. Apart from these high G-values for the acids the yield~~s~~ from chlorides is generally low. The colour change of a pH indicator has been used in dosimetry in conjunction with these halogen systems as aqueous chloroform where the hydrogen chloride yield is small or aqueous/

aqueous chloral hydrate where the hydrogen chloride yield is high and a more sensitive dosimeter results.

The alcohols and aldehydes both give oxidised products, the former giving as well as the carbonyl compound, the dimeric alcohol and hydrogen. In deaerated solutions of ethanol[36], glycol and acetaldehyde are formed indicating abstraction by the radicals produced from water; in oxygenated solutions three times as much acetaldehyde is produced[36]. At higher concentrations of ethanol (1M) the glycol yield is suppressed completely and acetaldehyde is produced with G = 6[37].

Hydrogen abstraction by radicals is also evident in the radiolysis of aqueous, oxygen free solutions of carboxylic acids. In the higher acids this is followed by dimerisation but formic acid yields the disproportionation products, carbon dioxide and hydrogen[38]. The addition of hydrogen peroxide or oxygen suppresses the yield of hydrogen and gives the following net reactions respectively:

$$\mathrm{H.COOH} + \mathrm{H_2O_2} \longrightarrow 2\mathrm{H_2O} + \mathrm{CO_2}$$

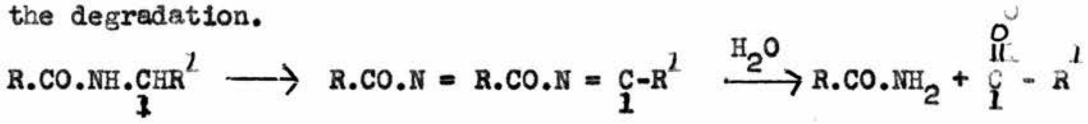
$$\mathrm{H.COOH} + \mathrm{O_2} \longrightarrow \mathrm{H_2O_2} + \mathrm{CO_2}$$

The aromatic acids mainly yield the products of ring substitution by the hydroxyl radical. For example benzoic acid[28] yields o-, m- and p-hydroxybenzoic acids with G-values of 0.74, 0.42 and 0.33 respectively. Similarly for salicylic acid[28] the 2:3 and 2:5 dihydroxy isomers are formed in the ratio 1.6:1 with no evidence of the other isomers. Both these acids produce carbon dioxide, with G = 0.7 for benzoic and G = 1.53 for salicylic, indicating decarboxylation.

The study of aqueous solutions of naturally occurring products receives considerable attention in relation to radiotherapy and health hazards.

In/

In polysaccharides the initial break down is at the bond between the sugar units[39]. For glucose[40] itself the primary products formed are glyoxal and erythrase from the fission of carbon-carbon bonds with the oxidation products D-glucuronic and D-gluconic acids. The radiolysis of simple amino acids in aqueous solutions is comparatively well understood and the formation of NH_2. $\dot{C}H$. COOH and $\dot{C}H_2$. COOH radicals from degassed glycine solutions has been observed[41]. The irradiation of proteins is of course more complex but carbonyl groups have been reported[42] and this is consistent with the degradation.



$$R.CO.NH.\underset{|}{C}HR' \longrightarrow R.CO.N = R.CO.N = \underset{|}{C}-R' \xrightarrow{H_2O} R.CO.NH_2 + \overset{\overset{O}{\|}}{\underset{|}{C}} - R'$$

Steroids are either oxidised or reduced at selective sites in the molecule depending on the availability of molecular oxygen[43].

In all the foregoing examples the presence or absence, of oxygen is shown to exert a strong influence on the radiolysis products, not only are yields altered but products formed may also differ. This illustrates the care required in degassing samples and in stating the oxygen concentration and availability in all systems.

Irradiation of Pure Organic Systems

One of the most extensively investigated organic systems is that of the hydrocarbons. Early work by Lind and Bardwell[44] with X-rays and alpha particles on hydrocarbon gases paved the way for the product identification which has now been well established. The mechanisms involved have however only recently been elucidated mainly by the application of mass spectrometry. This indicates a mechanism involving free radical and ion-molecule reactions[45]. The mass spectrometric results for methane showed the main ions to be CH_4^+, CH_3^+, and CH_2^+ in 48%, 40% and 8% respectively. Hydrogen atoms must also/

also be produced and these have been detected by iodine scavenging[46].

The main reactions of the ions CH_4^+ and CH_3^+ are with methane thus:-

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3\cdot$$

$$CH_3^+ + CH_4 \longrightarrow C_2H_5^+ + H_2$$

with the neutralization of CH_5^+ yielding another methyl radical and hydrogen gas. The $C_2H_5^+$ neutralization probably produces an ethyl radical, although normally it would yield ethylene and a hydrogen atom. Ethylene is produced and its reaction with radicals is the source of higher molecular weight material.

The irradiation of higher hydrocarbons resembles that of methane with hydrogen an important product. The yield of dimer, corresponding to ethane from methane, increases with the change from gas phase to liquid phase[47]; some unsaturated products are also produced and these, as in methane, interfere with the primary reactions after quite short irradiations. The principal difference between methane and other hydrocarbons is the scission of carbon-carbon bonds in the latter[47]. This fission is more pronounced in the gas phase than the liquid phase corresponding to the inverse change in the proportion of dimerisation products. The relative importance of carbon-carbon and carbon-hydrogen fission is dependent on whether the alkane has a straight or branched chain. In the case of **n-hexane**[48] the ratio of carbon-carbon to carbon-hydrogen fission is in the ratio 1:2, which is in contrast to a 5:14 ratio if random fission had occurred, showing that the weaker carbon-carbon bonds are broken preferentially. The branched hydrocarbons show a definite tendency to undergo fission at secondary and tertiary carbon-carbon bonds and this effect is strikingly illustrated by the methane yield in the radiolysis of neopentane[49] which/

which agrees with mass spectrometric results. A similar result is observed in the series n-octane, 2, methylheptane, 2,2, dimethyl hexane[40] in the mass spectrometer where the percentage of the parent ion decreases in the above order of the series.

The mechanism of production of the individual products may vary; the higher hydrocarbon products probably originate from free radical mechanisms as indicated by iodine[50] and anthracene[51] scavenging. Some products may arise from unimolecular processes and the hydrogen yield is not all due to thermal hydrogen atoms as is illustrated in scavenging experiments with cyclohexane[52, 53].

In alkyl halides the effect of high energy radiation is more specific and the observed preferential homolytic fission of the carbon-halogen bond is consistent with its lower bond energy. The chlorides yield hydrogen chloride owing to hydrogen abstraction by chlorine atoms but this is not so for iodides where the corresponding abstraction is endothermic; hence the use of iodine as a radical scavenger.

Many of the alkyl halides undergo isomerisation to the more stable isomers. Thus n-propyl chloride[54] and 1,3, -dichloropropane[55] give isopropyl chloride and 1,2 -dichloropropane respectively in appreciable yield, $G = 60$ in the former. The mechanism is probably of the following type.

$$CH_3 . CH_2 . CH_2Cl + Cl. \longrightarrow CH_3 . \dot{C}H\ CH_2Cl + CH.Cl$$

$$CH_3 . CH . CH_2Cl \xrightarrow{\text{isomerisation}} CH_3 . CHCl\ CH_2\cdot$$

$$CH_3 . CHCl . CH_2 \xrightarrow{\text{H abs.}} CH_3 . CHCl . CH_3$$

The butyl chlorides also exhibit this isomerisation with n-butyl chloride converted to sec-butyl chloride and sec-butyl chloride isomerising to/

to tert-butyl chloride with G = 60 and 24 respectively[56]. Isomerisation has also been reported for butyl bromide[57] with an accompanying significant yield of olefin. Thus isobutyl bromide as well as giving tert-butyl bromide, G = 4.5, produces isobutylene with G = 6.2; the tert-butyl bromide gives yields of iso-butylene with G-values up to 9. No isomerisation is noted for iodides[58], indicating the rapid abstraction from molecular iodine formed in the reaction before any rearrangement of the radical can occur. The main products are the hydrocarbons of the same chain length with usually a slight preponderance of the unsaturated form. With halomethanes there is a similar carbon-halogen bond fission giving $CCl_3\cdot$ and $CHCl_2\cdot$ radicals along with chlorine atoms from carbon tetrachloride and chloroform respectively. The mechanism for carbon tetrachloride radiolysis was elucidated by Schulte[59] using radioactive chlorine exchange.

Although polymerisation reactions are the main source of interest in unsaturated systems the formation of dimeric products has thrown considerable light on the condensation reaction of alkenes. Chang et al[60] obtained evidence of monoölefinic dimer from hex-1-ene irradiation whereas the free radical dimerisation produces the diolefinic product from terminal olefins[61]. Similar results have been obtained with hexadec-1-ene[62], oct-1-ene[60] and 2,2,4-trimethylpent-1-ene[63]. A deviation from this monoölefinic predominance is in cyclohexene radiolysis[64] where bicyclohexenyl predominates over cyclohexylcycohexene, the respective G-values being 1.36 and 0.2. The presence of monoölefin is attributed to an ionic reaction mechanism with neutralization of the dimer monoölefinic cation.

Ionic intermediates in polymerisations have also been shown to be important for monomers which do not undergo polymerisation by a free radical/

radical mechanism but give good yields by a cationic mechanism; these include iso-butene at -78°C[65, 66], α-methylstyrene[67] and β-pinene[68]. The initiation is by carbonium ion formation and the chain transfer by a proton transfer from the propagating ion to the monomer[67]. The neutralization of the ion must be slow to allow for the chain lengths achieved by these polymerisations where chains of up to several thousand molecules per initiator are obtained. Acetylene[69] has been shown to undergo cationic polymerisation by the following mechanism:-

$$\cdot\ CH = \overset{+}{C}H + CH = CH \longrightarrow CH - CH = \overset{+}{C}H \longrightarrow \text{polymer}$$

Evidence for ionic intermediates in ethylene polymerisation at -196°C have also been noted with initiation by $C_2H_4^{\ +}$ and subsequent ion molecule reactions[70].

Free radical polymerisations are also widely known especially in vinyl and related monomers such as vinyl chloride, styrene and methyl methacrylate[71]. Ethylene[72] itself gives $G_{(-C_2H_4)}$ in the range 100 - 12,000 dependent on the pressure. Evidence of the free radical nature comes from scavenging and initiation rate studies; also the copolymerisation of styrene and methylmethacrylate gives a 1:1 ratio similar to the free radical initiation[73]. The formation of branched and graft polymers by radiolysis is a well known technique whereby a polymer-monomer combination is subjected to irradiation; the results are interpreted on a free radical basis[74].

The most important characteristic of polymer irradiations is the change in their molecular weight. This may increase by cross linking of chains or decrease by inducing main chain scission[75]. The hydrogen yield is indicative of this linking as the $G_{(H_2)}$ does not fall off, by double bond addition, on irradiations of polymers of high unsaturation although there is a decrease in the concentration of double bonds. As well as end-to-end linking/

linking, ring linkages have been observed in <u>cis</u>- and <u>trans</u>- polybutadienes[76,77]. The presence of free radicals in the solid have been confirmed by E.S.R. studies of irradiated polyethylene[78].

The physical changes in irradiated polymers make it an important commercial application. Polyethylene, for example, when cross-linked is no longer soluble in organic solvents and on heating to 120°C softens to give a rubber-like material whereas the original polyethylene melts at this temperature.

Aromatic compounds are very much more resistant to ionising radiation; benzene, for example, disappearing with $G_{(-C_6H_6)} = 0.8$. The gas yields are also very low with $G_{(H_2)} = 0.036$ and $G_{(C_2H_2)} = 0.020$[79]. Biphenyl exhibits this stability also and even lower G-values are obtained[80]. These aromatic compounds differ from aliphatic hydrocarbons by showing a L.E.T. effect illustrated by an increase in gas and polymeric material when benzene is subjected to the action of alpha particles; the increment in the gas yield is relatively more than the polymeric material[81]. The origin of this latter material is most likely to be the olefins detected, namely cyclohexadiene and bicyclohexadienyl[82].

Alkyl substituted benzenes give gas yields 3 - 5 times greater than benzene[83] but still much lower than the corresponding alkanes. Ethyl and iso-propyl benzenes give increased methane yields but toluene gives chiefly hydrogen and benzl radicals[84], indicating that the fission is not between the ring and the first carbon atom but tends to produce a resonance stabilised radical; the polymeric material is approximately the same as for benzene itself. These results are interpreted as a "sponge type" protection of the side chains by an intramolecular energy transfer to the benzene ring itself/

itself[85]. The protective effect is also in evidence in mixtures of organic compounds with benzene where the product yields do not follow those predicted by the electron fraction rule for mixtures; an example of this is the classic cyclohexane/benzene system[86] where the hydrogen gas yield is lowered. Similar examples have been illustrated by Chapiro et al[87] for mixtures of benzene with, (a) carbon tetrachloride and (b) chloroform.

The reason for this decrease is probably due to energy transfer from the excited molecule to the benzene molecule although chemical scavenging cannot be ruled out for the hydrogen decrease in the cyclohexane/benzene system which tends to be rather complex. Strong evidence of energy transfer comes from studies by Collinson et al[88] where there is considerable overlap of the ultraviolet spectrum of the solvent and solute. Here for solutions of ferric chloride in diphenyl ether just above the melting point and in the supercooled liquid $G_{(-FeCl_3)}$ was low and independent of solute concentration and dose but in the solid state $G_{(-FeCl_3)}$ became larger and increased with decrease in temperature and decrease in solute concentration. In solvents with no overlap of absorption bands these phenomena were not observed and $G_{(-FeCl_3)}$ was the same in solid and in liquid at temperatures near the melting point.

The present work involves the addition of halomethanes to olefins. Such additions were first reported in 1945 by Kharasch[89] who reported the formation of 1,1,1,3-tetrachlorononane and 1,1,1-trichlorononane by the addition of carbon tetrachloride and chloroform respectively to oct-1-ene. Earlier work, also by Kharasch, on the addition of hydrogen bromide and mercaptans to olefins had given a new interpretation of anti-Markownikoff, or as it is now termed, Kharasch addition.

In/

In general the addition of a compound A-B across a double bond in the presence of a peroxide initiator,

i.e. $$A\text{-}B + CH_2 = CHR \xrightarrow{R^1OOR^1} CH_2\ A\ CHBR \tag{1}$$

takes place through the following complex set of reactions

$$R^1OOR^1 \longrightarrow 2R^1O. \tag{2}$$

$$R^1O. + A\text{-}B \longrightarrow R^1OB + A. \tag{3}$$

$$A. + CH_2 = CHR \longrightarrow A.CH_2.\ CHR. \tag{4}$$

$$A.CH_2.\ CHR. + A\text{-}B \longrightarrow A.CH_2.\ CHRB + A. \tag{5}$$

$$2A. \longrightarrow A\text{-}A \tag{6}$$

$$2A\ CH_2CHR. \longrightarrow ACH_2.\ CH(R).\ CH(R).\ CH_2A \tag{7}$$

$$A. + ACH_2.\ CHR. \longrightarrow ACH_2.\ CHRA \tag{8}$$

The steps (2) and (3) represent chain initiation, (6) (7) and (8) represent chain termination and (4) and (5) chain propagation. The products are determined by reactions (4) and (5) where a very large number of such cycles may take place for every radical introduced into the system. In contrast, chain termination reactions destroy radicals and thus no more chain terminations than chain initiations can occur. The actual yield of products, under set experimental conditions, is determined by the overall reaction rate, and the kinetic chain length is therefore dependent on initiation, propagation and termination steps.

Initiation

The initiation step may be either by means of chemical additives or photochemical or high energy radiation. Of the chemical initiations the peroxides acetyl, benzoyl and tert-butyl are most widely used. With acetyl and benzoyl peroxides the thermal break down is such as to give a methyl or a phenyl radical and carbon dioxide. There is some evidence of/

of the benzoyloxy radical from benzoyl peroxide decomposition[90]. The break down of tert-butyl peroxide yields the tert-butoxy radical and then the subsequent formation of acetone and a methyl radical. Using these three named peroxides it is possible to study reactions from room temperature to 150°. The particular initiator chosen is dependent on the temperature since a continual supply of radicals is required over a few half-life periods of the initiators[91].

In photoinitiation the energy absorbed per absorbing molecule from irradiation $E = h\nu$ where h is Plank's constant and ν is the frequency of the radiation. For ultraviolet light of wavelength 4000-2000 Å this energy lies in the range 71.4 - 142.8 k.cals/mole; this energy is sufficient to cause bond dissociation in most cases. However, due to fluorescence or loss of energy by collision, reaction does not always occur. particularly in the liquid phase. The addition of bromotrichloromethane is initiated by ultraviolet light in the 3000 Å region. This is the lower limit of Pyrex glass and shorter wavelengths require quartz vessels.

For high energy radiation the implications will be discussed in more detail in the present work. The use of high energy radiation as a source of radicals gives a very convenient method of studying systems at various temperatures.

Propagation

As radicals disappear very quickly by recombination as in reactions (6), (7) and (8), the propagation steps (4) and (5) must occur within a time limit of about 1 second. Since a large number of reactions must occur in this space of time a rapid, low activation process is required for good yields. The yield is further dependent on the nature of the olefin and addend. Considerable investigation of different systems and varying olefin/addend ratios have been carried out by Lewis and Mayo[92] who found a definite molar ratio/

ratio for most efficient addition. This phenomenon is due to the rate determining step being either (4) or (5) where the olefin proportion is low or high respectively.

The rates of reaction (4) and (5) depend on the exothermicity of these reactions which is itself dependent on the resonance energies of the radicals A. and R.. As in reaction (4) the resonance of A. is lost and that of R. gained, a highly stabilized A. will decrease the exothermicity of this process whereas a suitably substituted R. may increase the stability of the radical formed and thus the exothermicity. In (5) the resonance energy of R. is lost and that of A. gained whereas in (4) the reverse situation occurs.

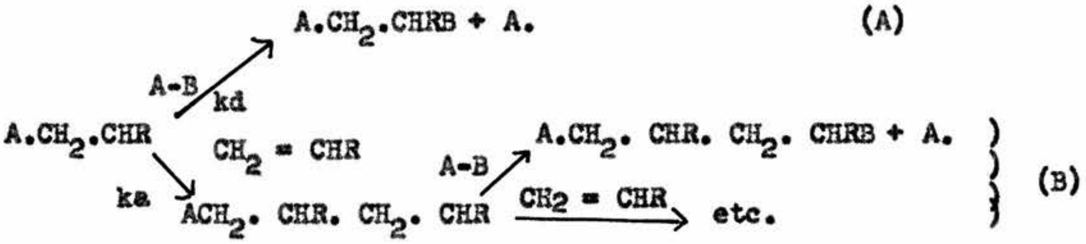
In reaction (5) the scission of the covalent bond A-B is also determined by the nature of B. For example in the halomethanes the reactivity increases in the sequence $H<Cl<Br<I$. Thus bromotrichloromethane undergoes addition more readily than carbon tetrachloride. In the addition of chloroform the entities are the trichloromethyl radical and the hydrogen atom with the stabilization of the trichloromethyl radical over-riding the weaker carbon-chlorine bond; bromoform, however, adds as dibromomethyl accompanied by bromine abstraction.

Factors other than the exothermic nature influence the rate of addition as indicated by reactions which are highly exothermic yet exhibit a considerable activation energy due to steric and polar effects[93]. The steric effect is emphasised in the more rapid addition to terminal olefins with the initial radical adding at the least substituted position. The stability of the resulting radical is however also influential in this addition step. The abstraction reaction tends to be free of any steric hindrances. The polar effect concerns the electron withdrawing and electron supplying tendencies of the substituent groups; this effect, plays an important role in the rate of displacement/

displacement as well as the addition step. Its nature is such that radicals with strong electron withdrawing groups are more reactive towards substrates containing electron supplying groups, and vice versa.

Telomer Formation

In the reaction sequence given previously the radicals formed in reaction (4) may add to another monomer molecule before displacement can occur. The resulting radical may also react competitively by addition or displacement giving the general sequence as follows, with the products ultimately formed by path (B) being known as telomers.

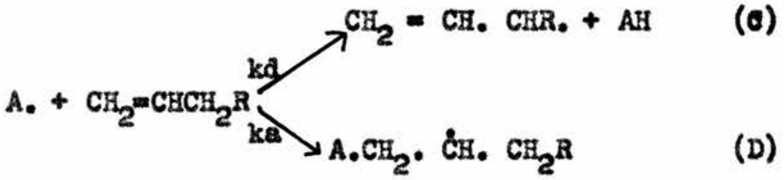


where kd and ka represent the rate constants for displacement and addition respectively. The telomer formation thus depends on the ratio kd/ka known as the transfer constant C. For systems with C«1 good yields of the 1:1 adduct may be obtained either by using high addend: olefin ratio or by slowly adding the olefin during the reaction. Raising the reaction temperature also improves the yield of 1:1 adduct as the transfer constant is increased. In practice telomerisation is an experimental problem in the halomethane system when compounds less reactive than bromotrichloromethane are used; it is very pronounced in halomethanes containing less than three halogen atoms in the molecule unless there is activation by another substituent.

Allylic Attack

The addition to olefins is further complicated by the displacement reactions at an allylic position in preference to double bond addition. This is most predominant in non-terminal olefins and its implications in the carbon tetrachloride/cyclohexene/

tetrachloride/cyclohexene system have been investigated by Israelashvili et al[94]. The competing reactions here are of the type,



with the ratio kd/ka giving a measure of the relative importance of the two reactions. Allylic radicals are highly resonance stabilized and may not restart a chain process but disappear by dimerisation or disproportionation thus reducing the yield. In some cases the allylic radical may re-enter the sequence as in the bromotrichloromethane and cyclohexene system[95].

$$C_6H_9\cdot + BrCCl_3 \longrightarrow C_6H_9\,Br + CCl_3\cdot$$

Huyser has examined the relative amount of allylic displacement and addition for various olefins[95]. In the case of non-terminal olefins the high kd/ka value are attributed to a decrease in ka due to steric hindrance rather than a large kd value. There is also evidence that secondary hydrogen atoms are more readily abstracted than primary and that tertiary are similarly more reactive than secondary[96] which may be explained on the stabilities of the radicals or it may be explained on an ionic type mechanism $Cl_3\overset{-}{C}\ldots H\ldots \overset{+}{CH_2}.CH = CH_3$; in either the radical or ionic intermediate the hydrocarbon stability will be in the order tertiary secondary primary.

Rearrangement

Various types of rearrangement may occur in radicals formed by addition of the chain carrier to the olefin, the best known being ring closure or opening, and 1,2-shifts. Ring opening is observed in the peroxide catalysed addition of carbon tetrachloride to β-pinene[97]. The converse reaction of ring closure is displayed in a similar addition of carbon tetrachloride to diallyl ether[98].

The/

The addition of bromotrichloromethane to 3,3,3,- trichloro-prop-1-ene and its derivatives affords the best example of halogen migration in 1,2-shifts[99]. The products formed here are CCl_3. CH_2. CHCl. CCl_2 Br, $CCl_3CH_2CH = CCl_2$ and CCl_2Br. CHCl. CH_2Cl or CCl_3. CHBr. CHCl. The product 1,1,4,4,4,- pentachlorobut-1-ene is formed by loss of a chlorine atom thus the terminating step provides an initiation for a further radical chain. A similar type of reaction is noted in the addition of bromotrichloromethane to allyl bromide[100].

SECTION I

APPARATUS AND TECHNIQUES

Cobalt-60 Source

The radiation unit used in this work was set up in conjunction with A.E.R.E. Harwell in 1954 and is similar in design to that described by Gibson and Pearce[101]. In July 1957 two cobalt-60 sources were installed: a 140 curie vertically positioned source and a 64 curie horizontal source, both being in form of ^{60}Co pellets in aluminium tubes which could be manipulated electrically from a concrete safety shield into a radiation chamber.

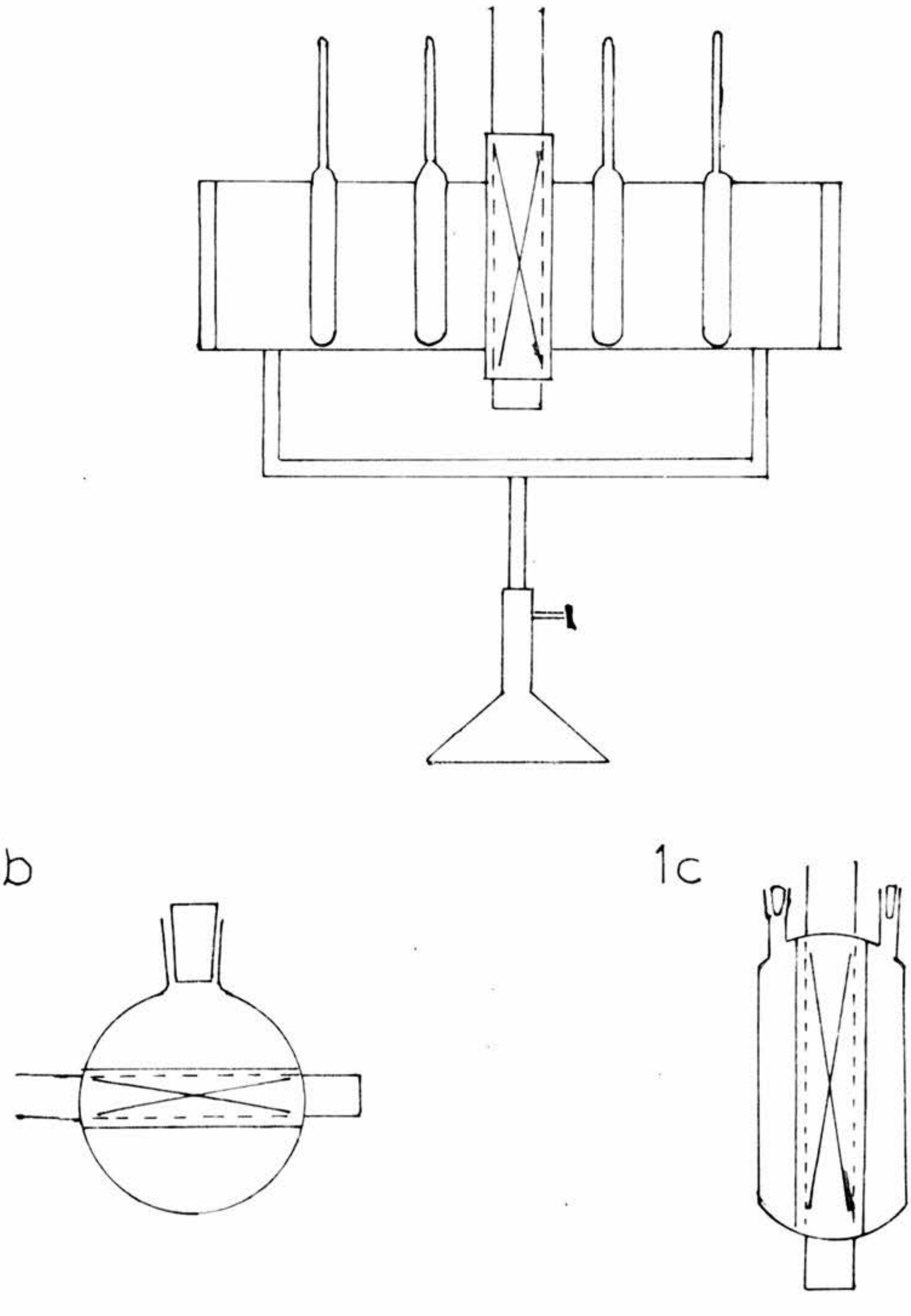
Solutions for which no rigorous precautions were taken to exclude air, were irradiated in annular Pyrex glass vessels of capacities ranging from 50 mls. to 2,000 mls. (Figures 1, (b) and (c))

However for accurate quantitative work irradiations were carried out in evacuated sealed Pyrex glass tubes of ca 80 mls. capacity. It was possible to irradiate eight of these tubes at the same time by placing them in fixed positions in a metal ring attached to the source tube with the source at the centre (Figure 1 (a)). Experiments confirmed that each tube in the ring received the same dose. Dose rate determinations were carried out for a set of experiments either before or after irradiation of the organic system, without altering the position of the metal ring at the source tube as this would record inaccurate dose rates.

FIGURE 1

IRRADIATION VESSELS

1a METAL RING WITH TUBES



1b

HORIZONTAL SOURCE

1c

VERTICAL SOURCE

Preparation of de-aerated samples

All glassware was cleaned by standing in chromic acid for several days before being thoroughly rinsed and dried. The organic samples were de-aerated by a repeated process of freezing in liquid nitrogen, pumping to high vacuum by a diffusion pump, and melting by immersion in cold water after the sample tube was isolated from the vacuum line. This latter process was found necessary to prevent expansion of the solid before liquifaction causing the tube to crack: the film of liquid formed next to the glass walls of the tube being able to expand into the neck of the tube. The melting of the solid was accompanied by the evolution of gas bubbles into the dead space above the liquid. When degassing was complete i.e. when no more bubbles appeared, the tube was sealed under vacuum.

In some of the later work dissolved oxygen was removed by refluxing the organic solution under a constant stream of dry oxygen-free nitrogen. This was carried out in a 3-neck flask equipped with a nitrogen inlet tube, a condenser and an outlet tube reaching to the bottom of the flask. After the reflux was complete, and the liquid cooled to room temperature in an atmosphere of nitrogen, the condenser end was closed and the flow of nitrogen forced the liquid through the outlet tube into a nitrogen flushed irradiation tube which was then sealed, while immersed in a cardice-acetone mixture.

Gas-Liquid Chromatography.

The identification of irradiation products was greatly facilitated by the use of gas-liquid chromatography (G.L.C.), as an analytical tool to compare retention times and estimate the G-values and on a preparative scale in the separation and purification of organic products. The model used in this work was a Perkin-Elmer 451 Fractometer equipped with a thermistor detector. In the analytical procedure dry hydrogen was used as a carrier gas but/

but nitrogen was employed in the preparative scale separations. The columns used were 1 metre or 2 metre stainless steel tubes, asbestos lagged; the columns were packed as required. The liquid sample injection was by a Hamilton 10 microlitre syringe (# 701N). The stationary phases used throughout the work were:- silicone elastomer E301 (S.E.), dinonyl phthalate (D.N.P.), tricresyl phosphate (T.C.P.), "Tween 60" ("TW60"), and polyethylene glycol adipate 1500 (P.E.G.ad); the abbreviations given after each will be used throughout the text. The column packing was Gas Chromatography G-cel (60 - 80 mesh) with a 25% w/w ratio of the appropriate stationary phase; the packing G-cel is referred to as "C" e.g. 25% P.E.G.ad/C.

In the preparative scale a 0.9 metre column was found sufficient for the separation of most compounds. Larger columns were available on a laboratory constructed apparatus using 25 mm internal diameter Pyrex Glass columns with a Katharometer detector (Gow - Mac W2) and injection system as shown in figure II(a).

The traps used consisted of two parts, as shown in fugure II(b) and (c), joined by a quickfit joint; the first part was cooled in cardice-acetone or ice-water depending on their efficiency of trapping; the second part, also cooled, was filled with $\frac{1}{4}$" glass helices to condense any fog which passed over from the first trap. The recovery of the fraction condensed in the second part was achieved by heating it in an electric jacket and passing a slow stream of nitrogen over the helices, into the first part which was immersed in the appropriate coolant. The major fraction condensed in the first part and ran down into the well which could then be cut off to obtain the sample. All samples collected from the preparative scale column were distilled before measurement of infrared spectra or the submission for elementary/

elementary analysis to remove any stationary phase stripped during the elution of the product.

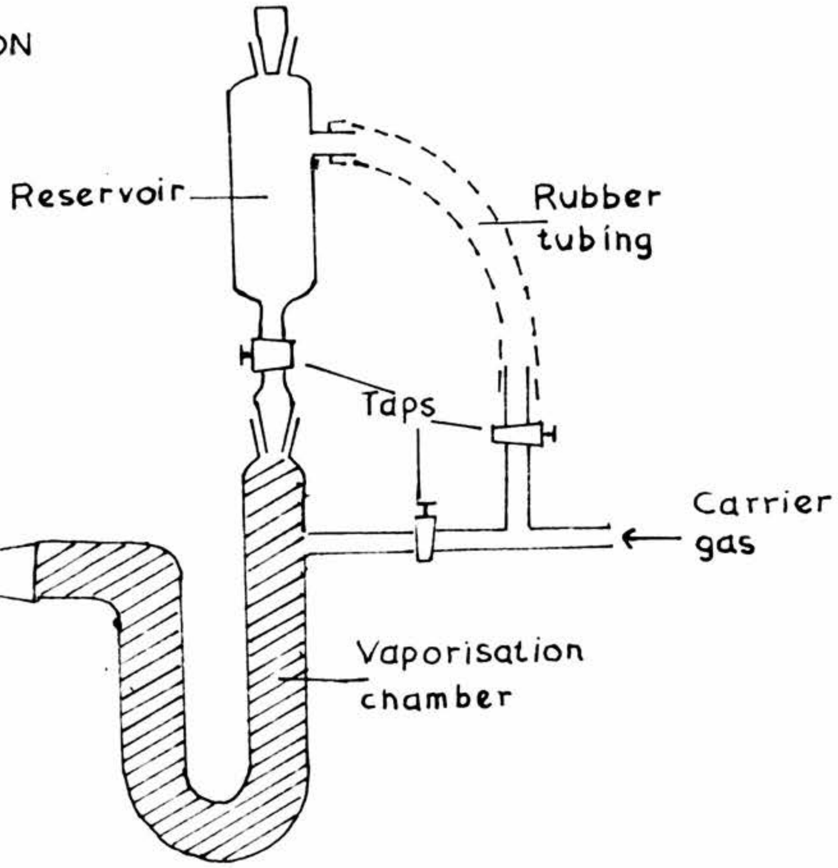
The flow rate for the preparative column was measured by the soap bubble technique using a graduated tube of 500 mls. total volume.

In some cases where the proportion of product was small, the separation was difficult, or an infrared spectrum only was required, the products were condensed directly onto a sodium chloride plate from the analytical column effluent for infrared investigation. This method proved quite successful when the plates were cooled over evaporating cardice in a calcium chloride desiccator; the gas flow was maintained about 40 mls. per minute and in this way 10 µl. samples on the analytical column were sufficient to give two samples for investigation after about three injections. Greater care was required for samples present in smaller proportions since surface evaporation caused a loss of product, this being especially the case for the more volatile products. Under such conditions it was found most efficient to pass the effluent gas stream onto a small droplet of Nujol or some other satisfactory "solvent" thus eliminating the evaporation.

FIGURE 2

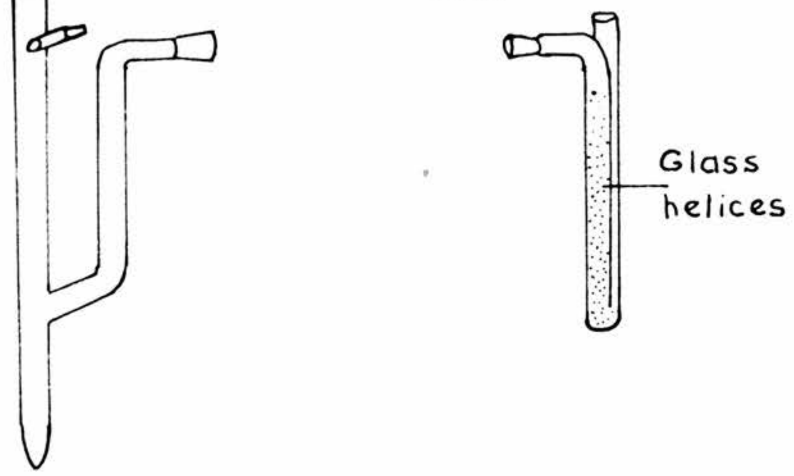
PREPARATIVE SCALE G.L.C.

2a INJECTION SYSTEM



TRAPS

2b 2c



First part

Second part

SECTION II

The Irradiation of Mixtures of Hydrocarbons and Carbon Tetrachloride.

SECTION II(A) (a) Cyclohexene and Carbon Tetrachloride.
(b) Cyclohexene and Chloroform.

SECTION II(B) Acetylene and Carbon Tetrachloride.

SECTION II(C) Cyclopropane and Carbon Tetrachloride.

SECTION II(D) Acenaphthylene and Carbon Tetrachloride.

Introduction.

Previous workers [102a.b.] in this department have studied various carbon tetrachloride-hydrocarbon systems and the present approach is an extension of this investigation to other hydrocarbon solutions. The previous work had dealt with saturated and aromatic hydrocarbons; the present investigation was concerned with the irradiation of solutions of unsaturated hydrocarbons in carbon tetrachloride.

The pertinent features of the radiolysis of unsaturated hydrocarbons are their addition and polymerisation reactions which have been discussed in the general introduction where the important mechanistic interest of such reactions was noted.

Although little is reported of the radiolysis of halomethane-olefin mixtures such systems with peroxide catalysed initiation have been extensively investigated; the present approach is to compare and contrast the peroxide and radiation induced reactions.

In the benzoyl peroxide catalysed addition of carbon tetrachloride to cyclohexene at the reflux temperature of the mixture the main product is the 1:1 adduct with other products being formed only in minor amounts: such minor products as 3-chlorocyclohexene and the dimer 3,3'-bicyclohexenyl, have been identified by Kooyman and Farenhorst[90]. This same system was investigated by Israelashvil~~l~~i and Shabatay[94] whose researches confirmed the role of allylic hydrogen abstraction when the initiation was brought about by acetyl or benzoyl peroxide. These workers postulated that Kharasch type addition only occurs with large radicals which are excluded from allylic substitution by steric interference. This hypothesis was based on the identification of addition products containing the benzoyloxy fragment of benzoyl peroxide i.e. 2-chlorocyclohexyl-1-benzoate, but no such product from the methyl radicals produced from acetyl peroxide decomposition;

allylic/

allylic substitution by methyl radicals was however observed but not for the larger benzoyloxy or chain carrying trichloromethyl radicals.

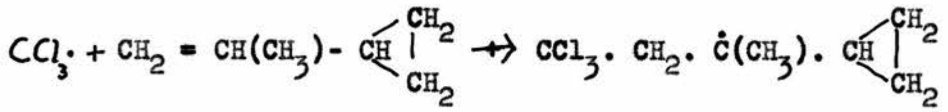
A similar mixture consisting of bromotrichloromethane and cyclohexene has been investigated by Huyser[95] with the purpose of estimating the relative reaction rates of addition and allylic attack, the rate constants being denoted by ka and kt respectively. This factor ka/kt is given by: (moles $BrCCl_3$ reacted-moles $CHCl_3$ formed)/(moles $CHCl_3$ formed) and values for a mixture of 2 mls. olefin and 0.5 mls. bromotrichloromethane, were 1.20 and 1.80 at 78° and 40° respectively. This same mixture was studied at room temperature by Heiba and Andersen[103] with a 4/1 molar ratio of bromotrichloromethane to olefin; radical production was initiated by irradiation with a 3.5 kilocurie cobalt-60 source. Products identified, and their relative percentages, were 3-bromocyclohexene (12%), cis-1,2-dibromocyclohexene (8%), 1,2-di(trichloromethyl) cyclohexane (2.5%), and 2-bromo-1-trichloromethylcyclohexane (63.5%).

Other systems which have been investigated by radiolysis are the ethylene-chloroform and ethylene-chloroform-carbon tetrachloride mixtures[104] where the main products identified are these formed by the addition of one molecule of halomethane to one or more ethylene molecules giving compounds of general formula $CCl_3\ (CH_2.\ CH_2)_nX$ where X = hydrogen or chlorine dependent on whether the displacement reaction occurs with chloroform or carbon tetrachloride; the value of n is related to the ethylene pressure. G-values of up to 3,000 were obtained at 100°C and of 300 at 28°C for disappearance of ethylene monomer.

The unsaturated character of cyclopropane is in evidence in its reactions with chlorinating agents where the formation of 1,3-dichloropropane indicates the addition of chlorine to cyclopropane with concomitant/

concomitant ring-opening. Walling and Fredricks[105] carried out the chlorination using chlorine itself and with tert-butyl hypochlorite, both in the liquid phase, and found cyclopropyl chloride and 1,3-dichloropropane as the primary products; higher chlorinated products were attributed to the secondary reaction of 1,3-dichloropropane to give the 1,2,3-trichloropropane and 1,1,3-trichloropropane. With chlorine the addition product predominates at low temperature (0°) but at higher temperatures (68°) the substitution product cyclopropyl chloride is the major product; tert-butyl hypochlorite gives less addition product at both temperatures with the substitution reaction predominating.

A study of the decomposition of biscyclopropylformyl peroxide in carbon tetrachloride[106] at 70° showed among the products cyclopropyl chloride with no observable isomerisation of the cyclopropyl radical to the more stable allyl radical. However, in the addition of bromotrichloromethane and carbon tetrachloride to 2-cyclopropylpropene[107] at 80°C the 1:1 addition products are 1,1,1-trichloro-3-methyl-6-bromohex-3-ene and -6-chlorohex-3-ene, respectively and these products are consistent with the following process:



$$\text{A}\cdot \longrightarrow \text{CCl}_3.\ \text{CH}_2.\ \text{C(CH}_3\text{)} = \text{CH}.\ \text{CH}_2.\ \underset{\text{B}\cdot}{\text{CH}_2.}$$

$$\text{B}\cdot + \text{BrCCl}_3 \rightarrow \text{CCl}_3.\ \text{CH}_2.\ \text{C(CH}_3\text{)} = \text{CH}.\ \text{CH}_2.\ \text{CH}_2\text{Br}$$

which indicates the isomerisation to a more stable radical by opening of the cyclopropyl ring.

SECTION II(A)

The Irradiation Of

(a) Cyclohexene - Carbon Tetrachloride

(b) Cyclohexene-Chloroform.

Purification

A sample of cyclohexene (B.D.H.) was shown by G.L.C. to contain several higher boiling impurities and one more volatile constituent. Distillation of this cyclohexene in a 2' silvered vacuum-jacketted fractionating column packed with $\frac{1}{4}$" glass helices gave cyclohexene free of the low boiling impurity after one distillation. However, after several such distillations it was found that two higher boiling impurities persisted and these (ca 0.5-1%) could not be removed even by use of a 4', 20 mm i.d. column, packed with Stedman stainless steel gauze rings surrounded by an electrically heated jacket. After drying over calcium chloride the cyclohexene was distilled in an atmosphere of oxygen-free nitrogen.

Carbon tetrachloride was purified by slow distillation using the 4' column mentioned above. The removal of chloroform and dichloromethane was noted and the last 10% was discarded. The final distillation was carried out under nitrogen after drying over calcium chloride for 2-3 days.

The irradiation of 10 mole % cyclohexene - 90 mole % carbon tetrachloride solution.

A 2 litre solution was irradiated for four weeks at a dose rate of 1- 1.5 eV/ml./min.

The irradiated solution was light brown in colour and the evolution of hydrogen chloride and phosgene was noted. The distillation was commenced using a 9" Vigreux column lagged with asbestos rope; the distillate was frequently monitored by G.L.C. for an indication of its composition. The early distillate (ca. 20 mls) boiling 70-75°C was collected, followed by a large fraction of mainly unreacted starting material. This left a residue of about 300 mls which was tested by G.L.C. for a tentative identification of the products.

Examination/

Examination of the Early Distillate

Examination by G.L.C. on a 1 metre 25% S.E./c at 50°C indicated two irradiation products of shorter retention times than carbon tetrachloride. The compound of shortest retention time corresponded to dichloromethane: this product was present only in very small quantities. The next eluted product corresponded to chloroform which was present in a greater amount.

The use of 25% T.C.P/C and 25% D.N.P./C confirmed these observations.

Thus the irradiation products more volatile than carbon tetrachloride are :

(1) Hydrogen chloride
(2) Carbonyl chloride (owing to presence of oxygen)
(3) Dichloromethane (minor)
(4) Chloroform.

Examination of residue after distillation at atmospheric pressure.

Frequent examination of the distillate by G.L.C. showed that there was no irradiation product in the large middle fraction, and all the higher boiling irradiation products remained in this residue. "Tween 60" was found to be the most successful stationary phase for separation of these products: on a 2 metre 25% "Tween 60"/C column at 160°C with a flow rate of 55 mls hydrogen per minute, 13 irradiation products were revealed, which will be referred to as A - M, with the following retention times.

Product A - retention time 1 minute
Product B - retention time 1½ minutes
Product C - retention time 2 minutes
Product D - retention time 4 minutes
Product E - retention time 5 minutes
Product F - retention time 6 minutes
Product G - retention time 9 minutes/

Product H - retention time 15 minutes

Product I - retention time 15½ minutes

Product J - retention time 30 minutes

Product K - retention time 35 minutes

Product L - retention time 37 minutes

Product M - retention time 42 minutes

For complete identification of the above products the residue was fractionally distilled at reduced pressure using a 9" Vigreux column to give a series of fractions and an oil residue. On recombination the distillate was refractionated and gave four distinct fractions (1) Boiling over the range 90-100°C/13 mm containing predominately the products (A), (B), (C) and (D); similarly fraction (2) boiling 100-110°C/13mm contained (E) and (F), fraction (3) boiling over range 110-120°C/10 mm contained (G), (H), and (I) and fraction (4) boiling over range 125-135°C/10 mm contained (J), (K), (L) and (M).

Further fractionation of these mixtures was achieved by preparative scale gas chromatography using an 18", 25 mm i.d. column packed with 25% S.E./C and a flow rate of 300 mls nitrogen per minute; the column temperature was varied in order to obtain the appropriate product in a reasonable time. The results obtained with each of the four fractions are described below.

Fraction (1) containing (A), (B), (C) and (D).

The product (D) was present in very small quantity and no further investigation as to its nature was carried out; work on the irradiation of different distillate fractions of cyclohexene with carbon tetrachloride indicated that this product was due to an impurity in the cyclohexene. It was not possible to separate the three products on the preparative scale column but a/

a sample, free of any residual starting material or higher boiling products, was eluted after 10 minutes when a column temperature of 100°C was used.

Runs on 25% S.E./C, 25% D.N.P./C and 25% "TW60"/C all indicated that the products were (A)-chlorocyclohexane or 1-chlorocyclohexene, (B) 4-chlorocyclohexene, (C) 3-chlorocyclohexene; samples of 1-, 3-, and 4-chlorocyclohexene were prepared (see appendix) and a sample of chlorocyclohexane was obtained commercially. The infrared spectrum of the mixture indicated that (A) was chlorocyclohexane since no absorptions due to 1-chlorocyclohexene were observed. The infrared spectra of synthetic mixtures of 3- and 4- chlorocyclohexene with (a) chlorocyclohexane and (b) 1-chlorocyclohexene in the appropriate quantities as indicated by the peak heights confirmed that in fact the compounds were (A) chlorocyclohexane, (B) 4-chlorocyclohexene (C) 3-chlorocyclohexene.

Fraction (2) containing products (E) and (F).

The presence of hexachloroethane was obvious from the formation of the characteristic white crystals in the condenser during the distillation. The two products (E) and (F) were not separated on the preparative scale column at 100°C and the trapped sample, retention time 20 mins., contained both products. An authentic sample of trans (±) - 1,2-dichlorocyclohexane gave an infrared spectrum identical with that of the irradiation product except for the strong hexachloroethane absorption at 680 cm^{-1} and 785 cm^{-1}. A comparison of the infrared spectrum of this irradiation mixture with that of cis-1,2- dichlorocyclohexane[108] confirmed that only the trans-isomer was formed.

Fraction (3) containing products (G), (H) and (I).

Gas/

Gas chromatography on a silicone elastomer stationary phase indicated only two product peaks and consequently the preparative scale column used gave only two fractions with retention times of 40 mins. and 60 mins. respectively at a column temperature of 100°C. The "Tween 60"/C analytical column showed these two fractions to be (a) pure (G) and (b) the products (H) and (I).

The infrared spectrum confirmed that (G) was trichloromethylcyclohexane by comparison with an authentic spectrum of this compound[102b].

The infrared spectrum of the mixture of (H) and (I) showed the presence of unsaturation and the low chlorine content indicated by the weak carbon-chlorine stretching band was confirmed by chemical analysis (C,79.6; H,10.4; Cl,9.8;%); bromination of these products removed both (H) and (I) to longer unestimated retention times, thus both appear to be unsaturated. Tentative identification of (H), present in greatest amount, by comparison of retention times would indicate that it was 3, 3^{1}- bicyclohexenyl, as formed in the benzoyl peroxide initiated reaction of the same mixture[90]; no definite formula could be attributed to the minor product (I) although 3-trichloromethylcyclohexene is a possibility.

<u>Fraction (4) containing products (J), (K), (L) and (M).</u>

The peaks corresponding to (K) and (L) were incompletely separated on "Tween 60"/C and no further separation could be achieved: silicone elastomer showed three incompletely separated peaks. Under the same column conditions a specimen of 1-chloro-2-trichloromethylcyclohexane prepared from carbon tetrachloride and cyclohexene with (a) benzoyl peroxide (b) cupric chloride and ethanolamine as catalysts was resolved into only two components attributed to the <u>cis</u>- and <u>trans</u>- isomers (see appendix); the irradiation product (J) and (L) had identical retention times to these two isomers on all/

all stationary phases used i.e. T.C.P. , D.N.P., P.E.G.ad., and "Tween 60". The infrared spectrum of the irradiation product exhibited no distinguishing features and was more characteristic of a mixture. However elementary analysis gave C,36.9; H,4.7; Cl,58.2%; and $C_7H_{10}Cl_4$ requires C,35.6; H,4.2; Cl,60.2%; thus as a basis for investigation of the nature of components (K) and (M) two possibilities were considered; (a) that these compounds were positional isomers of (J) and (L), and (b) that their structures were based on a cyclopentane skeleton formed by ring-contraction during an ion-molecule reaction. In order to decide between these possibilities a method was developed for replacement of the halogen atoms by hydrogen to give the parent hydrocarbon(s). Trial experiments with the mixture of (J) and (L) from the peroxide initiated reaction showed that catalytic hydrogenation was ineffective (see appendix) but that reaction with sodium ethanethiolate gave a mixture of two sulphur compounds which was converted by treatment with Raney nickel, into methylcyclopentane, identified by gas chromatography and infrared spectroscopy.(See appendix). A similar reaction carried out on the mixture of irradiation products gave a mixture of four sulphur compounds which was again converted by Raney nickel solely into methylcyclohexane, thereby showing that no ring-contraction had taken place.

It now seemed probable that compounds (K) and (M) were secondary products arising by free radical attack on one or more of the primary irradiation products, and this view was supported by the observation that their yields increased, relative to those of (J) and (L) with increasing dose. Accordingly mixtures of (a) chlorocyclohexane, (b) compounds (A), (B) and (C), and (c) trichloromethylcyclohexane, with carbon tetrachloride were irradiated. No products of comparable retention time were formed in the first two mixtures but compounds (K) and (M) together with a trace of (L)/

(L) were formed in the last mixture. Compounds (K) and (M) are clearly, therefore, chlorotrichloromethylcyclohexanes with ring substituents in relative positions other than 1:2 and are formed from trichloromethylcyclohexane; the appearance of (L) may be due to one of the 1,2- isomers or another isomer of comparable retention time.

Oil residue after the removal of the above products.

Further distillation of this residue afforded two ill-defined, oily fractions showing diffuse infrared spectra; the elementary analysis for these two fractions (in order of increasing boiling point) were C,56.9; H,7.0; Cl,36.0%; and C,59.9; H,7.5; Cl,32.4%; this may be mixtures of higher telomers.

(b) The irradiation of cyclohexene-chloroform mixture.

Investigation of this system was merely exploratory. A 10 m% solution (2 litres) of cyclohexene in chloroform was irradiated and examined as described for the cyclohexene-carbon tetrachloride system. Four products (W - Z) less volatile than cyclohexane were obtained:- (W) mainly chlorocyclohexane by infrared evidence; (X) analysis (C,50.8; H,6.8; Cl,42.4%; $C_7H_{11}Cl_2$ requires C,50.2; H,7.2; Cl,42.5%;) suggests dichloromethylcyclohexane; (Y) trichloromethylcyclohexane by infrared evidence; (Z) unidentified with elementary analysis C,74.4; H,9.8; Cl,14.6%; and an infrared spectrum similar to that of products (H) and (I) from the carbon tetrachloride-cyclohexene system, indicating 3,3'-bicyclohexenyl as a possible component. No further investigation was carried out on this system.

To summarise, the products formed in the irradiation of (a) a 2 litre solution of 10 m% cyclohexene - 90 m% carbon tetrachloride and (b) a 2 litre solution 10 m% cyclohexene - 90 m% chloroform were:

(a)/

(a)(1) Hydrogen chloride.
(2) Dichloromethane (possible).
(3) Chloroform.
(4) Chlorocyclohexane (A).
(5) 4-chlorocyclohexene (B).
(6) 3-chlorocyclohexene (C).
(7) Hexachloroethane(E).
(8) *trans*-(±)- 1,2-dichlorocyclohexane(F).
(9) Trichloromethylcyclohexane(G).
(10) $3,3'$-bicyclohexenyl(H)(probable).
(11) Unidentified chloro-compound(I).
(12) Chlorotrichloromethycyclohexane isomers (J) (K) (L) and (M).

(b)(1) Hydrogen chloride.
(2) Dichloromethane.
(3) Chlorocyclohexane.
(4) Dichloromethylcyclohexane.
(5) Trichloromethylcyclohexane.
(6) $3,3'$- bicyclohexenyl + unidentified chlorinated compound.

The irradiation of Degassed solutions of cyclohexene and Carbon tetrachloride

The purification of the starting material was as described previously for the 2 litre irradiation. Six tubes of 80 mls solution were made up and degassed: all tubes were of the same composition i.e. 10 m% cyclohexene and 90 m% carbon tetrachloride.

The irradiation dose was over the range 0.62×10^{20} to 2.27×10^{20} eV/ml./min. at a dose rate of 1.43×10^{16} eV/ml./min.

Measurement of Products.

Hydrogen Chloride.

The contents of each tube were transferred to a separating funnel containing an accurately known excess of dilute standard sodium hydroxide ($\sim 0.1\bar{N}$) and the stoppered funnel shaken several minutes to ensure neutralization of the hydrogen chloride. After separating the aqueous and organic layers, the latter was washed twice with distilled water, the washings being added to the excess aqueous sodium hydroxide solution. Back titration with approximately decinormal standard hydrochloric acid using methyl red as indicator then gave the amount of sodium hydroxide used up by the irradiation produced hydrogen chloride and thus a quantitative estimation of its production in moles per ml. This was the general procedure for the estimation of hydrogen chloride in all irradiations.

Organic Products.

The estimation of products more volatile than the starting materials was carried out by direct injection of a sample of the irradiated solution into a gas chromatographic column; owing to the low G-value of chloroform formation in this system it was not possible for an estimation to be carried out.

The measurement of less volatile organic products was carried out by the following general procedure. After removal of hydrogen chloride and drying over/

over anhydrous calcium chloride the organic liquid was transferred to a 250 ml. R.B. flask fitted with a short fractionating column. Unchanged starting material was distilled off and when the volume was reduced to about 25 mls., the residue was transferred to a 50 ml flask, again fitted with a short fractionating column and the volume reduced to less than 5 mls. Monitoring of the last few mls. of distillate by gas chromatography showed that no loss of lower boiling products occurred in this way. The residue was transferred to a suitable graduated flask and the fractionating column and distillation flask were subjected to thorough repeated rinsings with small volumes of distillate which were then added to the residue to ensure complete transfer of the products. The graduated flasks were made up to the mark and tightly stoppered to prevent evaporation.

The amount of organic product in each standard flask was measured by G.L.C. using peak heights when ever possible or peak areas in other cases. The standard solutions were prepared in graduated flasks using a range of concentrations similar to the concentrated irradiated solutions.

Optimum conditions for measurement were such that the peak was completely resolved from any others and had a retention time not greater than 20 minutes; if possible more than one product was estimated per injection, the corresponding standard then containing a number of compounds of known concentration.

Calculation of G-values

The expression for G-values is given by

$$G = \frac{S \times 100}{E(abs)}$$

S = number of molecules formed during the absorption of E(abs) eV of energy

$$\therefore G = \frac{\text{moles} \times 6.023 \times 10^{23} \times 10^{2}}{E(abs)}$$

The total dose = dose rate (eV/ml/min) X volume X minutes irradiated.

= y e.V. for ferrous sulphate solution.

E(abs) = energy absorbed by the organic solution /

E(abs) = energy absorbed by the organic solution

$$= y \times \frac{Ne(org)}{Ne(ferrous)}$$

Ne (ferrous) = 0.5675N.

The electron density Ne of the organic material i.e. 8 mls. cyclohexene/72 mls carbon tetrachloride is then:

$$Ne(org) = \frac{8}{80} \times \frac{0.81}{82.15} \times N \times 46 + \frac{72}{80} \times \frac{1.59}{153.8} \times N \times 74$$

as for cyclohexene $d^{20} = 0.81$ gm/ml; M.W. = 82.15; $\sum Z = (6 \times 6 + 10 \times 1) = 46$.

as for carbon tetrachloride $d^{20} = 1.59$ gm/ml; M.W. = 153.8; $\sum Z = (12 + 4 \times 17)$

$= 74$

$\therefore$ Ne (org) = 0.7336 x N.

$\therefore$ E(abs)/ml/min = y eV/ml/min x $\frac{0.7336}{0.5675}$

and as y = 1.1×10^{16} eV/ml/min.

then E(abs)(org) = 1.43×10^{16} eV/ml/min.

From this value of E(abs) and the known times of irradiation of the tubes the energy (E) absorbed in e.V./ml. can be calculated and a plot of E against moles of product formed per ml. gives a graph which is normally linear for relatively low doses. The gradient of the linear portion of the graph can then be used to calculate the G-values. Thus hydrogen chloride production, which is linear over the whole range investigated gives:

E(abs) = 2.1×10^{20} eV/Ml

for H Cl production = 13.8×10^{-6} moles/ml.

$$\therefore \quad G_{HCl} = \frac{13.8 \times 10^{-6} \times 6.023 \times 10^{2}}{2.1 \times 10^{20}} \times 10^{23}$$

= 3.95 molecules per 100 eV.

The G-values for organic compounds were similarly estimated and are listed in Table II.

The/

The G-values of most productswere constant over the range investigated:- 0.62×10^{20} - 2.27×10^{20} eV/ml but a reliable G-value for the 1:1 adduct would only be obtained in the lower part of this range, owing to the formation of the secondary products (K) and (M). Although it was found that the total chlorotrichloromethylcyclohexane production was linear with dose, inspection of the peak areas of the individual products (J), (K), (L) and (M) indicated that the cis- and trans- 1,2-adducts fell off at higher doses and the secondary products increased to compensate this; this would indicate a destruction of the primary adduct in a similar proportion to the trichloromethylcyclohexane. Again from the peak areas, at early doses, the G-values for the cis- and trans- 1-chloro-2-trichloromethylcyclohexane was found to be approximately 5 molecules per 100 eV.

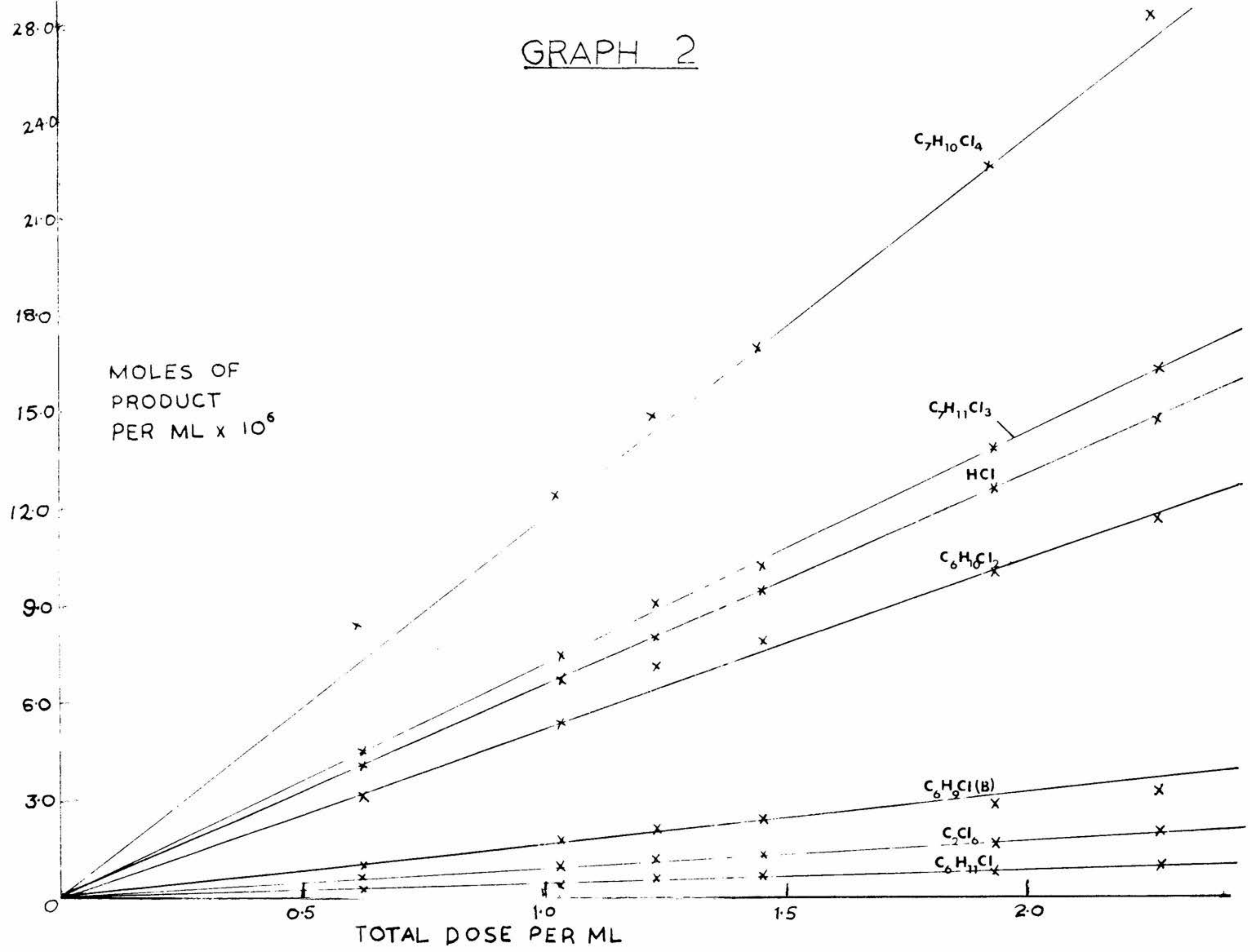
The ratio of monochloro-compounds changed with increasing dose owing mainly to the consumption of 4-chlorocyclohexene. The 3-chlorocyclohexene had a G-value of less than unity (ca 0.5) but, owing to the presence of some other peak interfering (probably an impurity), a true value was not obtainable.

From inspection of peak area the products (H) and (I) probably had a total G-value of 1.5-2 with the suspected $3,3'$- bicyclohexenyl (H) contributing over threequarters of this.

TABLE 11

Product / Dose eV/ml x 10^{-20}	HCl moles/ml x 10^6	$C_6H_{11}Cl$(A) moles/ml x 10^6	C_6H_9Cl (B) moles/ml x 10^6	C_2Cl_6 (E) moles/ml x 10^6	$C_6H_{10}Cl_2$(F) moles/ml x 10^6	$C_6H_{11}CCl_3$(G) moles/ml x 10^6	$C_7H_{10}Cl_4$ (J)(K)(L)(M) Moles/ml x 10^6
0.62	4.08	0.28	0.94	0.63	3.12	4.50	8.39
1.03	6.66	0.43	1.78	0.93	5.36	7.51	12.40
1.23	8.03	0.53	2.18	1.14	7.14	9.13	14.83
1.45	9.53	0.64	2.50	1.30	7.94	10.10	16.91
1.93	12.63	0.75	2.97	1.60	10.01	14.01	22.70
2.27	14.87	1.00	3.35	1.99	11.70	16.40	27.51
G	3.95	0. 2	1. 0	0. 5	3. 2	4. 4	7. 1

GRAPH 2



28·0
24·0
21·0
18·0
15·0
12·0
9·0
6·0
3·0
0
MOLES OF PRODUCT PER ML x 10^6
0·5
1·0
1·5
2·0
TOTAL DOSE PER ML
$C_7H_{10}Cl_4$
$C_7H_{11}Cl_3$
HCl
$C_6H_{10}Cl_2$
C_6H_9Cl (B)
C_2Cl_6
$C_6H_{11}Cl$

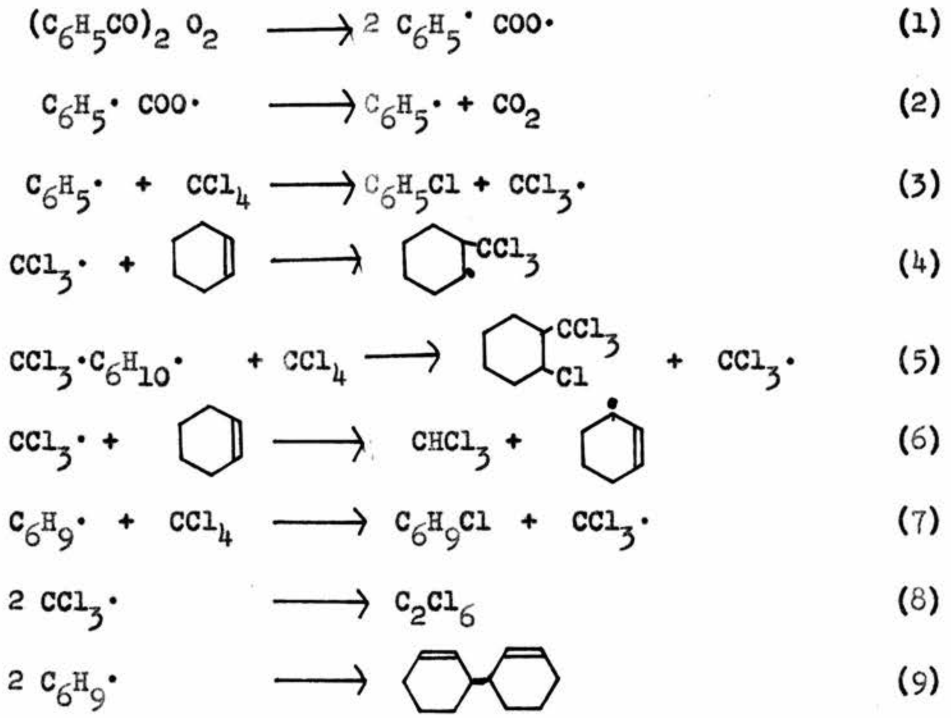
Comparison of the benzoyl peroxide initiated reaction and the irradiation.

The benzoyl peroxide initiated reaction of a mixture containing 10 m% cyclohexene and 90 m% carbon tetrachloride was carried out as described in the appendix for the preparation of the 1:1 adduct. The ratio of products formed here was strikingly different from that observed in the room temperature irradiation in that about 85% of the product in the former consisted of the 1:1 adduct, 5-10% 3-chlorocyclohexene, and about 5% 3,3' bicyclohexenyl, only traces of other compounds i.e. hexachloroethane and trichloromethylcyclohexane being formed. The irradiation of a 1 litre solution of similar composition with regard to olefin and carbon tetrachloride at the refluxing temperature of this mixture, 78-80°C indicated that the difference was caused almost entirely by the difference in temperature at which the reactions were carried out. The proportions of products in the peroxide catalysed reaction and in this high temperature irradiation differed only in a small amount of 4-chlorocyclohexene and some trans-1,2-dichlorocyclohexane produced in the latter.

Although the ratio of products changed strikingly with the increase in temperature giving a large predominance of 1:1 adduct the G-values calculated indicated that some of the other products also increased with respect to the lower temperature irradiation: 1,2-dichlorocyclohexane increased from G = 3.2 to G = 3.8 and the 3-chlorocyclohexene from ca. 0.5 to 2; the trichloromethylcyclohexane and the 3,3'-bicyclohexenyl were considerably reduced, the former to a very small value and the latter to about a third of its room temperature value. Of the monochloro-compounds, only a trace of chlorocyclohexane was detected while the 4-chlorocyclohexene was produced in similar quantities at both temperatures. The yield of 1-chloro-2-trichloromethylcyclohexane increased four fold at the higher temperature.

Discussion

In the benzoyl peroxide initiated addition of carbon tetrachloride to cyclohexene the following reaction sequence is postulated to account for the products isolated[90].



Addition of a trichloromethyl radical to cyclohexene (reaction 4) followed by abstraction of a chlorine atom from carbon tetrachloride (reaction 5) results in the formation of 1-chloro-2-trichloromethylcyclohexane and these two reactions constitute a chain process. An alternative chain process (reactions 6 and 7) indicated by allylic abstraction, results in the formation of 3-chlorocyclohexene. The formation of $3,3^{1}$-bicyclohexenyl is attributed to the low reactivity of the resonance stabilized 3-cyclohexenyl radical which may disappear by dimerisation (reaction 9) in preference to abstracting a chlorine atom from carbon tetrachloride. That the benzoyloxy radical, $(C_6H_5\cdot COO\cdot)$ is formed and has an appreciable lifetime is proved by the isolation of 2-chlorocyclohexyl benzoate.

In the radiolysis of such a mixture the primary act is the breakdown of the/

the carbon tetrachloride giving chlorine atoms and trichloromethyl radicals,

$$CCl_4 \rightsquigarrow CCl_3\cdot + Cl\cdot \qquad (10)$$

which then attack the cyclohexene.

The trichloromethyl radical may undergo a chain reaction as illustrated by reactions (4) and (5), or form chloroform by allylic displacement. At high temperatures (80°C) this is in fact found to be the case and the yield of 1-chloro-2-trichloromethylcyclohexane (G = 20) is indicative of this chain. The detection of chloroform also confirms the hydrogen abstraction by this radical. However, at room temperature (15°C) the trichloromethylcyclohexyl radical also abstracts hydrogen from cyclohexene to form trichloromethyl:cyclohexane i.e.

$$CCl_3\cdot C_6H_{10}\cdot + C_6H_{10} \longrightarrow CCl_3\cdot C_6H_{11} + C_6H_9\cdot \qquad (11)$$

That reaction (11) takes place in comparable yield to the chlorine abstraction at room temperature whereas the chlorine abstraction predominates at the higher temperature indicates that the hydrogen abstraction is the lower activation energy process, the higher activation process being the one favoured by increasing the temperature. The hydrogen abstraction probably has the lower activation energy because of (a) the resonance energy of the forming cyclohexenyl radical is greater than that from the forming trichloromethyl radical in the transition state and (b) the lower steric repulsion between the neighbouring trichloromethyl group and the atom being abstracted when the latter is hydrogen than when it is chlorine. Certainly factor (a) would give predominately hydrogen abstraction as the resonance energy of stabilization of the cyclohexenyl radical will be about 25 k.cals. per mole by comparison to the allyl radical itself; this is well in excess of the 12 k.cals. per mole for the trichloromethyl radical[109]. The steric factors (b) of the neighbouring group to the radical site will be considered in more detail in reference to the comparative hydrogen and chlorine abstractions

of/

of the chlorocyclohexyl radical.

The reactions of the chlorine atoms produced by radiolysis are similar to those of the trichloromethyl radicals: addition or abstraction to give either a chlorocyclohexyl radical or 3-cyclohexenyl radical and hydrogen chloride.

$$Cl\cdot + C_6H_{10} \longrightarrow ClC_6H_{10}\cdot \qquad (12)$$

$$Cl\cdot + C_6H_{10} \longrightarrow C_6H_9\cdot + H\,Cl \qquad (13)$$

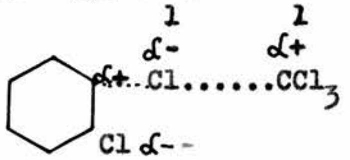
The chlorocyclohexyl radical would then either give 1,2-dichlorocyclohexane or chlorocyclohexane by reactions similar (5) and (11). It was found that in fact the dichloro-compound predominated greatly at both temperatures of irradiations, this behavious being in contrast to that of the similar trichloromethylcyclohexyl radical which at 15°C has G = 5 for chlorine abstraction and G = 4.4 for hydrogen abstraction.

The possibility that the dichlorocyclohexane may be produced by heterolytic addition of molecular chlorine may be discounted on the following argument. In the radiolysis of pure carbon tetrachloride it was found that $G(Cl_2) = 0.8$ linear at 23°C over the range 0-8 x 10^{19}eV/ml[110]. Therefore, as the $G(C_6H_{10}Cl_2)$ was found to be 3.2 here (dose rate range 0.62-2.27 x 10^{20} eV/ml) the chlorine yield is insufficient to account for its total production. Moreover, it is to be expected that the rate of reaction of chlorine atoms with cyclohexene will be much greater than the rate of their reaction with each other. Further evidence that the chlorine atoms do attack the double bond is provided by the low G_{HCl} (3.95) found for cyclohexene-carbon tetrachloride compared with that found in a similarly constituted mixture of cyclohexane and carbon tetrachloride where $G_{HCl} = 8.23$[102b].

Now to explain the low G-value for hydrogen abstraction (0.2) compared

to/

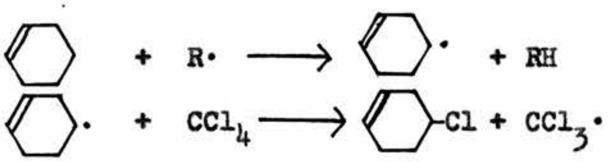
to chlorine abstraction (3.2) for the chlorocyclohexyl radical, which is in contrast to the ratios found for the trichloromethylcyclohexyl radical, two factors may be responsible - a steric factor and/or a polar factor. Considering the steric factor, the neighbouring large trichloromethyl group may introduce larger repulsive forces into the transition state for chlorine abstraction by the trichloromethylcyclohexyl radical than into the transition state for the corresponding hydrogen abstraction; the smaller chlorine atom in the chlorocyclohexyl radical would not show the same differential effect. This suggests that the steric factor is the dominant factor in causing the larger activation energy for chlorine abstraction by the trichloromethylcyclohexyl radical. However, the G-value for hydrogen abstraction by the chlorocyclohexyl radical appears to be low and does not show an increase with temperature rise which would be expected if in fact it is the higher activation energy process. Also as noted previously, the hydrogen abstraction is strongly favoured from the resonance stability of the transition state. The different polar effects of the trichloromethyl and chlorine substituents adjacent to the radical site may then account for the different ratios of attack. The stronger electron attracting properties of the chlorine substituent would give greater electronic distortion, conferring a slight positive charge on the radical centre; this may then favour the attack on carbon tetrachloride since the transition state would appear as



It would be necessary to assume that the carbon tetrachloride is readily distorted by attraction of one of the chlorine atoms towards the positive centre;/

centre; on the same basis the hydrogen abstraction might be hindered. A neighbouring trichloromethyl group with its smaller electron attracting properties would not lead to such a preferred chlorine abstraction.

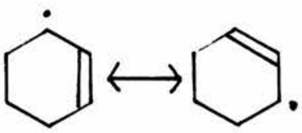
Just as the formation of 3-chlorocyclohexene is explained by reaction (6) and (7), the 4-chlorocyclohexene is presumably formed by the following sequence:-



(14)

(15)

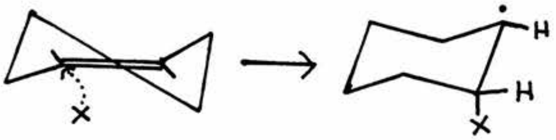
Formation of the 3-cyclohexenyl radical may be brought about by either trichloromethyl radical or chlorine atom abstraction and both hydrogen chloride and chloroform were identified; other radical intermediates may also contribute to the abstraction. However, since no 4-chlorocyclohexene was observed in the benzoyl peroxide initiated reaction, where chlorine atoms are absent and the trichloromethyl radical is the chain carrier, it may be that the chlorine atom is less selective and attacks both positions; that it is not a temperature factor is borne out by the identification of 4-chlorocyclohexene when the irradiation was carried out at the same temperature as the benzoyl peroxide experiment. A similar reaction has been noticed in the free-radical chain reaction of tert-butyl hypochlorite with pent-1-ene where as well as the allylic abstraction product, 4-chloropent-1-ene was detected[111]. The rise in the yield of 3-chlorocyclohexene from 0.5 at 18° to 2 at 78°C is accompanied by a fall in the yield of $3,3'$-bicyclohexenyl at the higher temperature. The allylic radical precursor of 3-chlorocyclohexene is resonance stabilized by the structures:-



and/

and its low reactivity allows these to disappear mainly by dimerisation at the low temperature. However, on increasing the temperature the abstraction of chlorine from carbon tetrachloride occurs before dimerisation; the 4-cyclohexenyl radical having no such stabilizing structures reacts immediately at both temperatures to give 4-chlorocyclohexene.

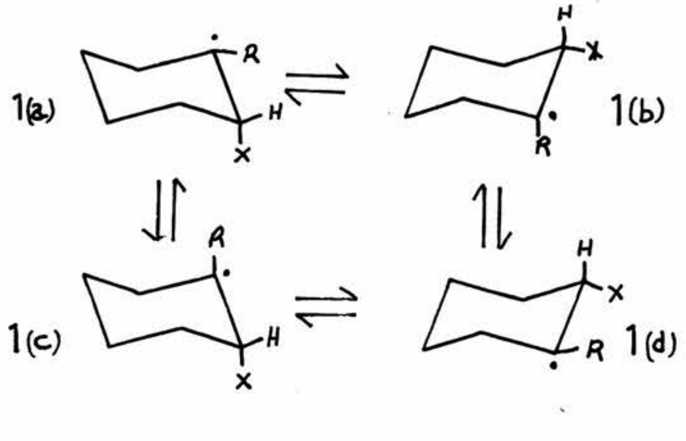
The stereochemistry of the 1,2-dichlorocyclohexane and of the 1-chloro-2-trichloromethylcyclohexane exhibit a very noteworthy difference: the dichlorocompound is entirely trans whereas the chlorotrichloromethyl compound is 50% trans-/ 50% cis- adduct. It is generally acknowledged that the initial attack on cyclohexene is via the least hindered route to give an axial substituent in the resulting free radical[112] i.e.



where X = CCl_3 or Cl.

The intermediate radical thus formed results in an odd electron centre which may be either (a) pyramidal, so that the substituent (H in this case) may be axial or equatorial, or (b) planar.

Considering the first hypothesis, which is the one favoured by Brand and Stevens[113] and Bordwell and Hewitt[114], there are four possible intermediates owing to ring inversion and inversion about the radical centre:



where X = incoming group and R is the substituent already present (e.g. R = H for cyclohexene).

The postulates are then that:

(a) the radical produced initially is represented by 1(a);

(b) the ring inversion reaction 1(a) ⟷ 1(b) and 1(c) ⟶ 1(d) are slow compared with abstraction reactions.

Now if the inversion at the radical site i.e. 1(a) ⟶ 1(b) is rapid compared with the abstraction, the result will be a mixture of <u>cis</u>- and <u>trans</u>- isomers as an equilibrium between 1(a) and 1(c) is achieved. Thus the essential features are the rate of conversion of 1(a) to 1(c) and the relative stabilities of these intermediates.

The stereospecific additions of hydrogen bromide to 1-methylcyclohexene[115] and 1-chlorocyclohexene[116] and of dinitrogen tetroxide (N_2O_4) to 1-methylcyclohexene[113] (all by free radical processes) are attributed to the short lifetime of radical 1(c) owing to the large 1-3 repulsions acting on the two axial substituents. However, for cyclohexene no such repulsions are applicable and N_2O_4 adds both <u>cis</u> and <u>trans</u> as equilibration is achieved between 1)a) and 1(c)[113]. Such a thermodynamically controlled reaction explains the non-stereospecific addition of carbon tetrachloride to cyclohexene where the intermediate 1(a) is allowed to equilibrate with 1(c) before final abstraction of chlorine; radical 1(a) gives <u>trans</u>- isomer and radical 1(c) gives <u>cis</u>-isomer.

On the other hand the fact that the 1,2-dichlorocyclohexane is entirely <u>trans</u>- would require a rapid chlorine abstraction before 1(a) to 1(c) inversion occurs in the radical where X = Cl and R = H. That such a difference in the rates of abstraction by the chlorocyclohexyl and trichloromethylcyclohexyl radicals is in fact real was noted previously (Page 57) and accounts/

accounts for the difference in the amount of chlorine relative to hydrogen abstraction by the two radicals. That the abstraction rate is a determining factor in stereospecificity is demonstrated by the reaction of thiols with 1-methylcyclohexene[117] where both <u>cis</u>- and <u>trans</u>- addition occurs in contrast to the more reactive chain transfer reagent hydrogen bromide which only yields <u>trans</u>- addition products. Also in the addition of bromotrichloromethane to cyclohexene the 1:1 addition product has been reported as the <u>trans</u>- isomer[103]. This is consistent with the greater ease of bromine abstraction from bromotrichloromethane compared to chlorine abstraction from carbon tetrachloride. However, the evidence for the exclusive formation of this isomer is not conclusive (cf <u>cis</u>-1,2-dibromocyclohexane is reported).

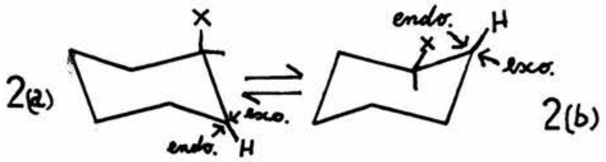
The exclusive formation of <u>trans</u>-1,2-dichlorocyclohexane in free radical reactions was noted previously by Brand and Stevens using nitryl chloride (NO_2Cl) for addition to cyclohexene[113], but this result was explained on the following basis:

$$NO_2Cl \longrightarrow NO_2\cdot + Cl\cdot \qquad (16)$$

$$Cl + NO_2Cl \longrightarrow NO_2 + Cl_2 \qquad (17)$$

with the molecular chlorine then adding heterolytically to the cyclohexene. However, as pointed out previously no such reaction can possibly account for all the <u>trans</u>-1,2-dichlorocyclohexane in the present reaction. The photochemical addition of bromine to cyclohexene has been observed to give only the <u>trans</u>-1,2-dibromocyclohexane[118], thus confirming that cyclohexene can undergo stereospecific addition if the chain transfer is rapid enough.

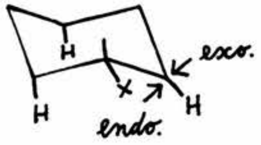
In considering a reaction pathway involving intermediates with a planar free radical centre the two possible confirmations for the substituted cyclohexyl radical will be 2(a) and 2(b) where 2(a) is the primary intermediate and 2(b) results from it by ring inversion./



Stereospecificity could then be the result of preferred attack _exo_ or _endo_ on 2(a) or 2(b).

In the present case there are two possible factors which might lead to stereospecific attack. Firstly the substituent group (i.e. chlorine or trichloromethyl) may effect the entrance at the radical site; if this was so then the preferred attack would be _endo_ in 2(a) and _exo_ in 2(b) and would give the _trans-_ isomer preferentially, but in order to explain the observations it would be necessary to assume that the smaller chlorine atom has a greater steric effect than the trichloromethyl group so this possibility may be neglected.

The second and probably more important factor is the steric effect of the axial β-hydrogen atoms which would tend to favour _exo-_ attack relative to _endo-_ attack. Stereospecific formation of the _trans-_ product could then result from the addition to the intermediate 2(b) where the _endo_ attack is least favoured.



2(b)

i.e. the _endo-_ attack is hindered by the β-hydrogen atoms; this mode of steric interaction is favoured by consideration of models[114].

This however, would imply that the chlorine atom causes inversion to 2(b) faster than the trichloromethyl group which is the reverse of the expected result; the larger trichloromethyl group will have a greater tendency to go to the more favoured equatorial position.

It appears therefore that although the formation of the _cis-_ and _trans-_ isomers of 1-chloro-2-trichloromethylcyclohexane is consistent with either/

either a pyramidal or a planar radical site the exclusive formation of the trans- dichloro-compound requires this site to have a pyramidal nature; this is in agreement with the explanation offered for most other additions to cyclohexene and 1-substituted cyclohexenes.

The other isomers (other than 1,2-) of chlorotrichloromethylcyclohexanes are probably secondary products formed by a hydrogen-chlorine exchange chain reaction of the type envisaged for cyclohexane itself, i.e.

$$CCl_3\cdot C_6H_{11} + Cl\cdot(\text{or } CCl_3\cdot) \longrightarrow CCl_3\cdot C_6H_{10} + HCl\ (\text{or } CH\,Cl_3)$$

$$CCl_3\cdot C_6H_{10} + CCl_4 \longrightarrow CCl_3\cdot C_6H_{10}CL + CCl_3\cdot$$

This type of chain reaction, in the production of chlorocyclohexane from cyclohexane and carbon tetrachloride has been noted to have a G-value of about 80[102b]. The position of hydrogen abstraction was not ascertained but the site furthest removed from the trichloromethyl group will be most likely owing to the deactivating effect of this group.

SECTION II (B)

THE IRRADIATION OF AN ACETYLENE-CARBON TETRACHLORIDE SOLUTION

The irradiation of an acetylene saturated carbon tetrachloride solution.

This system was studied previously in this department[102b] in relation to the radiolysis of benzene-carbon tetrachloride mixtures where acetylene may be produced by the breakdown of benzene. The absence of hydrogen chloride and chloroform was noted and attributed to the high carbon-hydrogen bond dissociation energy of 121 k. cals. per mole. The residue, after removal of carbon tetrachloride and more volatile compounds by distillation at atmospheric pressure, was shown to contain tetrachloroethylene (minor product) and hexachloroethane (major product); two unidentified peaks were tentatively identified as the *cis*- and *trans*- isomers of 1,3,3,3-tetrachloroprop-1-ene. The early distillate was shown to contain both *cis*- and *trans*- 1,2-dichloroethylene.

The above irradiation was carried out using an initially saturated solution of acetylene in carbon tetrachloride; the present approach was to maintain saturation of acetylene throughout the irradiation.

Experimental

A saturated solution of acetylene in carbon tetrachloride was obtained by passing a stream of the gas into 2 litres of purified carbon tetrachloride for a period of 5 hours. The acetylene, from a cylinder, was purified by first passing through a solution of 2,4-dinitrophenylhydrazine in $2\overline{N}$ hydrochloric acid and then through three concentrated sulphuric acid (Analar) scrubbers, a plug of wool being inserted in the gas stream after the dinitrophenylhydrazine solution and final sulphuric acid scrubber to remove any droplets of liquid in the gas stream; carbon tetrachloride was purified as described for the cyclohexene mixture.

When saturation was achieved the vessel was placed at the Cobalt-60 source and a slow stream of similarly purified acetylene was passed into the solution/

solution during the period of irradiation, from a cylinder outside the irradiation chamber. The sulphuric acid scrubbers were changed regularly throughout the irradiation to maintain maximum drying efficiency and removal of any impurities in the acetylene.

Examination of the irradiated solution.

After irradiation at an unmeasured total dose (dose rate approx. 1.3×10^{16} eV/ml/min.) the solution was subjected to a fractional distillation.

The early fraction distilled off slowly and examination by G.L.C. (1 metre 25% S.E./C at 50°C) showed the presence of both cis- and trans- isomers of 1,2-dichloroethylene but these were present only as minor products.

The remainder of the carbon tetrachloride was distilled off at atmospheric pressure, the absence of chloroform being noted. The residue (ca. 100 mls) was then investigated by G.L.C. for the less volatile irradiation products.

Examination on a 2 metre 25% S.E./C. column at

(a) 98°C, 55 mls hydrogen per minute showed:-

(1) A major product with small tail to the peak - retention time 8 minutes.

(2) Smaller peak corresponding to hexachloroethane-retention time 27 minutes.

(b) At 131°C, 55 mls. H_2 per minute:-

(2) Hexachloroethane - retention time 8 minutes.

(3) Small peak corresponding to 1,1,1,2,3,3- hexachloropropane - retention time 17 minutes, followed by a series of smaller peaks.

(c) At 181°C, 70 mls. H_2 per minute:-

(3) Asym-hexachloropropane - retention time 4½ minutes.

(4) Peak of ½ area of (3) - retention time 25 minutes.

(5) Peak of twice the area of (3) - retention time 43 minutes.

The/

The first peak eluted corresponded to about 85% of the products detectable by G.L.C. with hexachloroethane the other main product (ca 10%); all products eluted after hexachloroethane were only in minor quantities about 5% of detectable products.

This solution was further fractionated at reduced pressure using a 9" Vigreux column and this gave a fraction containing the hexachloroethane and the more volatile products and a residue of higher boilers.

Investigation of the reduced pressure distillate.

A refractionation of this gave a product boiling 78-79°C/73mm which contained less than 5% hexachloroethane and no more volatile components. As this was the major product of the irradiation (70 gm. being obtained) the investigation was mainly concerned with the elucidation of its structure. It had been tentatively suggested by Patterson[102b] that this product was a mixture of the cis- and trans- 1,3,3,3-tetrachloroprop-1-enes. Examination of the product obtained in this work and that obtained by Patterson on a 1 metre 25% P.E.G. ad/C column at 67°C, indicated that although the latter product resolved into two definite peaks, the former only gave a small tail of corresponding retention time to the second of the two peaks. Thus, as the present irradiation had been carried out at continuous acetylene saturation, it would indicate that the latter of the two peaks eluted was probably a secondary product. The presence of a small quantity of tetrachloroethane was observed under the above chromatographic conditions and examination on columns with other stationary phases (D.N.P., "TW60", and S.E.)confirmed the probability of such a product.

A pure sample of the irradiation product (1) free from any hexachloroethane and the small tail observed on the P.E.G.ad/C column was obtained by preparative scale gas chromatography using a 0.9 metre column of/

of 25% S.E./C. packing at 90°C and a flow rate of 500 mls N_2 per minute where a retention time of forty five minutes resulted. Only the first two thirds of this peak was trapped out and the asymmetry of the latter part was indicative of a partial separation of the two irradiation products. Examination of the trapped fraction on an analytical "Tween 60"/C column confirmed the removal of the small tail.

An elementary analysis gave:- C,20.94; H,1.44; Cl,76.71%; required for $C_3H_2Cl_4$:- C,20.00; H,1.22; Cl,78.88% and chlorination in carbon tetrachloride solution gave (asym) 1,1,1,2,3,3-hexachloropropane. These findings indicated that, in fact, the product was the 1,3,3,3-tetrachloroprop-1-ene and from infrared and n.m.r. evidence, combined with the G.L.C. detection of only one peak, the trans- isomer was favoured.

The 1,3,3,3-tetrachloropropene was then prepared by an independent route (see appendix) which should give the trans- isomer[120]. The product of this reaction, however, showed two peaks by G.L.C. analysis; (a) the main product of corresponding retention time to the main irradiation product and (b) a tail similar to that observed in the irradiation product but considerably larger (approximately 20% of the total product). This result is similar to that observed with Patterson's irradiation product.

The infrared evidence clearly demonstrated that, although there was a resenblance between the irradiation product and the chemically prepared sample, there were important differences. The infrared spectrum of the chemically prepared product showed two absorption bands in the 920 cm^{-1} - 935 cm^{-1} region which is believed to be characteristic of the trans- isomer thus the indication was that this other product was not the cis- isomer of the 1,3,3,3-tetrachloroprop-1-ene but was possibly some other rearranged tetrachloropropene since an elementary analysis of the mixture gave results consistent with the formula $C_3H_2Cl_4$ (found C,20.72; H,1.23; Cl,77.93%).

This/

This possibility was in fact proved to be the case.

The addition of anhydrous aluminum chloride (catalytic quantities) to the irradiation product gave a complete conversion to the second product obtained in the chemical preparation of the 1,3,3,3-tetrachloroprop-1-ene. Similarly, this latter mixture was converted into a homogeneous product by the action of aluminum chloride. Comparing an analagous reaction[126] whereby 3,3,3-trichloroprop-1-ene was converted to the isomeric 1,1,3-trichloroprop-1-ene the above result can be interpreted as a conversion to 1,1,3,3-tetrachloroprop-1-ene. The preparation of this 1,1,3,3-tetrachloroprop-1-ene was achieved by an independent method (see appendix) which gave an infrared spectrum identical with that of the aluminum chloride-treated product. A partial conversion of the 1,3,3,3-tetrachloroprop-1-ene to the 1,1,3,3-tetrachloroprop-1-ene was also achieved by refluxing the former in carbon tetrachloride with benzoyl peroxide or standing at room temperature over mercuric chloride; spontaneous conversion also occurred at a very slow rate.

The preceeding findings by G.L.C. investigations were confirmed by infrared spectroscopy where a mixture of the two tetrachloro-compounds gave a spectrum identical with that of the mixture from the supposed preparation of the 1,3,3,3-tetrachloro-isomer. Irradiation of a 10% solution of 1,3,3,3-tetrachloroprop-1-ene in carbon tetrachloride showed the build-up of the other isomer, again confirmed on infrared evidence.

Residue from the above distillation.

This residue contained three main peaks, all of which were present in greater proportions in the irradiation where the acetylene concentration was allowed to become depleted thus indicating that their production was due to a secondary reaction.

Distillation/

Distillation of the residue at a reduced pressure gave a series of fractions in the boiling point range 25 - 140°/0.01 mm. Infrared evidence from the early fraction boiling 25 - 30°/0.01 mm. confirmed 1,1,1,2,3,3-hexachloropropane as a product.

The higher boiling fractions did not give a good separation and G.L.C. showed the changing composition with variation in concentration of the two high boiling products; the later stages of distillation yielded a yellow viscous oil giving an elementary analysis of C,21.01; H,1.22; Cl,77.10%. About 70 gm of this material, including the charred residue was obtained indicating the importance of some chain reaction incorporating approximately one molecule of acetylene per molecule of carbon tetrachloride.

As it was expected that the main source of secondary products would be attack on the 1,3,3,3-tetrachloropropene, 10% solutions of this compound and of the 1,1,3,3-tetrachloro-isomer, both in carbon tetrachloride were irradiated. A G.L.C. analysis of the resultant solutions showed peaks corresponding to 1,1,1,2,3,3-hexachloropropane and the next higher boiling irradiation product; both isomers gave the same mixture of products except that the 1,3,3,3-tetrachloroprop-1-ene was converted to the other isomer whereas no reverse conversion was observed. Reduced pressure distillation of the irradiation mixtures yielded products boiling point 60 - 62°C/0.005mm. with identical infrared spectra; these spectra were rather diffuse and no confirmatory evidence was obtainable, the absorption due to the unsaturation being very small and probably caused by some remaining starting material.

The highest boiling product detectable by G.L.C. was unidentified but may not be a secondary product as its proportion was not so markedly increased in the irradiation where the acetylene concentration was allowed to become depleted.

The/

The irradiation products of a saturated acetylene-carbon tetrachloride mixture can then be tabulated, in order of increasing boiling point as follows:-

(a) *trans*- and *cis*- 1,2-dichloroethylene (minor product)

(b) 1,1,2,2-tetrachloroethane (?) (very small secondary product)

(c) 1,3,3,3-tetrachloroprop-1-ene (major product)

(d) 1,1,3,3-tetrachloroprop-1-ene (minor secondary product)

(e) hexachloroethane (major product)

(f) 1,1,1,2,3,3-hexachloropropane (minor secondary product)

(g) addition product of (c) and carbon tetrachloride (minor secondary product)

(h) unidentified product (minor secondary product)

Discussion

The high yield of 1,3,3,3-tetrachloroprop-1-ene from this mixture requires a chain mechanism with the following propagation steps

$$CCl_3\cdot + CH \equiv CH \longrightarrow CCl_3\cdot CH = CH\cdot \qquad (1)$$

$$CCl_3\cdot CH = CH\cdot + CCl_4 \longrightarrow CCl_3\cdot CH = CHCl + CCl_3\cdot \qquad (2)$$

The source of the trichloromethyl radical being, as for all carbon tetrachloride radiolysis:-

$$CCl_4 \rightsquigarrow CCl_3\cdot + Cl\cdot \qquad (3)$$

The chlorine atoms will undergo reaction similar to the trichloromethyl radicals but of course no such chain reaction is possible for a product which is dependent on the radiolysis for initiating chlorine atoms

$$Cl\cdot + CH \equiv CH \longrightarrow ClCH = CH\cdot \qquad (4)$$

$$ClCH = CH\cdot + CCl_4 \longrightarrow ClCH = CHCl + CCl_3\cdot \qquad (5)$$

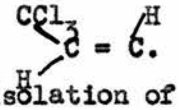
Reaction (4) in fact starts another chain sequence as shown in reaction (1) and (2).

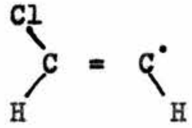
The 1,3,3,3-tetrachloroprop-1-ene and 1,2-dichloroethylene were the only primary products identified. The absence of hydrogen chloride and chloroform was noted and attributed to the high carbon-hydrogen bond dissociation energy in acetylene (121k. cals per mole).

The 1,2-dichloroethylene produced here was a mixture of <u>cis</u>- and <u>trans</u>- isomers in approximately equal quantities. However, the 1,3,3,3-tetrachloroprop-1-ene appeared only as one isomer as shown by gas chromatographic and n.m.r. evidence. The spin-spin coupling constant (J) for <u>cis</u>- olefinic protons is normally in the range 6 - 14 cycles/sec. and for the <u>trans</u>- isomer J = 11-18 cycles /sec. The tetrachloropropene gave J = 13 cycles/sec. which is ambiguous but may favour a <u>trans</u>- configuration since/

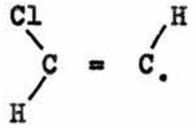
since a rule of J(cis) < J(trans) and a ratio of approximately = 0.5 holds in many cases. Further indications that the isomer is the trans are given in the infrared spectrum where the absorption in the region 922 cm^{-1} is near to that (935 cm^{-1}) expected for the carbon-hydrogen out-of-plane bending mode of a trans- CH = CHCl group[119] whereas there is no absorption below 720 cm^{-1}, the region most characteristic of cis- disubstituted olefins. However, the evidence is not confirmatory, since the rearrangement product, 1,1,3,3-tetrachloroprop-1-ene, also has an absorption band at 925 cm^{-1} which may be due to carbon-chlorine stretching. The source of the independent sample of 1,3,3,3-tetrachloroprop-1-ene would also favour its being the trans- isomer since the trans- isomer of 2-chlorovinylmercuric chloride was used and this has been shown to maintain its configuration during the exchange reaction with radioactive mercury[120]. However, here again there is some doubt since during the production of 1,3,3,3-tetrachloroprop-1-ene from this mercury compound some cis-2-chlorovinylmercuric chloride has been isolated[121]. It is concluded that, although the possibility of a cis- configuration cannot be ruled out, since only one isomer is produced the trans- isomer is strongly favoured.

Little is known of the stereochemistry of addition to acetylene and its derivatives by free radical processes but the ionic mechanism has been noted to give trans- addition and most results on this issue are concordant. In the free radical field the examinations have been carried out with bromine[122] and hydrogen bromide[123]. Skell and Allen[123] have shown that the homolytic addition of hydrogen bromide to 1-methylacetylene (1-propyne) is entirely trans and that any cis-isomer detected is produced by the reversible attack of bromine atoms on the trans- addition product initially formed. It was also found, for 1-substituted acetylenes, that bromine added mainly by a trans-mechanism/

mechanism except when the substituent group was large e.g. tert-butyl, and 2-hydroxy - and 2-acetoxy -isopropyl^{122}. It would thus appear that the intermediate radical has a fixed configuration or alternatively, since the resultant product, (e.g. of *trans*- addition of hydrogen bromide to methyacetylene) is the sterically compressed isomer, that the configuration in the transition state may be the controlling factor (i.e. kinetic control). The second possibility would then explain why the addition of carbon tetrachloride to acetylene is exclusively *trans* since the intermediate  is the more favoured one for approaching the substrate. The isolation of both *cis*- and *trans*- 1,2-dichloroethylene requires a free radical process since the heterolytic addition of molecular chlorine is entirely *trans*. The isomers appear in approximately equal quantities and the detection of only a very small quantity of a product which may be tetrachloroethane makes the isomerisation of one isomer by reversible attack of chlorine unlikely (addition should exceed isomerisation - later work on dichloroethylene-carbon tetrachloride); also the large concentration of acetylene and the major product 1,3,3,3-tetrachloroprop-1-ene would be expected to scavenge most of the chlorine atoms. This mixture of *cis*- and *trans*- isomers is in accordance with the free radical addition of bromine to acetylene where the addition product is 55% *trans*^{122}. The mixture of isomers probably results from the two intermediates (A) and (B) which give the *cis*- and *trans*- isomers respectively:



(A)



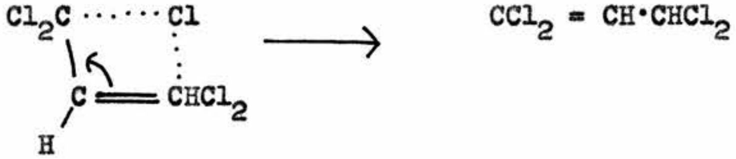
(B)

Presumably the *cis*- isomer can be formed here as the smaller chlorine atom exerts less of a steric hindrance in the transition state.

The/

The formation of the secondary product 1,1,3,3-tetrachloroprop-1-ene requires the shift of a chlorine atom from one end of the molecule of the 1,3,3,3-tetrachloropropene to the other. This involves two possible modes of rearrangement (a) the direct 1,3-shift via a four membered transition state or (b) the initial attack by a chlorine atom at the 1-position to give a radical which then loses a chlorine atom from the 3-position either directly or after a 1,2-shift of the type envisaged by Nesmeyanov and his co-workers[99].

Considering the first possibility the following intermediate is envisaged,



(6)

The possibility that this process does contribute towards the rearrangement is suggested by the auto-rearrangement observed when the 1,3,3,3-tetrachloropropene is allowed to stand at ambient temperatures; the change is, however, slow and no temperature coefficient was detectable.

In the other instance where the rearrangement is attributed to the radical formed by a chlorine atom attack on the double bond, the rearrangement is faster. That the chlorine atom is responsible can be deduced from the fact that during irradiation of a 10% solution of the compound in carbon tetrachloride, the rearrangement was more pronounced than observed on standing or by refluxing the same solution with some benzoyl peroxide; only in the irradiation is there a ready supply of chlorine atoms available. The intermediate will be the 1,1,1,3,3-pentachloropropyl radical which may lose a chlorine atom directly to give the 1,1,3,3 tetrachloropropene or rearrange to the more stable 1,1,2,3,3-pentachloropropyl radical before giving the propene.

$$CCl_2 = CH{\cdot}CHCl_2 + Cl/$$

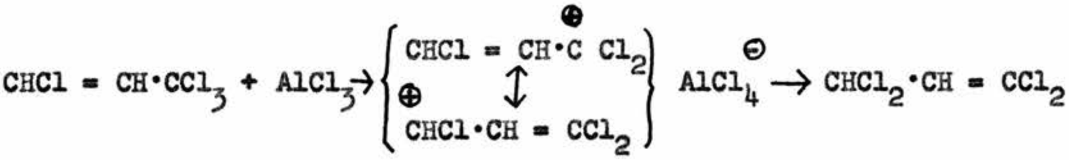
$$CCl_3\cdot\dot{C}H\cdot CHCl_2 \begin{cases} \longrightarrow CCl_2 = CH\cdot CHCl_2 + Cl\cdot & (7a) \\ \longrightarrow \dot{C}Cl_2\cdot CHCl\cdot CHCl_2 \rightarrow CCl_2 = CH\cdot CHCl_2 + Cl\cdot & (7b) \end{cases}$$

This radical rearrangement has been shown to be favoured by Nesmeyanov[99]. The increase in isomerisation caused by the benzoyl peroxide addition may be attributed to the action of chlorine atoms produced in reactions of the type.

$$CCl_3\cdot + CHCl = CH\cdot CCl_3 \longrightarrow CCl_3\ CHCl\cdot\dot{C}H\cdot CCl_3 \qquad (8)$$

$$CCl_3\cdot CHCl\cdot\dot{C}H\cdot CCl_3 \longrightarrow CCl_3\cdot CHCl\cdot CH = CCl_2 + Cl\cdot \qquad (9)$$

The rearrangement induced by aluminum chloride can be explained by an ionic intermediate,



$$CHCl = CH\cdot CCl_3 + AlCl_3 \rightarrow \left\{\begin{array}{c} CHCl = CH\cdot \overset{\oplus}{C}\ Cl_2 \\ \updownarrow \\ \overset{\oplus}{C}HCl\cdot CH = CCl_2 \end{array}\right\} \overset{\ominus}{AlCl_4} \rightarrow CHCl_2\cdot CH = CCl_2 \qquad (10)$$

whereby the chlorine is transferred from end to end. A similar effect may be induced by mercuric chloride thus explaining the isomerisation during its preparation. It is probable that the slow auto-rearrangement could be due to some ionic intermediate, either with the glass vessel or with the drying agent. Certainly no similar 1,3-rearrangements have been reported previously. There is also the possibility of chlorine atoms or hydrogen chloride being produced by decomposition of the chloropropene as this is a known reaction of polychlorinated compounds.

The similarity of the product isolated from the irradiation of 10% solutions of both tetrachloropropenes, 1,3,3,3- and 1,1,3,3-, in carbon tetrachloride is not easily explained: it requires the rearrangement of the 1,3,3,3-tetrachloropropene intermediate to the same as that from the 1,1,3,3-tetrachloropropene which may be achieved by reaction 6(b). Subsequent reaction with a trichloromethyl radical would then yield the addition product.

If/

If reactions of the type (7) and (8) are the source of this high boiling material then the two isomers would be expected to give different products; similarly dimeric material would be expected to differ but this possibility may be neglected as the product is formed at very low concentrations of the tetrachloropropenes.

SECTION II (c)

THE IRRADIATION OF CYCLOPROPANE-CARBON TETRACHLORIDE SOLUTIONS.

The irradiation of a cyclopropane saturated carbon tetrachloride solution.

The carbon tetrachloride was purified as described previously.

The cyclopropane (British Oxygen Gases Ltd.) was not subjected to any purification and was used directly from the cylinder.

A saturated solution of cyclopropane was obtained by the slow passage of a stream of the gas into 1800 mls carbon tetrachloride; when saturation was achieved this volume was increased to 2 litres which was irradiated in a 2 litre stoppered flask at the horizontal source. After irradiation for several days, at an unmeasured dose, the volume decreased and resaturation by further passage of cyclopropane restored the volume to 2 litres.

Examination of products.

The 2 litres of solution was subjected to a slow distillation and the first fraction (20 ml) consisting largely of carbon tetrachloride was examined on a 2 metre 25% "TW60"/C column which gave maximum resolution: a typical run at 75°C, 50 mls H_2 per min. gave peaks of the following retention times:- (1) ½ min. (2) 1 min. (3) 2 min. (4) 2½ min. (5) 3 min. (6) 4 min.

The products corresponding to peaks (1) and (5) were the starting materials, cyclopropane and carbon tetrachloride, respectively; peak (6) was chloroform and its presence was confirmed by use of S.E. and D.N.P. columns.

The main product peak was (3) with (2) and (4) only constituting minor fractions. By comparison of retention times on columns of D.N.P./C and S.E./C and "TW.60"/C these products were identified as (2) iso-propyl chloride (3) n-propyl chloride (4) either cyclopropyl chloride or allyl chloride (The above columns did not resolve cyclopropyl and allyl chlorides which were also eluted together on a 4 metre column consisting of a 2 metre 25% S.E./C. and a 2 metre 25% "TW60"/C). The peak (4) constituted about 2% of the total monochlorocompounds; a similar quantity of iso-propyl chloride was present.

The/

The large volume of carbon tetrachloride was then distilled off with frequent G.L.C. testing for products, and the residue (ca 5 mls) examined for products: optimum gas chromatographic conditions being a 1 metre 25% D.N.P./C column at 105°C with a flow rate of 55 mls hydrogen per minute; the following retention times of irradiation products and known samples were obtained:-

(7) Retention time - 1 minute - small unidentified peak.

(8) Retention time - $1\frac{1}{2}$ minutes - corresponds to 1,2-dichloropropane.

(9) Retention time - 2 minutes - corresponds to tetrachloroethylene.

(10) Retention time - $2\frac{1}{2}$ minutes - corresponds to 1,3-dichloropropane.

(11) Retention time - 4 minutes - unidentified.

(12) Retention time - 6 minutes - corresponds to 1,1,3-trichloropropane.

(13) Retention time - 8 minutes - corresponds to 1,2,3-trichloropropane.

(14) Retention time - 11 minutes - unidentified.

(15) Retention time - $12\frac{1}{2}$ minutes - corresponds to hexachloroethane.

at a column temperature of 131°C.

(15) Retention time - 7 minutes - corresponds to hexachloroethane.

(16) Retention time - 13 minutes - unidentified.

(17) Retention time - 30 minutes - unidentified.

Reference samples of 1,3-dichloropropane and 1,1,3-trichloropropane were obtained by liquid phase chlorination of cyclopropane as described by Walling[105]; 1,2,3-trichloropropane was produced by chlorination of allyl chloride.

The major products 1,3-dichloropropane, hexachloroethane, and the two unidentified peaks (16) and (17); the other products - viz. (9), (11), (12), (13) and (14) were about equal and each was about 10% of the 1,3-dichloropropane yield; the products (7) and (8) were only formed in very minor amounts.

Using/

Using a 0.9 metre 25% S.E./C column at 80°C and a flow rate of 400 mls nitrogen per minute preparative scale separation gave the three monochlorocompounds, 1,3-dichloropropane and 1,1,3- and 1,2,3-trichloropropanes in sufficient quantities to confirm their structures by infrared spectral comparisons. No further identification of the products (11) and (14) was carried out.

The large excess of hexachloroethane was removed by repeated chilling of the solution in ice-water and filtration. The unidentified product (16) was condensed onto an infrared sodium chloride plate from the effluent of an analytical column (1 metre 25% P.E.G. ad/C at 128°C, 60 mls hydrogen per minute) and its infrared spectrum was identical with a similarly trapped sample from the benzoyl peroxide initiated reaction between 5 mole % allyl chloride and chloroform at the refluxing temperature of the mixture. The product was therefore assumed to be 1,1,1,4-tetrachlorobutane since (a) the infrared spectrum indicated an open-chain chlorocompound (no characteristic cyclopropyl absorptions) for the irradiation compound, and (b) this structure is to be expected from the reaction of allyl chloride with chloroform by analogy with the corresponding allyl chloride-carbon tetrachloride reaction[124].

The second of the unidentified products (17) following hexachloroethane was separated from the concentrated irradiation solution using the preparative scale column, (0.9 m, 25% S.E./C at 118°C, flow rate of 300 mls nitrogen per minute, retention time 1½ hours). An elemental analysis of this product gave C,23.42; H,2.92; Cl,73.0%, which may indicate a pentachlorobutane ($C_4H_5Cl_5$ requires C,20.8; H,2.27; Cl,76.9%) formed by the hydrogen-chlorine exchange chain reaction between the primary 1,1,1,4-tetrachlorobutane and carbon tetrachloride. Other possibilities are: (a) 1,1,1,5,5,5-hexachloropentane which would, however, be rather high boiling (the unidentified product appears to boil in the range 200 - 210°C from its retention time on the non-polar silicone/

silicone elastomer stationary phase) (b) 1,6-dichlorohexane which, however can be neglected since the analysis results indicate a much greater percentage of chlorine.

If the pentachlorobutane is in fact formed by a fast chain reaction as indicated above then it would be expected that 1,1,1,3-tetrachloropropane and the 1,1,1,5-tetrachloropentane would undergo similar reactions but irradiation of 10% solutions of both these compounds in carbon tetrachloride gave no indication of a hydrogen-chlorine exchange chain reaction.

The sample eluted just before hexachloroethane, corresponding to product (14) was trapped in very small quantity from the above column and its infrared spectrum was very similar to that obtained for 1,1,1,4-tetrachlorobutane, a result which may indicate that this product is 1,1,1-trichlorobutane.

Estimation of products.

The estimation of products was only carried out on a relative scale, the actual G-values not being calculated.

Product	Percentage of total products.
n-propyl chloride	11%
1,3-dichloropropane	21%
1,1,1,4-tetrachlorobutane	36%
unidentified product (17)	24%
other products	8%

These percentages exclude hexachloroethane which was produced in about five fold excess of the 1,3-dichloropropane. The "other products" refers to those eluted between 1,3-dichloropropane and the hexachloroethane *viz.* 1,1,3- and 1,2,3-trichloropropane and the two unidentified peaks. The chloroform yield was small, about 5% of the n-propyl chloride.

The irradiation of cyclopropane in carbon tetrachloride at the reflux temperature of the latter.

(a)/

(a) Products more volatile than carbon tetrachloride.

The only products observed here were cyclopropyl chloride and chloroform with the latter only in small yield; the absence of any n-propyl chloride was noted.

(b) Products less volatile than carbon tetrachloride.

These products were in small yield except for a large excess of hexachloroethane. Other products were tetrachloroethylene, 1,3-dichloropropane, 1,1,3-trichloropropane and 1,2,3-trichloropropane; the yield of the 1,2,3-isomer was in excess of the 1,1,3-isomer by a factor of four with approximately equivalent yields of the 1,3-dichloropropane and the 1,1,3-trichloropropane.

The higher boiling products were unidentified and a S.E./C column showed that the two main peaks, one of shorter retention time than hexachloroethane and the other slightly longer, both in about equal quantities, approximately equal to the amount of 1,2,3-trichloropropane.

Discussion

The formation of n-propyl chloride and 1,3-dichloropropane is representative of the unsaturated character of cyclopropane, 1,3-dichloropropane being formed by the following process:-

$$\mathrm{Cl\cdot} + \text{cyclo-}\,\mathrm{C_3H_6} \longrightarrow \mathrm{C_3H_6Cl\cdot} \qquad (1)$$

$$\mathrm{C_3H_6Cl\cdot} + \mathrm{CCl_4} \longrightarrow \mathrm{CHCl_2\cdot\, CH_2\cdot\, CH_2Cl} + \mathrm{CCl_3\cdot} \qquad (2)$$

The trichloromethyl radical produced radiolytically and otherwise (e.g. reaction 2) will also undergo addition to the cyclopropane ring giving the 4,4,4-trichlorobutyl radical which by chlorine abstraction yields 1,1,1,4-tetrachlorobutane:

$$\mathrm{CCl_3\cdot} + \text{cyclo-}\mathrm{C_3H_6} \longrightarrow \mathrm{CCl_3\cdot\, C_3H_6\cdot} \qquad (3)$$

$$\mathrm{CCl_3\cdot C_3H_6\cdot} + \mathrm{CCl_4} \longrightarrow \mathrm{CCl_3\cdot C_3H_6Cl} + \mathrm{CCl_3\cdot} \qquad (4)$$

Thus a chain reaction is established. The radical produced by reaction (1) and, presumably, that produced by reaction (3) can also abstract hydrogen to give n-propyl chloride and 1,1,1-trichlorobutane; this latter product was not identified but it may account for one of the minor products eluted before hexachloroethane.

The source of this hydrogen seems to be the open chain products since very little cyclopropyl chloride, which would be formed by reactions (5) and (6), was isolated.

$$\mathrm{ClC_3H_6\cdot} + \text{cyclo-}\mathrm{C_3H_6} \longrightarrow \mathrm{C_3H_7Cl} + \text{cyclo-}\mathrm{C_3H_5\cdot} \qquad (5)$$

$$\text{cyclo-}\mathrm{C_3H_5\cdot} + \mathrm{CCl_4} \longrightarrow \text{cyclo-}\mathrm{C_3H_6Cl} + \mathrm{CCl_3\cdot} \qquad (6)$$

Thus hydrogen abstraction from 1,3-dichloropropane and 1,1,1,4-tetrachloropropane may be the main reactions leading to n-propyl chloride

$$\mathrm{ClC_3H_6\cdot} + \mathrm{CH_2Cl\cdot CH_2\cdot CH_2Cl} \longrightarrow \mathrm{ClC_3H_7} + \mathrm{\dot{C}HCl\cdot CH_2\cdot CH_2Cl} \text{ or } \mathrm{CH_2Cl\cdot \dot{C}H\cdot CH_2Cl\cdot} \qquad (7)$$

Reaction/

Reaction (7) thus provides precursors for the formation of 1,1,3- and 1,2,3-trichloropropane i.e.

$$\dot{C}H\,Cl\cdot CH_2\cdot CH_2Cl + CCl_4 \rightarrow CH\,Cl_2\cdot CH_2\cdot CH_2Cl + CCl_3\cdot \qquad (8a)$$

$$CH_2Cl\cdot \dot{C}H\cdot CH_2Cl + CCl_4 \rightarrow CH_2Cl\cdot CHCl\cdot CH_2Cl + CCl_3\cdot \qquad (8b)$$

Reactions similar to (7), (8a) and (8b) will occur with the 1,1,1,4-tetrachlorobutane but no products of such reactions were unambiguously identified although the higher boiling unidentified product may be the result of such reactions. It would however be likely that such a product $CCl_3(C_3H_5Cl)Cl$ would be a mixture of positional isomers and not a single compound.

The presence of hydrogen chloride and chloroform confirms that these radicals abstract hydrogen but again perhaps mainly from the open chain propanes. The unreactive nature of cyclopropane towards abstraction accounts for the large quantity of hexachloroethane and the small proportion of chloroform; this large quantity of hexachloroethane is probably largely the source of the tetrachloroethylene which is known to arise from radiolysis of hexachloroethane solutions. Although reaction (9) is a possibility which is known to occur at high temperatures [125] (138°C).

$$CCl_3\cdot CCl_3 + R\cdot \rightarrow CCl_3\cdot CCl_2 + \dot{R}Cl;\quad CCl_3\cdot CCl_2 \rightarrow CCl_2 = CCl_2 + Cl\cdot \qquad (9)$$

Goldfinger et al.[128] maintain that the pentachloroethyl radical does not decompose until temperatures > 112°C. The exact mechanism of this tetrachloroethylene is not fully understood but the stoicheiometry appears to be reaction (10) as no molecular chlorine is found.

$$2\ CCl_3\cdot CCl_3 \longrightarrow 2\ CCl_4 + CCl_2 = CCl_2 \qquad (10)$$

The tenatively identified 1,2-dichloropropane can be produced by the reaction sequence (11) and (12).

$$CH_2Cl\cdot \dot{C}H_2\cdot CH_3 + R\cdot \longrightarrow RH + CH_2Cl\cdot \dot{C}H\cdot CH_3 \qquad (11)$$

$$CH_2Cl\cdot \dot{C}H\cdot CH_3 + CCl_4 \longrightarrow CH_2Cl\cdot CHCl\cdot CH_3 + CCl_3 \qquad (12)$$

where $R\cdot = Cl$; $CCl_3\cdot$ or any chloropropyl radical.

Even/

Even if the radical formed in reaction (11) does rearrange to the 2-chloropropyl radical[54], chlorine abstraction will still give the 1,2-dichloropropane. However the isolation of iso-propyl chloride and 1,2-dichloropropane may indicate the 1,3-dichloropropane as their source as this latter compound is known to produce these other chloropropanes on gamma radiolysis[55]. However, the 1,2-hydrogen shifts envisaged[54] for the production of the iso-propyl chloride and 1,2-dichloropropane are now thought improbable under normal conditions and that any rearrangements may be due to chlorine shifts instead[55]. If there was any propane impurity in the cyclopropane, iso-propyl chloride would be formed in excess of n-propyl chloride[126]: this proves n-propyl chloride is a product from the cyclopropane nucleus. It was found however that the repetition of the chlorination of cyclopropane under the conditions of Walling and Fredricks[105] produced no iso-propyl chloride from the same cyclopropane; this result indicates that the iso-propyl chloride is also a true irradiation product of the cyclopropane-carbon tetrachloride mixture.

Apart from the very small quantity of cyclopropyl chloride, no other cyclopropyl compound was isolated and no evidence of the rearrangement of the cyclopropyl radical to the allyl radical was observed (i.e. propylene or allyl chloride). Thus the main feature of this reaction mixture is the unreactivity of the cyclopropane ring towards abstraction by the trichloromethyl radical or chlorine atom, a result in contrast to those with cyclohexane where the production of cyclohexyl chloride has a G-value of 80 by the chain reaction:-

$$CCl_3\cdot + C_6H_{12} \longrightarrow HCCl_3 + C_6H_{11}\cdot \qquad (13)$$

$$C_6H_{11}\cdot + CCl_4 \longrightarrow C_6HCl + CCl_3\cdot \qquad (14)$$

The increased production of cyclopropyl chloride compared to other products in/

in the higher temperature irradiation is in agreement with the results obtained by Walling and Fredricks[105]. A much lower concentration of cyclopropane was obtained at this refluxing temperature despite constant passage of the gas and this was reflected in the very small amount of products formed. The 1,3-dichloropropane was detected only in very small yield but this can be attributed to the secondary process giving 1,1,3- and 1,2,3-trichloropropane, mainly the latter. No 1,1,1,4-tetrachloropropane was observed but other products detected by G.L.C. in the higher temperature but not in the room temperature irradiation may contain a substituted cyclopropyl ring.

SECTION II (D)

THE IRRADIATION OF A 10 mole % ACENAPHTHYLENE-CARBON TETRACHLORIDE SOLUTION.

The irradiation of a 10 mole % acenaphthylene - 90 mole % carbon tetrachloride.

As a final unsaturated hydrocarbon, acenaphthylene $C_{10}H_6\cdot(CH)_2$ was investigated. The system acenaphthylene-carbon tetrachloride at very low concentrations of acenaphthylene, had been shown to give a linear relationship between disappearance of the hydrocarbon and dose, the rate of disappearance of hydrocarbon having been measured spectrophotometrically by examination of the absorption at 324 mμ[127].

The present object was to identify any of the products formed in such a solution at higher concentrations of the hydrocarbon.

Experimental

Acenaphthylene (90 gm) was dissolved in carbon tetrachloride (1000 mls purified) and irradiated at an unmeasured dose rate (approx. 1.3×10^{16} eV/ml/min). Distillation of the unreacted carbon tetrachloride gave a heavy viscous residue which contained only a small percentage of hexachloroethane and unreacted acenaphthylene, both of which were distilled off to some extent.

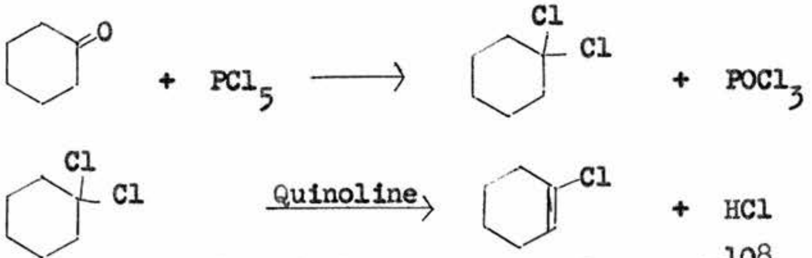
On addition of ether to the residue a white solid was precipitated out: filtration and several washings with ether removed any hexachloroethane and unreacted acenaphthylene and a pale yellow, non-crystalline solid remained. All attempts to crystallize the solid were fruitless as it was insoluble in acetone, ether or alcohol and gave a viscous syrup on addition of chloroform or carbon tetrachloride; mixtures of solvents also proved unsuccessful. The pure compound was obtained by taking it up in sufficient chloroform and slowly adding ether whereby reprecipitation occurred. After filtration and several washings with ether, alcohol, and acetone, the dry compound on elemental analysis gave C, 89.68; H, 4.63; Cl, 4.50% (total 98.81%) A similar compound obtained by the addition of benzoyl peroxide to the solution as prepared/

prepared for the irradiation gave a solid with C, 90.86; H, 4.86; Cl, 2.52% (total 98.24%). The infrared spectra were identical and the decomposition point was in the range 330 - 340°C.

All indications were of a polymeric material formed from the acenaphthylene with a very low percentage of chlorine incorporated. Presumably the initiating species were chlorine atoms and trichloromethyl radicals and termination was either by radical combination or abstraction from the substrate, carbon tetrachloride.

APPENDIX TO SECTION II

Preparation of 1-Chlorocyclohexene.



The method used was as described by Stevens and Grummit[108].

Cyclohexanone (20 gm.) was added slowly, from a dropping funnel, to phosphorus pentachloride (60 gm.). The reaction flask was cooled on an ice bath to eliminate the unpleasant evolution of hydrogen chloride; the resultant liquid was added to ice water to destroy excess phosphorus pentachloride and the organic layer extracted with dichloromethane, washed several times with 10% aqueous sodium bisulphite solution and dried over anhydrous sodium sulphate. After removal of the solvent, the residue was heated in a distillation flask with quinoline (50 gm.), the fraction boiling at 135° - 145°C being collected. Redistillation gave a product boiling at 140° - 142°C but the infrared spectrum showed the presence of cyclohexanone. Further extraction with aqueous sodium bisulphite removed these absorptions and the product was shown to be pure by G.L.C. analysis. Yield <u>10 gm.</u>

Boiling point = 140° - 142°C (lit.[108] 140° - 141.5°C)

Refractive index n_D^{20} = 1.4805 (lit. n_D^{20} = 1.4810)

Preparation of 3-Chlorocyclohexene.

The method used was as described by Walling et al[111] using *tert*-butyl hypochlorite as an allylic chlorinating agent. The overall reaction of *tert*-butyl hypochlorite in non-polar solvents, using light or chemical initiators may be represented by the equation:

$$RH + t\text{-}C_4H_9OCl \longrightarrow RCl + t\text{-}C_4H_9OH$$

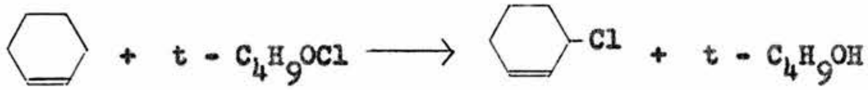
which/

which proceeds via the radical sequence

$$t - C_4H_9O\cdot + RH \longrightarrow t - C_4H_9OH + R\cdot$$

$$R\cdot + t - C_4H_9OCl \longrightarrow RCl + t - C_4H_9OH$$

The reaction of tert-butyl hypochlorite with cyclohexene.



Walling[128] reported that high yields of 3-chlorocyclohexene could be obtained by the above method but gave no details. The experiment was carried out under conditions similar to those described by Walling for a number of other olefins[128].

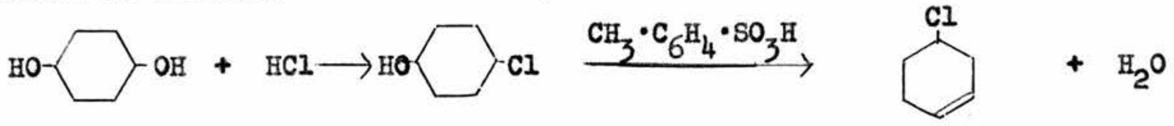
Tert-butyl hypochlorite[129] (25 gm.) was added to cyclohexene (45 ml) and a slow stream of nitrogen was passed through the mixturefor thirty minutes in the dark. The tube was then closed by a quickfit stopper, placed in a water bath at room temperature and irradiated by an incandescent lamp. The irradiation was continued for thirty minutes **after** the yellow colour had disappeared.

The reaction mixture was then distilled and the fraction boiling between 135 - 145°C, at 760 mm, was collected, washed repeatedly with water and finally dried over calcium chloride. Examination by G.L.C. showed some impurities which could not be removed by further washing. Further distillation at reduced pressure provided a purer product but still containing about 5 - 10% impurities. Final yield 5 gm.

Preparation of 4-Chlorocyclohexene.

The method used was as followed by Birch et al[130] except that the dehydration was carried out using p-toluene sulphonic acid instead of 2-naphthalene sulphonic acid. The 1,4-dihydroxycyclohexane (cyclohexane-1,4-diol) was obtained commercially. The overall reaction process is thought to proceed/

proceed as follows:-



Preparation of 4-Chlorocyclohexanol.

Cyclohexane-1,4-diol (20 gm.) was dissolved in conc. hydrochloric acid (50 ml) and heated for 16 hours at 85°C. This solution was then extracted with chloroform and the extract washed with 10% sodium carbonate solution. The organic layer was dried over calcium chloride and then distilled to give a mixture of the cis- and trans- isomers of 4-chlorocyclohexanol

Boiling point = 96-100°C/10 mm. Yield 6 gm.

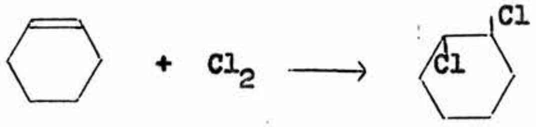
Dehydration to give 4-chlorocyclohexene.

4-chlorocyclohexanol (6 gm.) and p-toluene sulphonic acid (0.5 gm.) were heated in an oil bath at 200 - 240°C and the distillation taken through a fractionating column. The organic layer was shaken with water (10 ml), separated off and dried over calcium chloride. Fractionation yielded a product boiling 88 - 95°C/130 mm. taken as 4-chlorocyclohexene. Yield 2 gm.

Further fractionation was required to obtain a pure product and finally 0.5 gm. of pure product was obtained.

Preparation of trans- (±)-1,2-dichlorocyclohexane.

This product was obtained by the chlorination of cyclohexene in the absence of light according to Carrol et al[131]

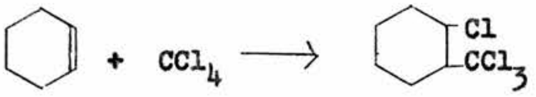


Cyclohexene (90 ml) was placed in a flask from which light was excluded and a slow stream of chlorine bubbled through a gas inlet tube. The gas flow was stopped when the gain in weight was 30 g (~ 50% theoretical). Distillation yielded the crude produce boiling point 186 - 190°C/760 mm. Fractionation of this product gave the pure dichlorocompound. Yield 30 gm.

Preparation/

Preparation of 1-Chloro-2-trichloromethylcyclohexane.

(a) The benzoyl peroxide initiated addition of carbon tetrachloride to cyclohexene to give the 1:1 adduct has been reported in the literature by Israelashvili and Shabatay[94] and by Kooyman and Farenhorst[90]. The procedure adopted here was that described by the former workers.



In a three-neck flask fitted with a reflux condenser, a dropping funnel, and a gas inlet tube, a mixture of cyclohexene, (55 ml) and carbon tetrachloride (550 ml) was refluxed for 18 hours under a continuous stream of dry nitrogen. At the beginning and, also 9 hours later, benzoyl peroxide (2.4 gm.) was added. The mixture boiled initially at 78°C and finally at 82°C. The solution was washed three times with 10% aqueous sodium bicarbonate and once with water before being dried over sodium sulphate. The low boiling fractions were removed by distillation and the fraction boiling at 140° - 142°C/13 mm. was collected. Yield 18 gm.

A G.L.C. run showed the presence of two peaks, presumably the cis- and trans-isomers. The infrared spectrum, however, indicated the presence of an ester group presumably to 2-chlorocyclohexyl benzoate.

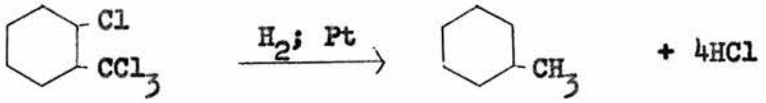
(b) An independent method of preparation of the 1-chloro-2-trichloromethyl-:cyclohexane which would eliminate telomerisation was put forward by Asscher and Vofsi[132] who used cupric chloride and ethanolamine to catalyse the addition of carbon tetrachloride to cyclohexene.

Cupric chloride dihydrate (50 mg.) in tert-butyl alcohol was added to a mixture of ethanolamine (3 gm.), cyclohexene (20.5 gm.), and carbon tetrachloride (75 gm) and the resultant blue solution was refluxed for 18 hours. After cooling, the solution was poured into water (500 ml) and the organic layer separated off. The aqueous layer was extracted twice with carbon tetrachloride and/

and extracts added to the original organic layer. This was then washed twice with water, separated and dried over calcium chloride; the solvent was removed by distillation and the fraction boiling at 140° - 142°C/13mm. was collected and its gas chromatograph again showed two peaks identical with those of the product from the benzoyl peroxide initiated reaction; the infrared spectrum was also the same except for the absence of the peaks at 1710 and 710 cm^{-1}, previously attributed to the ester as indicated above.

Hydrogenation of 1-Chloro-2-trichloromethylcyclohexane.

(a) The first attempt was the direct exchange of chlorine for hydrogen by catalytic hydrogenation using Adam's catalyst in methanol containing potassium hydroxide, i.e.

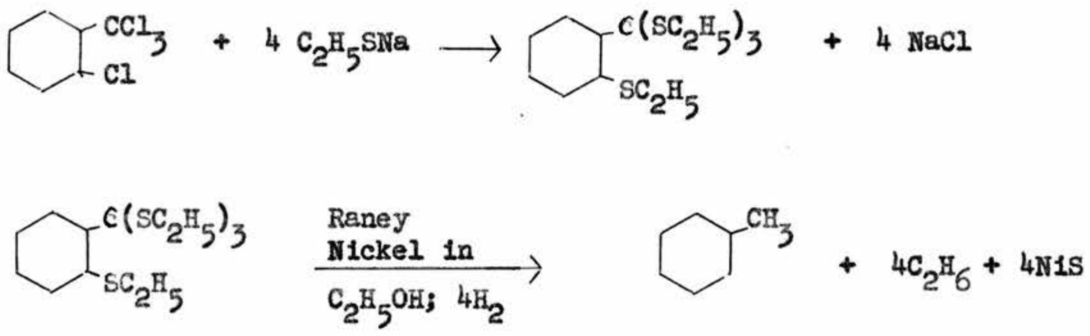


1-Chloro-2-trichloromethylcyclohexane (1.1 gm), potassium hydroxide (1 gm) and platinum oxide (70 mg) were dissolved in methanol and shaken with hydrogen at atmospheric pressure. When the hydrogen uptake stopped the solution was partitioned between ether and water and the separated ether layer washed several times with water, dried over calcium chloride and distilled. On evaporation of the ether a heavy layer separated out and this was then tested by G.L.C. The resulting gas chromatogram indicated that the main product had a boiling point close to that of bicyclohexyl and the infrared spectrum showed carbon-chlorine absorptions. The multiplicity of the products eliminated the possibility of obtaining any useful information from this experiment. Similar results were noted by Nesmeyanov et al[133] using alcoholic alkali with dehydrogenating agents.

An identical experiment was carried out in the absence of potassium hydroxide but the results did not give any indication of products in the appropriate/

appropriate boiling range i.e. corresponding to methylcyclohexane.

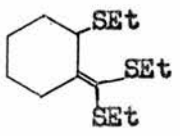
(b) The second method of removal of chlorine and replacement by hydrogen is based on the primary replacement of chlorine by the ethanetiyl group and hydrogenation of the latter using Raney nickel as illustrated by the following sequence of reactions:-



Ethanethiol (2.8 ml) was added to ethanol (50 ml) containing sodium ethoxide (from 1.1 gm sodium). The 1-chloro-2-trichloromethylcyclohexane (2.5 gm) was then added and a twelve hour reflux carried out.

The resultant solution was diluted with water (100 ml) and extracted twice with ether. The combined ether layers were washed four times with water (50 ml) portions, dried over calcium chloride, and distilled to remove the ether. A gas chromatogram of the residue indicated two products both of higher boiling point and in a ratio similar to that of the original cis- and trans- compounds. From the volatility of the compound (near the original chloro-compounds) and the possible unsaturation (infrared spectrum) the sulphur compounds may have been unsaturated - three ethanethiyl groups - $(SEt)_3$ rather than the saturated four ethanethiyl groups - $(SEt)_4$-

i.e.



Treatment of the sulphur compound with Raney nickel.

The sulphur compound (0.8 gm) was added to ethanol (40 ml) containing freshly prepared Raney nickel (8 gm) and this mixture/

mixture was left at room temperature for 1 hour and then kept under reflux for 6 hours. Continuous mechanical stirring ensured a free suspension of the catalyst during the reaction time. The solution was then extracted into ether and washed several times to remove the alcohol. The ether was then distilled off and the residue examined by gas chromatography and infrared. The G.L.C. analysis indicated the main peak as being methylcyclohexane. There were no other products in any measurable quantity. An infrared comparison with an authentic sample of methylcyclohexane confirmed the above indication.

Treatment of the irradiation products with sodium ethanethiolate followed by Raney nickel.

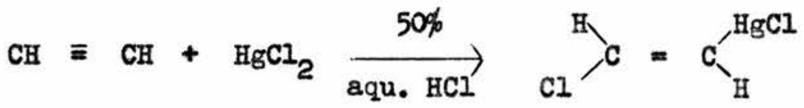
The above procedure was repeated using the irradiation products corresponding in boiling range to the 1:1 adduct.

Sulphur Compounds.

In this experiment four peaks were observed all with longer retention times than the parent chloro-compounds on a silicone elastomer column. The Raney nickel treatment again gave only one peak in the methylcyclohexane boiling range with complete conversion of the sulphur compounds to methylcyclohexane. This conclusion was again confirmed by comparison of the infrared spectrum with an authentic sample of methylcyclohexane.

Preparation of 1,3,3,3-tetrachloroprop-1-ene.

Nesmeyanov synthesised the above compound by the following reaction sequence[121]:



$$CH \equiv CH + HgCl_2 \xrightarrow[\text{aqu. HCl}]{50\%} \overset{H}{\underset{Cl}{}}C = C\overset{HgCl}{\underset{H}{}}$$

$$CHCl = CH\,HgCl + CCl_4 \xrightarrow{Bz_2O_2} CCl_3 \cdot CH = CHCl + HgCl_2$$

(1)/

(1) 2-Chlorovinylmercuric chloride[135].

Mercuric chloride (270 g) was dissolved in 50% hydrochloric acid (250 ml.) and acetylene was passed through the mixture. A white precipitate settled out and this was filtered off. Successive filtrations and passage of acetylene yielded a 50% theoretical yield (298 gm). This white product was dried under vacuum and gave a melting point of 120°C which was considered sufficiently pure for the next stage.

(2) 1,3,3,3-Tetrachloroprop-1-ene from the above compound.

2-Chlorovinylmercuric chloride (100 gm) was dissolved in carbon tetrachloride (1350 ml) and benzoyl peroxide (3 gm) was added. After reflux for 6 hours the solution was extracted with 10% aqueous sodium bicarbonate (1000 ml) and finally water (2 x 1000 ml) before drying over calcium chloride. After distilling off the unreacted solvent a product boiling 78° - 79°C/73 mm was obtained. Yield 50 gm.

$$\text{Found } n_D^{20} = 1{,}5076$$

$$\text{Literature } n_D^{20} = 1{,}5078$$

Inspection of this product by G.L.C. showed another smaller peak of similar retention time, the implications of which are discussed in reference to the acetylene-carbon tetrachloride irradiation.

Preparation of 1,1,3,3-tetrachloroprop-1-ene.

$$CH_3\cdot CO\cdot O\cdot CH = CH_2 + BrCCl_3 \longrightarrow CH_3\cdot CO\cdot O\cdot CHBr\cdot CH_2\cdot CCl_3$$

$$CH_3\cdot CO\cdot O\cdot CHBr\cdot CH_2\cdot CCl_3 \xrightarrow[\text{distillation}]{\text{steam}} (CCl_3\cdot CH_2\cdot CHO) \longrightarrow CCl_2 = CH\cdot CHO + HCl$$

$$CCl_2 = CH\cdot CHO + PCl_5 \longrightarrow CCl_2 = CH\cdot CHCl_2 + POCl_3$$

A solution of vinyl acetate (40 gm) and benzoyl peroxide (3 gm) in bromotrichloromethane (200 gm) was warmed up to 50° - 60°C and the reaction maintained at this temperature by occasional cooling for a period of three hours./

hours. After removal of excess of bromotrichloromethane, reduced pressure distillation gave a product boiling 65° - 70°C/0.5 mm. Yield 80 gm.

Found n_D^{20} = 1,4976

Literature for 1-bromo-3,3,3-trichloropropyl acetate[136]

n_D^{20} = 1,4976

Steam distillation of 1-bromo-3,3,3-trichloropropyl acetate (80 gm) from 5% aqueous sulphuric acid (800 ml) produced a yellow organic oil which was extracted with ether, washed with 5% aqueous sodium bicarbonate, then water and dried over calcium chloride. Distillation gave a colourless oil (B.pt. 85°C/35 mm). Examination, by G.L.C., indicated two small impurities and a further distillation was required to remove most of those until approximately 5% of impurity remained. The main product was the β,β-dichloroacrolein. Yield 25 gm.

2,4-dinitrophenylhydrazone melting point 163° - 165°C

Literature value[136] = 164 - 165°C

Action of phosphorus pentachloride on β,β- dichloroacrolein.

β,β-Dichloroacrolein was added dropwise with constant agitation to phosphorus pentachloride (50 gm) over a period of 2 hours with the temperature maintained at 0°C. Stirring was continued for a further 12 hours when the mixture was added slowly to ice water. The oil was extracted into ether, washed with water (2 x 100 ml) and dried over calcium chloride. Distillation yielded a product(80 gm) boiling point 80°C/74 mm. n_D^{20} = 1.5096.

Examination by G.L.C. showed only one main peak and two very small impurities (ca. 2-3%) of longer retention time on a silicone elastomer stationary phase.

Analysis gave C,20.72; H,1.23; Cl,77.93%

required for $C_3H_2Cl_4$: C,20.00; H,1.22; Cl,78.88%.

SECTION III

The Irradiation of 10 mole% chlorinated ethylene-90 mole% halomethane mixtures

(A) Trichloroethylene with 90 m% - (1) Carbon Tetrachloride (2) chloroform and (3) dichloromethane.

(B) 1,2-dichloroethylene with 90 m% - (1) bromotrichloromethane
(2) carbon tetrachloride.

Introduction

The peroxide and photochemically initiated addition of halomethanes to various halogen substituted ethylenes has been the source of considerable study, the general line of research depending on whether the ethylene is symmetrically or asymmetrically substituted.

In the latter category the trifluoroethylene-dibromodifluoromethane reaction illustrates the problem which concerns the ratio of addition at one carbon atom of the ethylene linkage relative to the other. It has been shown here[143] that the addition product is a mixture, the frequency of addition of the bromdifluoromethyl radical to CFH and CF_2 being in the ratio 2.4/1 at 100°C but 1/1 at 120°C. However in the case of 1-chloro-1,2,2-trifluoroethylene, the addition of trifluoroiodomethane proceeds exclusively by the addition of the trifluoromethyl radical to the carbon atom with two fluorine atoms;[144] similarly any polymerisation occurs by a tail to head mechanism[144]. The addition of bromotrichloromethane is propagated likewise with attack of the trichloromethyl radical at the difluoromethylene group[145].

Of the symmetrically substituted ethylenes the 1,2-dichloro-compound has been most fully investigated. The addition of bromotrichloromethane to this compound, and the similar dibromoethylene,[103] showed that, although the former gave a 1:1 adduct, identified as 1-bromo-1,2,3,3,3-pentachloropropane, no such product was identified in the reaction of the latter compound, where 1-bromo-3,3,3-trichloroprop-1-ene, along with sym-tetrabromoethane were the products isolated. The production of this propene by the elimination of a bromine atom from the 1,2-dibromo-3,3,3-trichloropropyl radical is analagous to the reaction which occurs during the attack on 1,2-dichloroethylene by the chlorodifluoromethyl radical, formed in the photolysis of 1,3-dichlorotetrafluoroacetone. Here a chlorine atom is eliminated to give 1,3-dichloro-3,3-difluoropropene but no addition product (1,1,2,3-tetrachloro-

3,3-/

(1,1,2,3-tetrachloro-3,3-difluoropropane) is produced by chlorine abstraction from the 1,3-dichlorotetrafluoroacetone.

The mechanism of the chlorine atom loss postulated in the above instance is a breaking of the carbon-chlorine bond to give a free chlorine atom since no corresponding disproportion product could account for the amount of 1,3-dichloro-3,3-difluoropropene formed. Isomerisation of the dichloroethylenes (the major reaction) could not unequivocally be attributed to a reversible attack by the chlorodifluoromethyl radical or the chlorine atom.

In the present researches the addition to trichloroethylene of the halomethanes, carbon tetrachloride, chloroform and dichloromethane under the action of gamma rays and by benzoyl peroxide initiation, the main product of interest was the 1:1 adduct. The identification of hexachloropropanes (the 1,1,2,2,3,3- and the 1,1,1,2,3,3-isomers) in prolonged radiolysis of chloroform led to the postulation of the formation of trichloroethylene[102ab]. as a product of chloroform radiolysis. The mode of formation of these hexachloropropanes is somewhat doubtful and the present study of the radiolysis of carbon-tetrachloride, chloroform and dichloromethane, with trichloroethylene, is concerned primarily with the elucidation of the mechanism of the 1:1 addition product formation.

The investigation was further extended to the 1,2-dichloroethylene-halomethane systems to further the elucidation of the above and other facets of the radiolysis of halogen substituted ethylenes and halomethanes.

SECTION III)A)

The Irradiation of 10m% trichloroethylene - 90m% (1) carbon tetrachloride (2) chloroform and (3) dichloromethane.

The irradiation of a 10m% trichloroethylene - 90 m% (1) carbon tetrachloride (2) chloroform and (3) dichloromethane.

The purification of the three halomethanes was carried out by the same general method: all were shaken with water several times, dried over calcium chloride and, after a slow distillation to remove traces of impurities as described previously for carbon tetrachloride, were finally distilled in an oxygen-free nitrogen atmosphere.

Trichloroethylene (B.D.H.) contains a basic stabilizer which was removed by shaking several times with dilute hydrochloric acid, then twice 10% aqueous sodium bicarbonate and twice with water. The compound was then dried over several portions of calcium chloride before distillation under nitrogen. The first and last 10% portions were rejected.

In all cases the irradiations were carried out at room temperature (15°-20°C) and the refluxing temperature of the mixture, and comparisons of these reactions were made with a benzoyl peroxide initiated reaction at the reflux temperature. The carbon tetrachloride-trichloroethylene reaction was also examined on a small scale with a trichloroacetyl peroxide initiator at ambient temperatures.

(1) Carbon tetrachloride-trichloroethylene

Room temperature radiolysis.

2 litres of a 10m% trichloroethylene solution in carbon tetrachloride were irradiated at an average dose rate of 1.2×10^{16} eV/ml/min. to determine the products formed in such a mixture; products more volatile than carbon tetrachloride were not examined although some hydrogen chloride was noted.

After distillation of the unreacted starting material a gas chromatographic analysis on a 1 metre 25% S.E./C. column at 102°C with a flow rate of 55 mls. H_2 per minute gave the following peaks :-

(a) /

(a) Retention time - $1\frac{1}{2}$ minutes corresponding to tetrachloroethylene (minor)

(b) Retention time - $3\frac{1}{2}$ minutes corresponding to sym-tetrachloroethane(minor)

(c) Retention time - 6 minutes corresponding to pentachloroethane

(d) Retention time - 9 minutes unidentified product

(e) Retention time - 11 minutes corresponding to hexachloroethane

(f) Retention time - 49 minutes corresponding to 1,1,3,3,4,4-hexachlorobut-:1-ene i.e. dimer of trichloroethylene

(g) Retention time-62 minutes unidentified-possible sym-heptachloropropane

(h) Retention time-69 minutes unidentified-possible asym-heptachloropropane

The application of a 1 metre P.E.G.ad/C column added support to the identifications made above i.e. (a), (b), (c), (e) and (f) and the following retention times were observed at 100°C for a similar flow rate.

Retention time - 6 mins. - pentachloroethane (c)
Retention time - 5 mins. - unidentified product (d)
Retention time - 7 mins. - hexachloroethane (e)
Retention time -52 mins. - 1,1,3,3,4,4-hexachlorobut-1-ene (f)
Retention time -62 mins. - 1,1,1,2,3,3,3-heptachloropropane (sym) (g)
Retention time -71 mins. - 1,1,1,2,2,3,3-heptachloropropane (asym) (h)

The irradiated solution was then subjected to a reduced pressure fractional distillation and the two main fractions obtained were collected, in the boiling point ranges (a) 55°-60°C/6mm., (b) 40°-43°C/0.1 mm.

Fraction (A) b.p. 55°-60°C/6mm.

A gas chromatographic analysis indicated that this fraction contained mainly the penta- and hexa-chloroethanes along with the unidentified product (d). The infrared spectrum confirmed the presence of penta- and hexachloroethanes and the presence of unsaturation absorptions (1600 cm^{-1}) was an indication that (d) was in fact 1,1,3,3,3-pentachloroprop-1-ene.

The products were separated on a preparative scale chromatography unit using a 0.9 metre 25% S.E./C. column at 110°C, flow rate of 300 mls N_2/min; the/

the required product (d) was eluted after 10 mins. and condensed in an ice-water cooled trap. The purity of the trapped sample was confirmed by analytical scale G.L.C. and elementary analysis gave C, 17.62; H, 1.1; Cl, 81.3% required for C_3HCl_5. C, 16.6; H,0.6; Cl,82.8%.

The refractive index $n_D^{16} = 1.5266$; literature value[146] for 1,1,3,3,3-pentachloroprop-1-ene $n_D^{16} = 1.5254$

Further confirmation of the structure was obtained by chlorination, in carbon tetrachloride solution, when the only product was sym- heptachloropropane.

Fraction (B)

This fraction contained mainly the products suspected as the dimer, and the sym- and asym-heptachloropropanes. A further distillation gave a fraction containing only these three products and with the asym- and sym- compounds in the ratio of 4:1. An infrared spectrum of these mixed irradiation products and that of a mixture of the authentic compounds (dimer, sym- and asym-heptachloropropanes) in the same proportion were identical. The sym-heptachloropropane was prepared as described in the appendix, while samples of the asym-isomer and of the dimer were available.

This completed the product identification as (f) 1,1,3,3,4,4-hexachlorobut-1-ene (g) 1,1,1,2,3,3,3-heptachloropropane (h) 1,1,1,2,2,3,3-heptachloropropane.

During the distillation to obtain the above fractions it was noticed that a solid product precipitated as the volume was reduced; this product was not hexachloroethane which was only produced in small quantities and could be distilled over. The solid was filtered off and recrystallized from chloroform; the infrared evidence confirmed the product as identical with that obtained in the radiolysis of pure trichloroethylene[147] which gave an elementary analysis corresponding to a formula of $C_6H_4Cl_{10}$.

The irradiation of trichloroethylene - carbon tetrachloride at the refluxing temperature of the mixture./

This irradiation was carried out at the horizontal source by heating a 2 litre irradiation flask, containing 1500 mls of mixture (same composition as the room temperature irradiation), on an isomantle.

A G.L.C. analysis of the reaction mixture showed that the proportion of products had changed but no new products were observed. However, the examination for products in the heptachloropropane region indicated that these products were not formed at this temperature.

Benzoyl peroxide initiated reaction.

A solution of the same composition (500 mls) was used and the benzoyl peroxide initiator (2.4 gm) was added to the refluxing solution at the beginning and every 12 hours thereafter during a 48 hour reaction period. The subsequent treatment of the reaction mixture was as described for the carbon tetrachloride-cyclohexene peroxide initiated reaction.

The product identification was carried out as described for the above irradiations and showed the presence of pentachloroethane, 1,1,3,3,3-pentachloroprop-1-ene and the trichloroethylene dimer; chlorobenzene was also present. There was no evidence of any heptachloropropanes having been produced.

Initiation by trichloroacetyl peroxide (see appendix for experimental detail).

This reaction was only carried out on a small scale and the products were identified by comparison of retention times on different stationary phases. The products found were :- pentachloroethane, 1,1,3,3,3-pentachloroprop-1-ene, a small amount of hexachloroethane, some unidentified product and finally as main product the dimer of trichloroethylene; no heptachloropropanes could be identified in the mixture even when it was concentrated to leave only the high boiling material.

During the reduction in volume of the reaction mixture in the three foregoing experiments the same solid product, as mentioned in the room temperature irradiation, was precipitated and was identified by its infrared spectrum.

(2) Chloroform - trichloroethylene

Previous work[102b] on this system had resulted in the identification of products such as *sym*- tetrachloroethane, pentachloroethane, hexachloroethane, *sym*- pentachloropropane, 1,1,2,2,3,3- and 1,1,1,2,3,3- hexachloropropane and the dimer of trichloroethylene as well as hydrogen chloride. A product eluted after tetrachloroethane on a silicone elastomer/C column was noted and tentatively identified as 1,1,3,3-tetrachloroprop-1-ene.

Room temperature radiolysis

An irradiation of 1 litre of 10 m% trichloroethylene in chloroform at a dose rate of 1.3×10^{16} eV/ml/min. confirmed the above results. There were, however, two unidentified products, one corresponding to that noted above. A 1 metre 25% S.E./C column at 105°C, with a flow rate of 55 mls H_2/min gave the following retention times.

Tetrachloroethane - retention time 3 minutes
Unidentified peak - retention time 4 minutes
Pentachloroethane - retention time 5 minutes
Unidentified peak - retention time 8 minutes
Hexachloroethane - retention time 10 minutes

The two unidentified products were produced in very small quantity and could not be isolated by preparative scale gas chromatography, but irradiation of 700 mls of an identical mixture at its reflux temperature greatly increased the proportion of these two peaks. The latter of the two unidentified products, as eluted under the above conditions, behaved identically with the previously identified sample of 1,1,3,3,3- pentachloroprop-1-ene and further confirmation was provided by varying the stationary phase to P.E.G.ad, "TW60", and D.N.P. Proof of the structure ($CCl_3 \cdot CH = CCl_2$) was provided, as before, by addition of chlorine to give *sym*- heptachloropropane.

The unidentified product eluted first was also unsaturated and its chlorine/

chlorine-addition product was a hexachloropropane. Fractional distillation of the irradiation mixture gave a fraction containing mainly tetrachloroethane and the desired product; infrared evidence then confirmed the identity of this irradiation product as 1,1,3,3-tetrachloroprop-1-ene (for preparation see appendix to Section II)

Hexachloropropanes.

It was not possible to separate the 1,1,2,2,3,3- and the 1,1,1,2,3,3-hexachloropropanes by gas chromatography using any of the stationary phases available, either with a single column of 2 metres or mixed columns of 4 metres. The estimation of the proportions of these products was carried out previously[102b] by infrared analysis and the ratio was found to be 3:1 of symmetrical to asymmetrical compound.

Radiolysis at room temperature of varied trichloroethylene concentration in chloroform.

The concentrations used were 1%, 5%, 10%, 15% and 20% of trichloroethylene in chloroform. The samples were made up in 80 ml ampoules and sealed before irradiation. The relative amounts of hexachloropropane to dimer was measured and the results are tabulated in Table III (C).

The irradiation of trichloroethylene-chloroform at the refluxing temperature of the mixture.

The radiolysis of the refluxing solution was carried out at a similar dose to that used in the room temperature experiment. The products identified were the same but, owing to the very small quantity of hexachloropropanes relative to the dimer, their individual ratios were not assessed by infrared analysis.

Benzoyl peroxide initiated reaction.

This reaction was carried out with 500 mls of solution of the same composition (10 m% C_2HCl_3); the experimental conditions were as described for the carbon tetrachloride-trichloroethylene reaction. The products identified were tetrachloroethane, pentachloroethane, 1,1,3,3,3-pentachloroprop-1-ene and the dimer. The absence of any hexachloropropanes was noted.

(3) Dichloromethane-trichloroethylene.

Room Temperature Radiolysis.

2 Litres of 10 m% trichloroethylene in dichloromethane were irradiated at an average dose rate of 1.2×10^{16} eV/ml/min.

After distilling off the bulk of the dichloromethane a gas chromatographic test on a 2 metre column of 25% S.E./C at 105°C with a flow of 50 mls hydrogen per minute gave the following chromatogram:-

(1) Retention time - 3 mins. corresponds to 1,1,2-trichloroethane
(2) Retention time -4½ mins. corresponds to tetrachloroethylene
(3) Retention time -5½ mins. unidentified - (1,1,3-trichloropropene?)
(4) Retention time - 7 mins. corresponds to sym- tetrachloroethane
(5) Retention time -8½ mins. corresponds to 1,1,3,3-tetrachloropropene
(6) Retention time -11 mins. corresponds to pentachloroethane
(7) Retention time -13 mins. unidentified
(8) Retention time-14½ mins. corresponds to 1,1,2,3-tetrachloropropane
(9) Retention time -23 mins.) probable pentachloropropanes:-
)
)
(10)Retention time -24 mins.) 1,1,1,2,3- and 1,1,2,2,3-isomers
(11)Retention time-26½ mins. corresponds to sym-pentachloropropane

At a temperature of 145°C

(11)Retention time -10 mins. corresponds to sym-pentachloropropane
(12)Retention time -16 mins. corresponds to hexachloropropanes
(13)Retention time -26 mins. corresponds to 1,1,3,3,4,4-hexachlorobut-1-ene

The identities of products (1), (2), (4), (5), (6), (11), (12) and (13) were confirmed by use of a P.E.G.ad/C column; the trichloroethane and tetrachloroethylene were only present in minor quantities. The unidentified product (7) was also present only in very small quantity and no further investigation was carried out as to its nature. An authentic sample of 1,1,3-trichloroprop-1-ene (see appendix) corresponded in retention time to the irradiation/

irradiation product (3) and the addition of chlorine to a fraction containing this product gave a pentachloropropane corresponding to an authentic sample of the 1,1,1,2,3-isomer (for preparation see appendix). The chlorination required strong illumination at a temperature of 40°C.

The compared retention times of an authentic sample of 1,1,2,3-tetrachloropropane and of irradiation product (8) gave proof of its identity. Chromatography of the irradiation products on the 1 metre 25% P.E.G.ad/C at 105°C gave the following peaks:-

1,1,3,3-tetrachloroprop-1-ene	- retention time 3 minutes
Pentachloroethane	- retention time 7 minutes
Tetrachloroethane	- retention time 10 minutes
Unidentified peak (A)	- retention time 14 minutes
1,1,2,3 tetrachloropropane	- retention time 16 minutes
Unidentified peak (B)	- retention time 20 minutes

Samples of the pentachloropropanes suspected as products (A) and (B) above were prepared (see appendix) and these gave the following retention times:-

1,1,1,2,3-pentachloropropane	- 14 minutes
1,1,2,2,3-pentachloropropane	- 20 minutes

An analysis on the S.E./C column previously described for this mixture identified (9) as the 1,1,2,2,3-isomer and (10) as the 1,1,1,2,3-isomer.

Preparative scale gas chromatographic separation gave a mixture of (A) and (B) (retention time 50 mins. on a 0.9 metre 25% S.E./C column at 105°C with a flow rate of 600 mls N_2 per minute), the infrared spectrum of which was identical with that of a synthetic mixture, in suitable proportions of the two pentachloropropanes. Measurements made with the P.E.G. ad/C column indicated that the ratio of 1,1,2,2,3- to 1,1,1,2,3- pentachloropropane was 3:2 and that the ratios of total pentachloro- to total hexachloropropanes was 3:1.

The irradiation of dichloromethane-trichloroethylene at the refluxing temperature of the mixture./

The products identified here were the same as those for the ambient temperature radiolysis. However the yield of pentachloropropanes and hexachloropropanes were greatly reduced in proportion to the dimer. The yields of 1,1,3,3-tetrachloropropene and tetrachloroethane showed large increases over the corresponding room temperature irradiation. The absolute amounts of pentachloro- and hexachloropropanes were, however, unaltered from the room temperature radiolysis and the ratio of pentachloropropanes also remained the same.

Benzoyl peroxide initiated reaction.

This experiment was carried out as described for the previous halomethane-trichloroethylene mixtures but as the reflux temperature of this mixture was much lower (ca. 45°C) considerable undissociated benzoyl peroxide was recovered after the 48 hour reaction period. The main product was the dimer of trichloroethylene, with small amounts of tetrachloroethane, pentachloroethane (very small) and 1,1,3,3-tetrachloropropene; no pentachloropropanes or hexachloropropanes were detected.

Variation of dimer-hexachloropropane ratio.

In the previous investigations[102b] of the irradiation of the chloroform-trichloroethylene system a 1:1 ratio of dimer to hexachloropropanes was reported for a solution of similar molar concentration but the present irradiation of a 700 ml sample in a 1 litre flask at the same temperature gave a 5:1 ratio of dimer to hexachloropropanes. This difference could have been due to (a) dose rate difference or (b) the presence of oxygen in the present system.

Irradiation of 75 ml samples in sealed ampoules (a system similar to that reported previously[102b]) at dose rates of 2.47×10^{16}, 1.44×10^{16}, and 0.85×10^{16} eV/ml/min. to the same total dose per ml. as the 700 ml. sample received at an average dose rate of 1.33×10^{16} eV/ml/min. all gave the 1:1 ratio found/

found previously; this difference in the larger radiation irradiation vessel was due to an increase in the dimer production and a decrease in the hexachloropropanes.

Saturation with oxygen and sealing the ampoule did not produce any significant difference over the same irradiation period, but passage of a slow stream of dry air at a dose rate of 1.44×10^{16} eV/ml/min. for a 75 ml. ampoule caused a slight depression of the hexachloropropane yield although the yield of dimer did not show any significant change.

Similar effects were found for the carbon tetrachloride and dichloromethane mixtures with respect to the proportion of hepta- and pentachloropropane relative to the dimer of trichloroethylene, even when the 700 ml. sample was previously flushed with nitrogen in the carbon tetrachloride mixture. In both these cases, where it was possible to separate the two polychloropropane isomers formed, no variation of the isomer ratio was found in the large scale irradiations compared with the sealed ampoules. It would therefore, appear that this variation can be attributed to the difference in the irradiation vessels; presumably the dose received at the extremities of the large vessel is well below the average dose recorded for this vessel (dose varies approximately inversely with the square of the distance from the source). It was also assumed for the comparison of the refluxing irradiation and the room temperature irradiation that with the identical geometry of the systems any differences could be attributed entirely to a temperature effect.

Addition of iodine.

Assuming a G(radical) of about 10 for chloroform radiolysis, sufficient iodine was added to scavenge all the radicals produced during a 72 hour irradiation at a dose rate of 2.47×10^{16} eV/ml/min. of 75 mls. of the chloroform-trichloroethylene mixture (10 m%).

A G.L.C. analysis indicated a suppression of the yield of hexachloropropanes to/

to near zero whereas the dimer was only cut to about half the previous value. This same phenomena was observed in the carbon-tetrachloride and dichloromethane solutions; here the ratio of isomeric hepta- and pentachloropropanes remained the same even though greatly reduced.

Estimation of products from the carbon tetrachloride and chloroform mixtures with trichloroethylene.

For both these systems the product estimation was carried out on a 700 ml. sample in a 1 litre flask at ambient temperatures and the reflux temperature of the mixture; comparisons were made at ambient temperatures with a 75 ml. sample in a sealed ampoule at a higher dose rate but for the same total dose per ml.

The 700 ml. sample was reduced by distillation to 50 mls. for the lower temperature irradiation and to 100 mls. for the refluxing irradiation; the 75 ml. sample was reduced to 10 mls.

Carbon tetrachloride-trichloroethylene.

The dose for the 700 ml. sample was 8.2×10^{19} eV/ml at an average dose rate of 1.37×10^{16} eV/ml/min. and for the 75 ml. sample an equal dose per ml. at a dose rate of 1.48×10^{16} eV/ml/min.

Chloroform-trichloroethylene.

For this mixture a similar system was employed at a dose rate of 1.33×10^{16} eV/ml/min. for the 700 ml. sample and 1.44×10^{16} eV/ml/min. for the 75 ml. sample both having a total dose of 11.5×10^{19} eV/ml/min.

The values for carbon tetrachloride and chloroform solutions are listed in Table III(a) and III(b) respectively.

TABLE III a

	700 ml. sample				75 ml.sample at room temperature
	Room temperature		Reflux temperature		
Product	Moles x 10^{-3}	G-value	Moles x 10^{-3}	G-value	G-value
C_2HCl_5	3	3.2	4.5	4.8	4
$CCl_3 \cdot CH = CCl_2$	0.6	0.6	6.1	6.3	0.6
$CCl_3 \cdot CCl_3$	1.1	1.2	0.8	0.8	1.2
$CHCl_2 \cdot CCl_2 \cdot CH = CCl_2$	6.5	6.9	150	160	3.6
$CCl_3 \cdot CHCl \cdot CCl_3$	0.2	0.2	-	-	0.6
$CCl_3 \cdot CCl_2 \cdot CHCl_2$	0.8	0.8	-	-	2.5

TABLE III b

	700 ml. sample				75 ml.sample at room temperature
	Room temperature		Reflux temperature		
Product	Moles x 10^{-3}	G-value	Moles x 10^{-3}	G-value	G-value
sym-$C_2H_2Cl_4$	0.86	0.66	8.7	7	0.66
$CHCl_2 \cdot CH = CCl_2$	0.41	0.31	4.2	3.6	0.25
$CHCl_2 \cdot CCl_3$	0.85	0.65	1.67	1.2	0.69
$CCl_3 \cdot CH = CCl_2$	ca.0.1	~ 0.1	8.9	7.2	ca.0.1
Hexachloropropanes	0.76	0.55	0.76	0.55	1
$CHCl_2 \cdot CCl_2 \cdot CH = CCl_2$	4.1	3.0	75.0	56	1

TABLE III c

m% C_2HCl_3	1	5	10	15	20
G-hexachloropropane	0.35	0.63	1.0	0.93	0.91
G-dimer	small	0.40	1.0	1.10	1.30

Benzoyl peroxide experiments.

The ratio of products here was compared with those found for the irradiations. For the benzoyl peroxide initiated reaction between carbon tetrachloride and trichloroethylene the ratio of pentachloroethane/pentachloropropene/dimer was approximately 1/3/16 whereas, for the room temperature and refluxing irradiations respectively, the same products were formed in the ratio 1/0.2 (0.18)/2.1(0.9) and 1/1.3/33; the figures in brackets refer to the 75 ml. sample.

Similarly, for the chloroform-trichloroethylene mixture the benzoyl peroxide reaction gave a ratio of tetrachloroethane/pentachloropropene/dimer equal to 1/3/10; the values for the room temperature and refluxing irradiations being 1/0.2/5(2) and 1/1/8 respectively.

Dichloromethane solutions.

No quantitative measurements were made for the dichloromethane solutions. However a rough estimate of the ratio of the products in a room temperature irradiation gave :-

Trichloropropene - 0.5; *sym*- tetrachloroethane - 0.5;
Tetrachloropropene - 1; pentachloroethane - 1;
Tetrachloropropane - 0.25; pentachloropropanes - 2;
hexachloropropanes - 1; dimer - 7.5.

The irradiation of pentachloroethane-halomethane mixtures.

As the present research into the radiation induced reactions of trichloroethylene were prompted by the postulation of this compound as a precursor of the hexachloropropanes formed in the prolonged radiolysis of chloroform, it was considered informative to study the effect of irradiating halomethanes in presence of pentachloroethane, another major product of chloroform radiolysis.

10 m% Solutions of pentachloroethane in carbon tetrachloride and in chloroform were irradiated in nitrogen flushed and sealed tubes. The resultant solution was only investigated for the content of hexa-, hepta- and octachloropropanes. The identification was by gas chromatography and further by infrared investigations of samples trapped out on the surface of a cooled sodium chloride plate from the effluent of an analytical G.L.C. column. The octachloropropane, a solid was trapped into a droplet of nujol placed on a cooled sodium chloride plate.

Results.

Pentachloroethane-carbon tetrachloride.

The products identified here were asym-heptachloropropane and, in larger amount octachloropropane.

Pentachloroethane-chloroform.

Hexachloropropanes were formed and were shown by infrared evidence to be mainly the (symmetrical) 1,1,2,2,3,3-isomer together with some of the 1,1,1,2,3,3-isomer. Only the asymmetric isomer of heptachloropropane was detected and a small yield of octachloropropane was also observed.

Discussion

In the free radical, peroxide initiated addition of halomethanes to trichloroethylene the products identified may be explained by a series of equations exemplified by the following for the reaction between carbon tetrachloride and trichloroethylene:-

$$(C_6H_5CO)_2\ O_2 \longrightarrow 2C_6H_5{\cdot}COO{\cdot} \qquad (1)$$

$$C_6H_5{\cdot}COO{\cdot} \longrightarrow C_6H_5{\cdot} + CO_2 \qquad (2)$$

$$C_6H_5{\cdot} + CCl_4 \longrightarrow C_6H_5Cl + CCl_3{\cdot} \qquad (3)$$

$$CCl_3{\cdot} + CHCl = CCl_2 \longrightarrow CCl_3{\cdot}CHCl{\cdot}CCl_2{\cdot} \qquad (4)$$

$$CHCl = CCl_2 + CCl_3{\cdot}CHCl{\cdot}CCl_2 \longrightarrow CHCl_2{\cdot}CCl_2{\cdot} + CCl_3{\cdot}CH = CCl_2 \qquad (5)$$

$$CCl_4 + CHCl{\cdot}CCl_2{\cdot} \longrightarrow CCl_3{\cdot} + CHCl_2{\cdot}CCl_3 \qquad (6)$$

$$CHCl_2{\cdot}CCl_2{\cdot} + CHCl = CCl_2 \longrightarrow CHCl_2{\cdot}CCl_2{\cdot}CHCl{\cdot}CCl_2{\cdot} \qquad (7)$$

$$CHCl_2{\cdot}CCl_2{\cdot}CHCl{\cdot}CCl_2 + CHCl = CCl_2 \longrightarrow CHCl{\cdot}CCl_2{\cdot}CH = CCl_2 + CHCl_2{\cdot}CCl_2 \qquad (8)$$

$$2\ CCl_3{\cdot} \longrightarrow C_2Cl_6 \qquad (9)$$

Thus chain reactions initiated by a trichloromethyl radical via reaction (4) produce pentachloroethane, 1,1,3,3,3-pentachloroprop-1-ene and the dimer of trichloroethylene, 1,1,3,3,4,4-hexachlorobut-1-ene. For the chloroform solution the reactions are similar, the only difference being that the abstraction reactions here involve the formation of a carbon-hydrogen bond instead of a carbon-chlorine bond, thus reactions (3) and (6) are replaced by (10) and (11) :-

$$C_6H_5{\cdot} + CHCl_3 \longrightarrow C_6H_6 + CCl_3{\cdot} \qquad (10)$$

$$CHCl_2{\cdot}CCl_2 + CHCl_3 \longrightarrow CHCl_2{\cdot}CHCl_2 + CCl_3{\cdot} \qquad (11)$$

In the case of dichloromethane solutions the chain sequence is initiated by the dichloromethyl radical giving the following reactions:- /

reactions:-

$$C_6H_5\cdot + CH_2Cl_2 \longrightarrow C_6H_6 + CHCl_2\cdot \tag{12}$$

$$CHCl_2 + CHCl = CCl_2 \longrightarrow CHCl_2\cdot CHCl\cdot CCl_2\cdot \tag{13}$$

$$CHCl_2\cdot CHCl\cdot CCl_2\cdot + CHCl = CCl_2 \longrightarrow CHCl_2\cdot CH = CCl_2 + CHCl_2 = CCl_2\cdot \tag{14}$$

$$CHCl_2\cdot CCl_2\cdot + CH_2Cl_2 \longrightarrow CHCl_2\cdot CHCl_2 + CHCl_2\cdot \tag{15}$$

All these compounds have been identified in the gamma irradiation of these solutions. However, the radiolytic breakdown of the halomethanes is the source of the initial radicals and for carbon tetrachloride (16), chloroform (17) and dichloromethane (18), this introduces into the system the following radicals[102ab].

$$CCl_4 \rightsquigarrow CCl_3\cdot + Cl\cdot \tag{16}$$

$$CHCl_3 \rightsquigarrow CHCl_2\cdot + Cl\cdot \tag{17}$$

$$CH_2Cl_2 \rightsquigarrow CH_2Cl\cdot + Cl\cdot \tag{18}$$

The chlorine atoms produced in this way may either attack the trichloroethylene double bond or abstract hydrogen from the halomethane solvent to give hydrogen chloride:-

$$Cl\cdot + CHCl_3 \longrightarrow HCl + CCl_3\cdot \tag{19}$$

$$Cl\cdot + CH_2Cl_2 \longrightarrow HCl + CHCl_2\cdot \tag{20}$$

(Carbon tetrachloride is inert to chlorine atom attack since the reaction $Cl\cdot + CCl_4 \qquad Cl_2 + CCl_3\cdot$ is endothermic).

The radicals produced in (19) and (20) are then capable of the normal reactions as noted for the peroxide initiated reactions.

The attack of the chlorine atom on the trichloroethylene molecule has been previously shown as giving exclusively the 1,1,2,2-tetrachloroethyl radical (e.g. reaction 5) and this is consistent with the isolation of only sym-tetrachloroethane[102b]; if any addition had occurred to give the 1,1,1,2-

tetrachloroethyl/

1,1,1,2-tetrachloroethyl radical then some 1,1,1,2-tetrachloroethane would have been detected in the chloroform and dichloromethane solutions. It is however possible that if any addition had occurred at the dichloromethylene end the resultant radical would, by chlorine migration, give the more stable 1,1,2,2-tetrachloroethyl radical[99] i.e.,

$$CCl_3{\cdot}CHCl{\cdot} \longrightarrow {\cdot}CCl_2{\cdot}CHCl_2 \qquad (21)$$

If the chlorine migration is a faster reaction than the hydrogen abstraction, addition of chlorine in this way would be masked. Similarly a reaction (21) faster than reaction (7) would give the observed form of dimer. There is thus no concrete evidence for the direction of addition of the chlorine atom although it is most likely that the 1,1,2,2-tetrachloroethyl radical is the only one formed. The subsequent reaction of this radical will then be as for the peroxide initiated reaction (i.e. addition to a further trichloroethylene molecule or abstraction from the halomethane substrate).

Part of the tetrachloroethane formed in the radiolysis of the chloroform solution may be produced directly by the reaction postulated for pure chloroform.[102]

$$2CHCl_2{\cdot} \longrightarrow CHCl_2{\cdot}CHCl_2 \qquad (22)$$

However the large increase in the G-value of tetrachloroethane with temperature rise indicates its production by reactions (5) and (11), certainly as the temperature increases. The tetrachloroethane in the dichloromethane solution has the same two possible sources of production since dichloromethyl radicals are produced by various hydrogen abstraction reactions.

If the tetrachloroethane production is by reaction (11) then a greater availability of chlorine atoms is required; this can in fact be accounted for by the increase in the G-value of 1,1,3,3-tetrachloropropene. The increase in dimer production which also furnishes chlorine atoms may only be due to an increase in the chain length of reactions (7) and (8) at the higher temperature.

The/

The production of 1,1,3,3-tetrachloropropene in the chloroform solution is dependent on the radiolytic production of dichloromethyl radicals, this being their only source. Another product dependent on this radical is the sym- pentachloropropane which is probably formed by reaction (13) followed by (23),

$$CHCl_2\cdot CHCl\cdot CCl_2 + CHCl_3 \longrightarrow CHCl_2\cdot CHCl\cdot CHCl_2 + CCl_3\cdot \qquad (23)$$

The increase in the 1,1,3,3-tetrachloropropene in the refluxed chloroform solution may be partly explained by a decrease in the dimerisation reaction of the dichloromethyl radicals and the suppression of reaction (23) in favour of (14). However, even if the total tetrachloroethane production at room temperature ($G = 0.66$) is due to dimerisation of these radicals this still does not account for the observed increase of tetrachloropropene (G room temperature = 0.31; G reflux temperature = 3.6) and the small amount of sym-pentachloropropane formed at the lower temperature does not differ significantly at the higher temperature.

Although any variation in the competitive hydrogen abstraction reaction of the dichloromethyl radical,

$$CHCl_2\cdot + CHCl_3 \longrightarrow CH_2Cl_2 + CCl_3\cdot \qquad (24)$$

was not fully investigated here due to the ready volatility of the dichloromethane at the refluxing temperature of the solution, it was assumed that the G-value of 1.16 found for reaction (24) in pure chloroform (at room temperature) would be an upper limit for the dichloromethyl radical disappearance by reaction (24) in the room temperature radiolysis. This was indeed confirmed by the nature of the products identified: those containing the trichloromethyl group from reaction (24) are of minor importance but a number of important products result from the reactions of the dichloromethyl radical with trichloroethylene. An increased production of the dichloromethyl radicals at the/

the higher temperature is therefore indicated.

Comparing the result observed for the chloroform solution with the carbon tetrachloride solution a similar situation is observed with an increase in the pentachloropropene G-value (G room temperature = ~ 0.6, G reflux temperature = 6.9). Here an increase in the availability of trichloromethyl radicals would be consistent with an increase in reaction (6) or a decrease in reaction (9). It was found that the hexachloropropane production decreased a little at the higher temperature but not by any significant amount (G room temperature = 1.2, G reflux temperature = 0.8); furthermore the pentachloroethane production increased from G = 3.2 to G = 4.8. However, neither of these results can explain the ten-fold increase in the yield of pentachloropropene and the elimination of the heptachloropropanes production, which will be discussed later, is also inadequate to account for this increase.

It therefore appears that the radiolytically produced radicals react more readily with the trichloroethylene at the higher temperature rather than by the back reaction e.g.

$$CCl_3\cdot \ + \ Cl\cdot \longrightarrow CCl_4 \qquad (25)$$

$$CHCl_2 \ + \ Cl\cdot \longrightarrow CHCl_3 \qquad (26)$$

This effect will also increase the availability of chlorine atoms in the system for reaction with trichloroethylene and will thereby contribute to the increases in dimer production and in the yields of tetra- and penta-chloroethanes in the chloroform and carbon tetrachloride solutions, respectively. The temperature increase may facilitate the suppression of reactions (24) and (25) by increasing the rate of diffusion of these radicals from their site of production.

It could be argued that an increase in the rate of a reaction of the type

$$CHCl_2\cdot CCl_2\cdot CHCl\cdot CCl_2\cdot \ + \ CCl_4 \longrightarrow CHCl_2\cdot CCl_2\cdot CHCl\cdot CCl_3 \ + \ CCl_3\cdot \quad (27)$$

might/

might increase the availability of trichloromethyl radicals at the higher temperature but, from work on the 1,2-dichloroethylene-carbon tetrachloride solutions it appears that the yield of this type of product is temperature independent (Section III (b)).

The pentachloroethane produced in the chloroform solution radiolysis may be explainable on the same basis as for pure chloroform radiolysis[102 ab].

$$CHCl_2^{\cdot} + CCl_3^{\cdot} \longrightarrow CHCl_2{\cdot}CCl_3 \qquad (28)$$

The increase in its production with temperature would then be explained by the increased availability of dichloromethyl radicals and the increased production of trichloromethyl radicals via reaction (11) and other hydrogen abstraction reactions. It has been shown however that these radicals react more readily with the trichloroethylene at higher temperatures; that this is the fate of the trichloromethyl radical is deduced from the large G-value for the 1,1,3,3,3-pentachloropropene in the refluxing chloroform solution radiolysis.

A possible source of pentachloroethane is then reactions (29) and (30) the second of which might occur close to the particle tracks where the local concentration of chlorine atoms is still high.

$$Cl^{\cdot} + CHCl = CCl_2 \longrightarrow CHCl_2{\cdot}CCl_2 \qquad (29)$$

$$CHCl_2{\cdot}CCl_2^{\cdot} + Cl^{\cdot} \longrightarrow CHCl_2{\cdot}CCl_3 \qquad (30)$$

The identification of pentachloroethane as a radiolysis product of the dichloromethane solution provides support for this reaction sequence since no trichloromethyl radicals are produced here. The observation that some pentachloroethane appears in the peroxide initiated reaction between chloroform and trichloroethylene (where there are no locally high concentrations of chlorine atoms) does not necessitate reactions (29) and (30) since a disproportionation reaction of the tetrachloroethyl radical could also account for its production.

$$2\,CHCl_2{\cdot}CCl_2^{\cdot} \longrightarrow CHCl_2{\cdot}CCl_3 + CHCl = CCl_2 \qquad (31)$$

Similar/

Similar collisions of the tetrachloroethyl radical with other radicals may also produce the pentachloroethane and an unsaturated compound. However, the very small amount of pentachloroethane formed in the peroxide initiated reaction indicates that any such reactions are unimportant.

In the benzoyl peroxide initiated reaction for the three halomethane solutions no 1:1 adduct with the trichloroethylene was isolated. These adducts would be for the carbon tetrachloride, chloroform and dichloromethane solutions respectively 1,1,1,2,3,3,3-heptachloropropane, 1,1,1,2,3,3-hexachloropropane, and 1,1,2,3,3-pentachloropropane assuming the initial addition to the trichloroethylene takes place at the carbon atom with one chlorine substituent; i.e. for carbon tetrachloride reaction (4) followed by (32):-

$$CCl_3\cdot CHCl\cdot CCl_2^{\cdot} + CCl_4 \longrightarrow CCl_3\cdot CHCl\cdot CCl_3 + CCl_3\cdot \qquad (32)$$

for chloroform reaction (4) followed by (33):-

$$CCl_3\cdot CHCl\cdot CCl_2^{\cdot} + CHCl_3 \longrightarrow CCl_3\cdot CHCl\cdot CHCl_2 + CCl_3\cdot \qquad (33)$$

and for dichloromethane reaction (13) followed by (34):-

$$CHCl_2\cdot CHCl\cdot CCl_2^{\cdot} + CH_2Cl_2 \longrightarrow CHCl_2\cdot CHCl\cdot CHCl_2 + CHCl_2\cdot \qquad (34)$$

Rather than these reactions occurring the radicals formed in reactions (4) and (13) lose a chlorine atom to give the chloropropene.

The mode of this chlorine atom loss has been represented previously (e.g. reaction 5) as a transfer direct to the molecule of trichloroethylene. However, two other possibilities can be considered, firstly a transfer of a chlorine atom from one radical to another (disproportionation) and secondly, a unimolecular decomposition of the radical to give the olefin and a free chlorine atom. In the first instance, the production of 1,1,3,3,3-pentachloropropene could be represented by the equation:-

$$2CCl_3\cdot CHCl\cdot CCl_2^{\cdot} \longrightarrow CCl_3\cdot CHCl\cdot CCl_3 + CCl_3\cdot CH = CCl_2 \qquad (35)$$

but since no <u>sym</u>- heptachloropropane was produced, this reaction is ruled out.

Another/

Another disproportionation possibility is with the 1,1,2,2-tetrachloroethyl radical to give pentachloroethane but the formation of the tetrachloroethyl radical itself requires a chlorine atom which must ultimately be derived from a hexachloropropyl radical, either by unimolecular decomposition or by bimolecular transfer to trichloroethylene.

Indeed most of the pertinent features of the chlorine atom loss can be explained on the basis of a bimolecular transfer to another molecule of monomer (e.g. the radical-chain production of dimer and high polymer from chlorinated ethylenes[102a]). The cis- trans- isomerisation in the liquid phase could also take place by a chlorine atom transfer from the 1,1,2-trichloroethyl radical (free rotation about the radical single bond) rather than by the now accepted mechanism for the gas phase of reversible addition of a chlorine atom[148]. However, results obtained by Schmerling and West[149] for the addition of hydrocarbons to chlorinated ethylenes in the liquid phase strongly suggests the presence of a free chlorine atom since hydrogen chloride is produced by a chain reaction consistent with equations (36) and (37)

$$R\cdot\ CXCl\cdot CXCl\cdot \longrightarrow R\cdot\ CX = CXCl + Cl\cdot \qquad (36)$$

$$RH + Cl\cdot \longrightarrow R\cdot + HCl \qquad (37)$$

This reaction occurs at temperatures as low as 110°C and there is no evidence of chlorine transfer to the chloroethylene (no 1,1,2-trichloroethane from dichloroethylene by the reaction $CHCl_2\cdot CHCl\cdot + RH \rightarrow CHCl_2\cdot CH_2Cl + R\cdot$, or dimer although the latter is formed at this temperature[149] in pure dichloroethylene). However, these types of radicals are known to decompose at elevated temperatures by a rupture of the carbon-chlorine bond[125, 128] so the same mechanism may not be applicable at room temperature.

The unimolecular loss of a chlorine atom may be considered as similar to the reversible addition of a chlorine atom to dichloroethylene in the gas phase where/

where it is assumed that the loss occurs from an excited 1,1,2-trichloroethyl radical and that the energy required to cause dissociation of the radical (20 k. cals/mole) is obtained from the bond formed. If a similar activated radical is produced in the liquid phase then it would be expected to be deactivated very rapidly by collisions and since the 1,2-dichloroethylenes show isomerisation even in the liquid phase the loss of a chlorine atom may probably take place by a bimolecular mechanism. However, the observation of a pressure effect here[150] whereby isomerisation is decreased by increasing pressure (1 to 300 atmospheres) may be attributable to the unimolecular process occurring.

Frequently there is no difference between the products which would result from a chlorine atom loss or a transfer, the only difference being that the former is a unimolecular reaction whereas the latter is a bimolecular reaction. Gas phase systems tend to favour the carbon-chlorine bond rupture with the postulation of a hot radical. A similar hypothesis for the liquid phase requires either a very rapid decomposition or a somewhat stabilized excited state[151]. If the liquid phase addition of hydrocarbons to chlorinated ethylenes[149] can be generalised as not being a thermal reaction then the unimolecular reaction does occur as bimolecular reaction would give a different chain reaction here (see page 126).

The addition of free radicals to haloethylenes can be generalized by the equation $X\cdot + CYZ = CY^{1}Z^{1} \longrightarrow CXYZ\cdot CY^{1}Z^{1}$ (38)
Then if the radical $CXYZ\cdot CY^{1}Z^{1}$ decomposes the bond that breaks preferentially will be the weakest. Therefore, in the addition of the trichloromethyl radical to trichloroethylene the carbon-chlorine bond breaks giving the observed pentachloropropene, a result similar to that obtained for the addition of the chlorodifluoromethyl radical to dichloroethylene[151]. Similarly, the formation of 1-bromo-2-chloroethylene by radical-chlorination of 1,2-dibromoethylene is consistent/

consistent with the fission of the weaker carbon-bromine bond rather than the carbon-chlorine bond[152].

The possibility of any saturated addition product being formed appears to be dependent on the lifetime of the intermediate and the ease of the displacement step. Comparing the results obtained for the three systems (a) $BRCCl_3/CHCl = CHCl$[103], (b) $BRCCl_3/CHBr = CHBr$[103], and (c) $CCl_4/CHCl = CHCl$ (present work Section IIIB) it was observed that only (a) gave any significant yield of 1:1 addition. However the intermediates formed in (a) and (c) by trichloromethyl radical attack are the same (the 1,2,3,3,3-pentachloropropyl radical) and the difference here can be attributed to the difference in the ease of the displacement reaction, the ease of bromine abstraction from bromotrichloromethane compared to chlorine abstraction from carbon tetrachloride being well known. The difference between (a) and (b) probably involves the lifetime of the two different intermediates since the displacement reactions are the same; this is consistent with the weaker carbon-bromine bond in the intermediate from dibromoethylene compared with the carbon-chlorine bond in that from dichloroethylene.

In the irradiation solutions, in contrast to the peroxide catalysed reactions, the product contains some 1:1 adducts. These addition products were shown to be peculiar to the irradiation and not a temperature dependent factor since the addition of carbon tetrachloride to trichloroethylene initiated at room temperature by trichloroacetyl peroxide gave no addition product. Furthermore irradiation of the chloroform and dichloromethane solutions at the same temperature as the benzoyl peroxide-initiated reaction gave the same amounts of hexa- and pentachloropropanes as a room temperature irradiation of these solutions.

It has been assumed previously that the (poly) chloromethyl radical addition takes place exclusively at the least substituted carbon atom and this/

this is in fact consistent with the exclusive formation of the olefins 1,1,3,3,3-pentachloropropene, 1,1,3,3-tetrachloropropene and 1,1,3-trichloropropene in the carbon tetrachloride, chloroform and dichloromethane solutions, respectively. If any addition had occurred at the disubstituted carbon atom, then other chloropropenes would have been isolated, e.g.

$$CCl_3\cdot \ + \ CCl_2 = CHCl \rightarrow CCl_3\cdot CCl_2\cdot CHCl\cdot \rightarrow CCl_3\cdot CCl = CHCl \ + \ Cl\cdot \qquad (39)$$

However, the formation of *asym*- heptachloropropane in the room temperature irradiation of the carbon tetrachloride-trichloroethylene solution could be attributed to the reaction:-

$$CCl_3\cdot \ + \ CCl_2{=}CHCl \rightarrow CCl_3\cdot CCl_2\cdot CHCl \xrightarrow{CCl_4} CCl_3.CCl_2\cdot CHCl_2 \ + \ CCl_3 \qquad (40)$$

and the formation of *sym*- hexachloropropane in the chloroform solution could be attributed to the reaction sequence (41)

$$\underset{(i)}{CCl_3\cdot + CCl_2{=}CHCl} \rightarrow \underset{(ii)}{CCl_3\cdot CCl_2\cdot CHCl\cdot} \rightarrow \underset{(iii)}{\cdot CCl_2\cdot CCl_2\cdot CHCl_2} \xrightarrow{CHCl_3} \underset{(iv)}{CHCl_2\cdot CCl_2\cdot CHCl_2} \qquad (41)$$

The step (ii) to (iii) requires a chlorine migration either by a 1,3-shift or by two 1,2-shifts along the chain to give the most stable radical (iii) and is to be expected from the work of Nesmeyanov et al[99]. (The formation of *sym*- heptachloropropane and *asym*- hexachloropropane in the carbon tetrachloride and chloroform solutions, respectively, could be attributed to the normal mode of radical-chain addition with initiation by a trichloromethyl radical at the less substituted carbon atom of the olefin). It must be noted however, that all these reactions involve the trichloromethyl radical which, judging by the low G-value of 1,1,3,3,3-pentachloropropene appears to be present in relatively small concentration in the room temperature irradiation of the chloroform solution. Moreover, radical-chain addition mechanism whether initiated by addition to the CHCl or the CCl_2 group of the olefin, is inadequate to explain the pentachloropropanes found in the dichloromethane solution. Initiation by a dichloromethyl radical would give *sym*- pentachloropropane if addition occurs at/

at the least substituted carbon atom or if addition occurs at the more substituted carbon atom then either the sym- isomer or the 1,1,2,2,3-isomer would be formed depending on whether or not a chlorine migration occurs to give the more stable radical:-

$$\begin{tikzcd}[column sep=small] \mathrm{CHCl_2\cdot} + \mathrm{CCl_2 = CHCl} \arrow[r] & \mathrm{CHCl_2\cdot CCl_2\cdot CHCl\cdot} \arrow[r, "\mathrm{CH_2Cl_2}"] \arrow[d, "\text{1,2-shift}"] & \mathrm{CHCl_2\cdot CCl_2\cdot CH_2Cl} \\ & \mathrm{CHCl_2\cdot \dot{C}Cl\cdot\ CHCl_2} \arrow[r, "\mathrm{CH_2Cl_2}"] & \mathrm{CHCl_2\cdot CHCl\cdot CHCl_2} \end{tikzcd} \qquad (42)$$

Therefore, no conceivable chain reaction is adequate to explain the production of the 1,1,1,2,3-pentachloropropane.

It seems clear then that free-radical attack on trichloroethylene occurs exclusively at the monochloro-substituted carbon atom and that trichloroethylene behaves identically with chlorotrifluoroethylene in this respect[143]. It follows therefore that the hepta-, hexa-, and penta-chloropropanes must be formed by a mechanism other than the radical-chain addition. Since the production of these products, apart from the heptachloropropanes, was temperature independent it was thought that an ion-molecule reaction might be occurring in the radiolysis but addition of iodine to the chloroform solution suppressed the hexachloropropane formation to a greater extent than the other products, an observation which is characteristic of a radical reaction.

If addition occurs exclusively at the monochloro-carbon atom of the trichloroethylene for either member of the pair of radiolytic species, produced by reactions (16) -(18), and the resultant radical reacts with the other member of the pair, the formation of the polychloropropanes can be accounted for according to the following reaction schemes:-

for carbon tetrachloride:-

$$\mathrm{Cl\cdot} + \mathrm{CHCl = CCl_2} \rightarrow \underset{\mathrm{A}}{\mathrm{CHCl_2{:}CCl_2\cdot}} \xrightarrow{\mathrm{CCl_3\cdot}} \mathrm{CHCl\cdot CCl_2\cdot CCl_3} \qquad (43a)$$

$$\mathrm{CCl_3}+ \mathrm{CHCl = CCl_2} \rightarrow \underset{\mathrm{B}}{\mathrm{CCl_3\cdot CHCl\cdot CCl_2\cdot}} \xrightarrow{\mathrm{Cl\cdot}} \mathrm{CCl_3\cdot CHCl\cdot CCl_3} \qquad (43b)$$

for chloroform:-/

for chloroform:-

$$\mathrm{Cl\cdot + CHCl = CCl_2 \rightarrow \underset{A^{1}}{CHCl_2\cdot CCl_2\cdot} \xrightarrow{CHCl_2\cdot} CHCl_2\cdot CCl_2\cdot CHCl_2} \qquad (44a)$$

$$\mathrm{CHCl_2\cdot + CHCl = CCl_2 \rightarrow \underset{B^{1}}{CHCl_2\cdot CHCl\cdot CCl_2\cdot} \xrightarrow{Cl\cdot} CHCl_2\cdot CHCl\cdot CCl_3} \qquad (44b)$$

for dichloromethane:-

$$\mathrm{Cl\cdot + CHCl = CCl_2 \rightarrow \underset{A^{11}}{CHCl_2\cdot CCl_2\cdot} \xrightarrow{CH_2Cl\cdot} CHCl_2\cdot CCl_2\cdot CH_2Cl} \qquad (45a)$$

$$\mathrm{CH_2Cl\cdot + CHCl = CCl_2 \rightarrow \underset{B^{11}}{CH_2Cl\cdot CHCl\cdot CCl_2\cdot} \xrightarrow{Cl\cdot} CH_2Cl\cdot CHCl\cdot CCl_3} \qquad (45b)$$

These reaction sequences (43)-(45) account for the production of all the polychloropropanes having molecular formulae equal to the sum of those of the reactants, without assuming radical attack at the more substituted carbon atom of the olefin. This scheme would be dependent on a high radical concentration and would therefore be peculiar to the radiation - induced reaction. The intermediates A, B etc. are all known and the subsequent reactions probable. The radicals B^{1} and B^{11} are probably also the source of sym- pentachloropropane and 1,1,2,3-tetrachloropropane, respectively since these compounds would be formed by displacement reactions with chloroform and dichloromethane respectively.

The formation of radicals in the radiolysis differs from the peroxide reactions in that the radiolytic breakdown does not give an equal distribution of radicals throughout the system but results in a high concentration of radicals along the electron tracks. The high concentration of radicals will then tend to disperse by diffusion into the bulk of the solution, or react with each other to give molecular products. There will thus be a concentration gradient from the electron track into the bulk of the solution and the likelihood of any radical-radical reactions occurring

will/

will decrease with the concentration decrease. Thus the radiolytic breakdown favours reactions (43)-(45) along the electron tracks and probably within a certain limited vicinity. If, however, these areas of high radical concentration overlap then the solution becomes nearly homogeneous with little variation of radical density. Such a situation would strongly favour the reactions (43)-(45) for the various solutes. This could explain the lower G-value of hexachloropropanes compared to dimer at the lower dose rate for the chloroform solution. The production of dimer will in fact decrease with an increase in reaction (44a), and increased pentachloroethane production by reaction (30).

Although there is a strong similarity in the results for the three different solutions there are also some important differences. In the dichloromethane solution hexachloropropanes are formed in similar yields at both temperatures during the irradiation but not in the peroxide-initiated reaction. These may be assumed to be formed via reactions (44a) and (44b). However, in the chloroform solution the corresponding reaction to form heptachloropropanes is not observed. These results are consistent with the observations, in the room temperature radiolysis, that the dichloromethyl radical is more important in the dichloromethane solution (the value of 1,1,3,3-tetrachloropropene is twice that of 1,1,2-trichloropropene) than the trichloromethyl radical is in the chloroform solution (only about a third the amount of 1,1,3,3,3-pentachloropropene compared with 1,1,3,3-tetrachloropropene).

Considering the relative reactivities of the dichloro- and monochloromethyl radicals to be inversely related to their resonance energies, it is seen that the former has three contributing structures compared with the latter's two and is therefore likely to be less reactive.

$$Cl\text{-}\dot{C}H\text{-}Cl \leftrightarrow \cdot\overset{+}{Cl}\text{-}\overset{-}{C}H\text{-}Cl \leftrightarrow Cl\text{-}\overset{-}{C}H\text{-}\overset{+}{Cl}\cdot \;;\quad Cl\text{-}CH_2\cdot \leftrightarrow \cdot\overset{+}{Cl}\text{-}\overset{-}{C}H_2$$

It/

It follows that the importance of abstraction from the solvent, relative to addition to trichloroethylene, is likely to be greater for the more reactive chloromethyl group than for the less reactive dichloromethyl radical. This difference between mono- and di- chloromethyl radicals is borne out by the results from the radiolysis of pure chloroform and pure dichloromethane[102a] where the G-value for hydrogen abstraction by the monochloro-radical is greater than that for the dichloro-radical ($G = 1.5$ compared with 1.1) and also that compounds containing the monochloromethyl group by radical-radical combinations in the dichloromethane radiolysis is less than compounds containing the dichloromethyl group in the chloroform radiolysis although the total G-values are approximately equal. There is therefore, a greater likelihood of dichloromethyl radicals being produced in the region of high radical concentration in the dichloromethane solution than of trichloromethyl radicals being produced in this region in the chloroform solution.

A further difference in these three solutions is the effect of temperature increase: the yields of hexa- and penta- chloropropanes are unaltered in the chloroform and dichloromethane solutions whereas the heptachloropropanes (disappear in the carbon tetrachloride solution. This disappearance of heptachloropropanes could be influenced by the faster diffusion of radicals from the areas of high concentration so that the required concentration of radicals is not obtained. Possibly the formation of the heptachloropropanes requires a higher radical concentration than the formation of hexa- and penta-chloropropanes owing to the shorter lifetime of the radicals A and B compared with the corresponding precursors of the hexa- and penta- chloropropanes. With the higher reflux temperature of the carbon tetrachloride solution (78°C) compared to chloroform (65°C) and dichloromethane solutions (45°C) the further reaction of A with a molecule of trichloroethylene will be enhanced. That radical B is more prone to lose a chlorine atom than the analagous radicals

B^1/

B^1 and B^{11} may be deduced from the fact that the room temperature radiolysis of chloroform and dichloromethane solutions give sym- pentachloropropane and 1,1,2,3-tetrachloropropane from radicals B^1 and B^{11} respectively whereas the room temperature peroxide initiated reaction between carbon tetrachloride and trichloroethylene gives no sym- heptachloropropane. If the loss of a chlorine atom is the result of an activation energy process then it would be expected that the hexa- and penta-chloropropanes would also decrease. It has however been postulated that this loss has zero or very little activation energy which is consistent with its loss at room temperature[151].

It would require a fuller understanding of the different factors influencing the production of the intermediates A, B etc. (e.g. activation energies and reaction rates of initial step) before any concrete conclusion could be arrived at as to why the G-values of the hexa- and penta-chloropropanes do not vary and why the ratio of the two pentachloro-isomers does not alter with temperature. Possibly the initial addition to trichloroethylene is an equal and low activation energy process for both the radiolytically produced species. The position is further complicated by the difference in the rates of diffusion of these radiolytic species; the largest difference between members of a pair is that between the trichloromethyl radical and a chlorine atom and the least difference is between the monochloromethyl radical and a chlorine atom. These differences and the variation of temperature increase will undoubtedly influence the reactions at the sites of high radical concentrations.

It can be seen from the variation of the concentration of trichloroethylene in the chloroform solution that a 10 m% trichloroethylene solution results in the maximum production of the hexachloropropanes. Presumably below this concentration of olefin excess radicals escape into the solution giving a radical concentration too low for reactions (44a) and (44b) to occur; at higher/

higher mole percentages the trichloroethylene will deplete the radical concentration by the initial production of A^1 and B^1, to below the concentration necessary for further radical combinations and will also scavenge A^1 to give dimer. The longer life of B^1 before a radical collision will facilitate reaction (14).

In conclusion it can be said that the reaction sequences (43) to (45) afford a satisfactory explanation of the formation of these polychloropropanes. The position of their formation with respect to the bulk of the solution and the electron tracks is, however, not fully understood. It can be assumed, however, that it is not in the bulk of the solution since the increased scavenging efficiency of the trichloroethylene at the higher temperature would probably suppress any radical combinations. The effect of iodine in reducing the yields of these compounds probably indicates that the reaction does not occur in the electron tracks or spurs but rather in an area just outside this where the diffusion of radicals gives a high local concentration. It may be that the two radical additions are very nearly simultaneous.

The production of hexachloropropanes during the radiolysis of pure chloroform is in accordance with an initial formation of trichloroethylene but the isolation of both _asym_- and _sym_- heptachloropropanes in the carbon tetrachloride solution probably indicates that trichloroethylene is not the precursor of the _asym_- heptachloropropanes in the pure chloroform radiolysis.

The results from the radiolysis of pentachloroethane-carbon tetrachloride and pentachloroethane-chloroform solutions suggest that the pentachloroethane, formed by radiolysis of pure chloroform, does not contribute directly to the chloropropane production. The isolation of octachloropropane and only _asym_-heptachloropropane in the carbon tetrachloride-pentachloroethane solution indicates that only pentachloroethyl and 1,1,2,2-tetrachloroethyl radicals are produced and that these react with trichloromethyl radicals according to the equations:-/

equations:-

$$CCl_3{\cdot}CCl_2{\cdot} \;+\; CCl_3{\cdot} \;\rightarrow\; CCl_3{\cdot}CCl_2{\cdot}CCl_3 \qquad (47)$$

$${\cdot}CCl_2{\cdot}CHCl_2 \;+\; CCl_3{\cdot} \;\rightarrow\; CHCl_2{\cdot}CCl_2{\cdot}CCl_3 \qquad (48)$$

The 1,1,1,2-tetrachloroethyl radical was evidently absent since it would have given rise to <u>sym</u>- heptachloropropane.

In chloroform-pentachloroethane solution these radicals would give octachloropropane (47), <u>asym</u>- heptachloropropane (48) and (49) and 1,1,2,2,3,3-hexachloropropane (50) only i.e.

$$CCl_3{\cdot}CCl_2{\cdot} \;+\; CHCl_2{\cdot} \;\rightarrow\; CCl_3{\cdot}CCl_2{\cdot}CHCl_2 \qquad (49)$$

$$CHCl_2{\cdot}CCl_2{\cdot} \;+\; CCl_3{\cdot} \;\rightarrow\; CHCl_2{\cdot}CCl_2{\cdot}CCl_3 \qquad (50)$$

$$CHCl_2{\cdot}CCl_2 \;+\; CHCl_2{\cdot} \;\rightarrow\; CHCl_2{\cdot}CCl_2\; CHCl_2 \qquad (51)$$

and all of these products were detected. Some 1,1,1,2,3,3-hexachloropropane was also produced but in the absence of 1,1,1,2-tetrachloroethyl radicals it must be assumed to arise from the same source as in pure chloroform, and not from the added pentachloroethane. The absence of octachloropropane amongst the radiolysis products from pure chloroform is another indication that pentachloroethane is not involved in the formation of polychloropropanes in this medium.

SECTION III (B)

The irradiation of 10 mole % 1,2-dichloroethylene with 90 mole % (1) carbon tetrachloride (2) bromotrichloromethane.

The irradiation of 10 m% 1,2-dichloroethylene with 90 m% 1(carbon tetrachloride (2) bromotrichloromethane.

These mixtures were examined on a similar basis to the trichloroethylene experiments: irradiation at ambient and reflux temperatures and comparison with the benzoyl peroxide initiated reaction at the reflux temperature of the mixture.

Irradiation.

The purification of carbon tetrachloride was carried out as previously described; the bromotrichloromethane (Eastman-Kodak Ltd.) was slowly distilled at atmospheric pressure and the resultant distillate was shown to contain a higher boiling impurity to the extent of about 1-2%. No further purification was carried out and since there was no preferential comsumption of the impurity during subsequent irradiations, its effect can be neglected. The drying and final distillation were carried out as for the carbon tetrachloride.

The 1,2-dichloroethylene (B.D.H.), a mixture of *cis*- and *trans*- isomers was purified as described for the trichloroethylene, the final distillation giving a mixture of the isomers. The room temperature irradiations were carried out with a 550 ml sample for the carbon tetrachloride solution with a 100 ml sample of the bromotrichloromethane solution, both in stoppered flasks.

Benzoyl peroxide experiments.

These experiments were carried out as described for the trichloroethylene experiments. The solution (300 mls for carbon tetrachloride and 150 ml for bromotrichloromethane) was refluxed for 36 hours (for carbon tetrachloride) or for 12 hours (for bromotrichloromethane) with additions of benzoyl peroxide (1.5 gm) at the beginning and at 9 hour intervals thereafter (6 hours for bromotrichloromethane).

Product identification (1) carbon tetrachloride - 1,2-dichloroethylene.

In the room temperature irradiation, the formation of polymer was noted; the rather gelatinous precipitate was filtered off and no further investigation was carried out/

out as to its nature but it was similar to that observed in the irradiation of pure 1,2-dichloroethylene[153]. (It was noted, at the higher dose rate used for the product estimation, that the formation of polymer was not observable in the original volume but that polymer began to separate as the volume was reduced).

The low yield of products other than polymer can be attributed to the competing polymerisation reactions. As the volume of solution was reduced further polymer was precipitated and this was again removed by filtration. Fractional distillation of the residual liquid at atmospheric pressure gave fractions boiling in the ranges 136°-144°C, 144°-150°C and 150°-155°C which were all shown to contain mainly <u>sym</u>- tetrachloroethane and 1,1,3,3-tetrachloropropene by G.L.C. and comparison of their infrared spectra with those of suitably constituted mixtures of these compounds. The last fraction contained quantities of the dimer of dichloroethylene, 1,3,4,4-tetrachlorobut-1-ene, as identified from the irradiation of dichloroethylene itself[154]. Further identification was by gas chromatography retention times only: a typical run on a 1 metre 25% S.E./C. at 125°C with a flow rate of 50 mls. hydrogen per minute gave the following retention times:-

Retention time - 3 minutes - corresponds to hexachloroethane.
Retention time - 4 minutes - corresponds to dimer
Retention time - 8 minutes - corresponds to hexachloropropane
Retention time -12 minutes)
Retention time -14 minutes) unidentified peaks.
Retention time -21 minutes)

The presence of hexachloroethane, dimer and hexachloropropane (probably the 1,1,1,2,3,3-isomer) was confirmed by examination on the P.E.G. ad/C column when the dimer gave two peaks indicating the presence of the two isomers[154]. The/

The latter of the two peaks was not completely separated from hexachloropropane but the asymmetry of the peak showed that it was a composite one.

The two peaks of retention time 12 minutes and 14 minutes were found to be identical with the products isolated from the addition of chlorine to 1,3,4,4-tetrachlorobutene, a reaction which afforded a liquid and a white crystalline solid (mpt. 104°-106°C), presumably the racemic and meso forms of 1,1,2,3,4,4-hexachlorobutane (elementary analysis gave, for the liquid C, 18.62; H, 2.16; Cl, 79.80%; and for the solid C, 17.64; H, 1.58; Cl, 79.40%; $C_4H_4Cl_6$ requires C, 18.15; H, 1.45; Cl, 80.39%).

The peak eluted after these hexachlorobutanes was not investigated further as it could not be isolated in a pure form by preparative scale gas chromatography owing to its high boiling point.

The irradiation at reflux temperature was carried out with a 500 ml sample at the horizontal source, heated by an isomantle. It was noted that no polymer was observed in the original volume even on cooling. Reduction of the volume of solution by slow distillation of unreacted carbon tetrachloride did, however, cause the precipitation of some gelatinous material but it was obvious that high molecular weight polymer was present only in small quantities compared with the irradiation at room temperature at a similar dose rate. A G.L.C. analysis showed the same products as previously identified but with a decrease in the proportion of products eluted after the dimer i.e. hexachloropropane, hexachlorobutane and higher boiling products. The ratio of these products to each other was, however, unaltered and their absolute amounts were approximately the same as in the room temperature irradiation.

The benzoyl peroxide reaction gave products in a similar ratio to that observed in the refluxing irradiation with, additionally, chlorobenzene, in about the same quantity as the 1,1,3,3-tetrachloropropene. There was, however, no evidence of any hexachloropropane formation here.

Estimation of Products.

An ampoule of 80 mls solution previously flushed with dry nitrogen and sealed was used for the estimation of products in the ambient temperature irradiation. For the refluxing irradiation the vessel was placed in a similar position and heated on an isomantle. After the irradiation at a dose rate of 1.41 x 10^{16} eV/ml/min for a total dose of 6.2 x 10^{19} eV/ml in both cases the volume was reduced to 10 mls and the G-values estimated.

For the benzoyl peroxide initiated reaction the volume was reduced to 50 mls and the molar quantities were measured.

All these values are listed in Table IV.

TABLE IV

Product	Room temperature		Reflux temperature		Bz_2O_2exp.[c]
	Moles x 10^{-4}	G	Moles x 10^{-4}	G	Moles x 10^{-3}
$CHCl_2 \cdot CHCl_2$	1.05	0.80	5.4	3.6	1.2
$CCl_2 = CH \cdot CHCl_2$	1.10	0.81	3.6	2.4	3.6
C_2Cl_6	0.60	0.41	-	-	-
$CHCl_2 \cdot CHClCH = CHCl_2$	3.60	2.46	30.0	20.4	10.5
$CCl_3 \cdot CHCl \cdot CHCl_2$	1.20	0.82	1.1	0.7	-
(liquid) $CHCl_2 \cdot CHCl \cdot CHCl \cdot CHCl_2$	0.80	0.50	-	-	-
$CHCl_2 \cdot CHCl \cdot CHCl \cdot CHCl_2$	0.60	0.40	-	-	-

Product identification (2) bromotrichloromethane- 1,2-dichloroethylene.

The mixture (100 mls) was irradiated for 7 days at a dose rate of approximately 2.5 x 10^{16} eV/ml/min; the refluxing irradiation was carried out at an equal dose rate for a period of 4 days.

No products more volatile than bromotrichloromethane were observed and the higher boiling products were examined after reduction of the volume by distillation. The solution obtained from the low temperature irradiation showed, by gas chromatographic examination, four major reaction products. On a 1 metre 25% S.E./C column at 55 mls hydrogen per minute the following retention times were recorded:-

(a) at 105°C,

Retention time - 4 minutes (1)

Retention time - 5½ minutes (2)

Retention time - 9 minutes (3)

(b) at 154°C,

Retention time - 2 minutes (3)

Retention time - 6 minutes (4)

Further examination on a 1 metre 25% P.E.G. ad/C column at 131°C caused resolution of peak (4) into two components (X) and (Y), the latter forming a tail to the major product (X). Examination of the solution from the refluxing irradiation and from the benzoyl peroxide experiment, on a silicone elastomer column showed that the same products were present (except for the absence of (3) in the benzoyl peroxide experiment) and no others could be detected. A similar result was obtained by examination on the P.E.G.ad/C column but, it was noted that the product (4) gave two definite peaks of about equal area.

Fractional distillation of the solution from the room temperature irradiation gave two main fractions: (a) containing products (1), (2) and (3), boiling range 50°-70°C/10 mm.; and (b) containing products (4) boiling point

50°-55°C/0.1 mm.

Complete separation of products (1), (2) and (3) was achieved by using the preparative scale gas chromatography unit. A 0.9 metre 25% S.E./C column at 100°C with a flow rate of 500 mls nitrogen per minute gave three peaks of retention times 35, 50 and 90 minutes respectively. The first of these was identified as 1,1,3,3-tetrachloropropene and the third as 1,2-dibromo-1,2-dichloroethane by comparison of their infrared spectra with those of authentic samples (see appendix for preparation). The other product in this fraction was suspected to be 1-bromo-1,2,2-trichloroethane and its infrared spectrum closely resembled that of <u>sym</u>-tetrachloroethane. Analysis gave C, 11.64; H, 1.28% required for $C_2H_2Cl_3Br$, C, 11.29; H, 0.94%.

The mixture of high boiling products (4) was distilled through a 9" Vigreux column under reduced pressure (0.1 mm.) and thus obtained free from other products. As noted previously this product consisted of a major component (X) and a minor component (Y) (about 5%). The infrared spectrum of the mixture exhibited characteristics very similar to those of the spectrum of 1,1,1,2,3,3-hexachloropropane and suggested the possible structure $CCl_3 \cdot CHCl \cdot CHClBr$. The isolated fractions corresponding to (4) from the benzoyl peroxide initiated reaction and from the refluxing irradiation, which contained equal quantities of (X) and (Y), gave identical spectra with very little difference from that produced in the room temperature irradiation. This result implies that the two compounds (4X)and (4Y) are in fact isomers of $C_3H_2Cl_5Br$; an elementary analysis of the product from the benzoyl peroxide experiment gave C, 12.76; H, 0.88% required for $C_3H_2Cl_5Br$, C, 12.18; H, 0.68%.

Two possibilities exist for (4X) and (4Y); either positional isomers of $C_3H_2Cl_5Br$ or diastereoisomers of $CCl_3 \cdot CHCl \cdot CHClBr$.

Considering the positional isomers attempts were made to synthesise the most/

most probable isomers, 1-bromo-1,2,3,3,3-pentachloropropane, 2-bromo-1,1,1,3,3-pentachloropropane and 1-bromo-1,1,2,3,3-pentachloropropane. The first of these was prepared by addition of chlorine to 1-bromo-3,3,3-trichloropropene (see appendix) and its retention time corresponded to the irradiation product (4X) on all the stationary phases used. However, attempts to prepare the other isomers were unsuccessful.

It was not possible to separate the products (4X) and (4Y) by preparative scale gas chromatography but by the injection of 10 μl. sample onto the 1 metre 25% P.E.G.ad/C column at 131°C (flow rate of 50 mls hydrogen per minute), it was found possible to condense the separated samples onto cooled sodium chloride plates for infrared investigation.

The infrared spectra of (4X) and (4Y) were found to be very similar and to differ only in the intensity of absorption at certain frequencies. The spectrum of the chemically prepared 1-bromo-1,2,3,3,3-pentachloropropane was identical in all respects with that of the product (4X) isolated from the irradiation at both temperatures and from the benzoyl peroxide initiated reaction. The product (4Y) was isolated but it showed no characteristic spectral features from which the structure could be assigned.

As the reaction progressed to 1,2-dichloroethylene depletion it was noticed that the ratio of the peak area of 1,1,3,3-tetrachloropropene to the peak area of 1-bromo-1,2,2-trichloroethane became significantly smaller. Comparison of reactions at low conversion of the dichloroethylene, however, gave a nearly 1:1 ratio of these products indicating that the phenomenon was a result of consumption of the propene in secondary reactions. No higher boiling product was isolated but such a product would probably decompose at the temperatures required for its identification by gas chromatography.

After irradiation, the solution had a slight brown colour similar to that produced by dilute solutions of bromine; this effect was most pronounced in the refluxing/

refluxing irradiation where, if irradiation was carried out towards dichloroethylene exhaustion, the solution had a distinct red-brown colour.

The disappearance of dichloroethylene was investigated and it was observed that the rate of disappearance of the trans- isomer was approximately four times that of the cis- isomer at room temperature. Isomerisation was not fully investigated but the isomerisation of the cis- to trans- isomer was noted to be rapid. A solution containing initially 2% trans- isomer after irradiation at a dose 4.95×10^{20} eV/Ml. gave a 1:1 mixture of cis- and trans- compounds. This is in comparison to a small percentage of isomerisation for the carbon tetrachloride- cis- 1,2-dichloroethylene.

Estimation of products.

The irradiation of 40 mls of the mixture in a 50 ml irradiation vessel, stoppered for the room temperature irradiation and fitted with a reflux condenser and calcium chloride drying tube for the refluxing irradiation gave a method of direct comparison as the vessel was maintained in an identical position for both temperatures. The dose rate was 11.5×10^{16} eV/ml/min. for a period of 24 hours; both samples were reduced to 10 mls for examination and the results are listed in Table V.

The 1,2-dichloroethylene uptake was estimated from the original volume on a 1 metre 25%S.E./C. column at 50°C and at room temperature the values were:

$G(-cis) = 7.57$; $G(-trans) = 25.46$

TABLE V

Product	Room temp. G-value	Reflux temp. G-value	Benzoyl peroxide ratio of products
$CCl_2 = CH \cdot CHCl_2$	1.72	22.51	1
$CHCl_2 \cdot CHClBr$.	1.93	23.02	1
$(CHCl\,Br)_2$	3.03	3.41	-
"$CCl_3 \cdot CHCl \cdot CHClBr$"	27.67	47.28	1.5

Discussion

The halomethanes irradiated with dichloroethylene were carbon betrachloride and bromotrichloromethane. The radiolytic breakdown of the latter compound may be represented mainly as,

$$\mathrm{Br\,CCl_3} \longrightarrow \mathrm{Br\cdot} + \mathrm{CCl_3\cdot} \qquad (1)$$

with the weaker carbon-bromine breaking[155]. The difference between the products from the halomethanes reflect the difference in the ease of free-radical displacement reaction at the carbon-bromine bond compared with the carbon-chlorine bond. In the carbon tetrachloride solution the major product fraction consisted of compounds incorporating two or more dichloro:ethylene molecules (including some polymer) whereas with the bromotrichloromethane there were no products incorporating more than one dichloroethylene molecule.

The refluxing irradiation and the peroxide-catalysed reaction at the same temperature gave very similar product analysis for both halomethane-1,2-dichloroethylene solutions. In the carbon tetrachloride solution the only difference resulting from the different methods of initiation was the production of 1,1,1,2,3,3-hexachloropropane in the irradiated solution and this hexachloropropane was also produced at room temperature in an almost equal amount. Therefore, by an analogy with the trichloroethylene solutions its formation may be assumed to occur via reactions (2a) and (2b).

$$\mathrm{CCl_3} + \mathrm{CHCl=CHCl} \rightarrow \underset{\mathrm{A^{111}}}{\mathrm{CCl_3\cdot CHCl\cdot CHCl\cdot}} \xrightarrow{\mathrm{Cl\cdot}} \mathrm{CCl_3\cdot CHCl\cdot CHCl_2} \qquad (2a)$$

$$\mathrm{Cl\cdot} + \mathrm{CHCl=CHCl} \rightarrow \underset{\mathrm{B^{111}}}{\mathrm{CHCl_2\cdot CHCl\cdot}} \xrightarrow{\mathrm{CCl_3\cdot}} \mathrm{CHCl_2\cdot CHCl\cdot CCl_3} \qquad (2b)$$

The unsaturated product expected from radical $\mathrm{A^{111}}$, after loss of a chlorine atom, would then be 1,3,3,3- tetrachloropropene:-

$$\mathrm{CCl_3\cdot CHCl\cdot CHCl\cdot} \longrightarrow \mathrm{CCl_3\cdot CH=CHCl} + \mathrm{Cl\cdot} \qquad (3)$$

However/

However only a possible trace of this compound was detected and the main unsaturated product isolated was 1,1,3,3-tetrachloropropene. This same compound was formed in the irradiation and the peroxide catalysed reactions of both halomethane solutions and its formation can be explained on the basis of a chlorine migration before a chlorine atom loss, either (a) a 1,3-migration or (b) one or two 1,2-shifts

$$\text{(a)}\quad \underset{(i)}{CCl_3\cdot CHCl\cdot CHCl\cdot} \rightarrow \underset{(ii)}{\cdot CCl_2\cdot CHCl\cdot CHCl_2} \rightarrow CCl_2 = CH\cdot CHCl_2 + Cl\cdot \qquad (4)$$

It is to be expected that the radical (ii) would be the more favoured form[99] and it is possible that the chlorine atom substituent on the trichloromethyl group is in close enough proximity for this migration to occur by a simultaneous bond-breaking and bond-forming process in a cyclic (four-membered) transition state. The alternative (b) requires one or two 1,2-chlorine migrations then involves the following intermediates, (ii) and (iii)

$$\begin{tikzcd}
\underset{(i)}{CCl_3\cdot CHCl\cdot CHCl\cdot} \arrow[r, "1{,}2\text{-shift}"] & \underset{(iii)}{CCl_3\cdot\dot{C}H\cdot CHCl_2} \arrow[d] \arrow[r, "1{,}2\text{-shift}"] & \underset{(ii)}{\cdot CCl_2\cdot CHCl\cdot CHCl_2} \arrow[dl] \\
 & CCl_2 = CH\cdot CHCl_2 + Cl\cdot &
\end{tikzcd} \quad (5)$$

The intermediate (iii) is not a favoured radical and certainly if formed would be expected to generate the intermediate (ii) which is the most favoured pentachloropropyl radical[99].

The possibility of two radical intermediates existing is found in the identification of two isomeric 1:1 addition products in the bromotrichloromethane solution. In the carbon tetrachloride solution further chlorine addition to the intermediates (i), (ii) or (iii) would give the same product (1,1,1,2,3,3-hexachloropropane) whereas the addition of bromine would be identical with the site of the unpaired electron of the radical precursor. Unfortunately, these two isomers could not be definitely assigned two of the possible structures. It would appear, however, that one of these isomers was 1-bromo-1,2,3,3,3-pentachloropropane since/

since it was identical with the chlorination product of 1-bromo-3,3,3-trichloropropene. This isomer was almost exclusively formed in the room temperature radiolysis (only 5% of the other isomer).

However the possibilities of these two compounds being diastereoisomers of $CCl_3 \cdot CHCl \cdot CHClBr$ cannot be ruled out as this compound has two asymmetric carbon atoms. The 1-bromo-3,3,3-trichloropropene may be entirely the trans-isomer and its chlorination via an ionic intermediate entirely trans to give only the meso form of 1-bromo-1,2,3,3,3-pentachloropropane, identical with the major product of the room temperature irradiation. It is possible that at the higher temperature the racemic form is more favoured. It was not possible to distinguishbetween the two possibilities of positional isomers or conformational isomers although it would be expected that the life-time of the intermediate radical would be sufficient for it to reach equilibrium among its confirmations before reaction with bromotrichloromethane even at the higher temperature[158]. This was in fact found to be the case for the hexachlorobutanes (see page 150) formed in the carbon tetrachloride solutions.

The halogen shifts, which are necessary to explain the 1,1,3,3-tetrachloropropene, can be considered as taking place either by a carbon-chlorine bond fission followed by a carbon-chlorine bond formation at the adjacent carbon atom or else by a direct transfer via some bridged intermediate whereby the chlorine atom is never a free entity. There are several arguments against the former mechanism being operative in related instances of halogen migration. For example, in the addition of mercaptans to 3,3,3-trichloropropene,[99] a rearranged 1:1 adduct is the major product and if the rearrangement occurred via a bond-breaking, bond-forming reaction, Walling[157] suggests that a free chlorine atom would be expected to react with the mercaptan preferentially:-

$$RSH + Cl\cdot \longrightarrow RS\cdot + HCl \qquad (6)$$

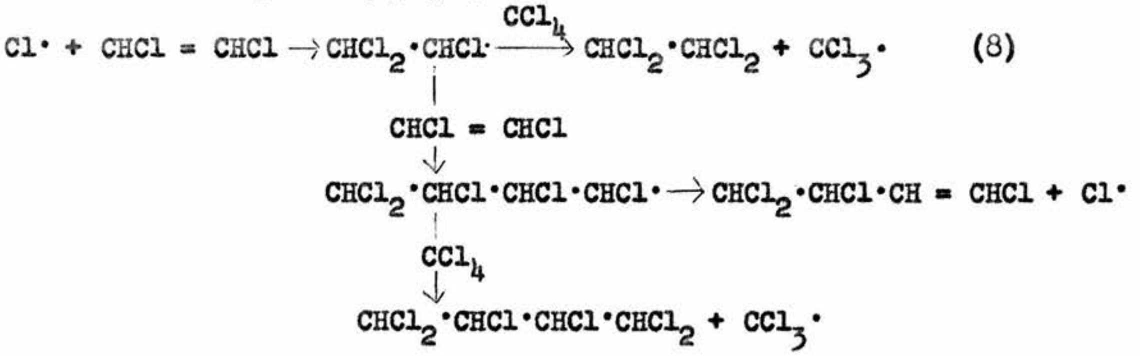
In the reaction between diazomethane and carbon tetrachloride, the structure of the/

the main product indicates that a halogen migration has taken place[156] and, if it had occurred by way of a free chlorine atom, then the reaction products would be expected to resemble those from the carbon tetrabromide-diazomethane reaction where a free bromine atom is produced. This difference in the carbon tetrachloride-diazomethane mixture, along with the apparently clear-cut mechanism, appears to favour a bridged intermediate. In the present work, if the migration process occurred by a bond-breaking-readdition mechanism the following reaction would be the first stage in the rearrangement:-

$$\mathrm{CCl_3\cdot CHCl\cdot CHCl\cdot \longrightarrow CCl_3\cdot CH = CHCl + Cl\cdot} \qquad (7)$$

Now the 1,3,3,3-tetrachloropropene is known, from the work on the irradiation of acetylene-carbon tetrachloride mixture, to isomerise to 1,1,3,3-tetrachloropropene under the influence of chlorine atoms but not at a rate sifficient to explain the complete isomerisation in all the halomethane-dichloroethylene mixtures. These results would then seem to favour the bridge type of intermediate, as suggested by Walling[157].

The other products identified in the solution can be explained by halogen atom attack on the dichloroethylene. For carbon tetrachloride this only involves chlorine atoms and the products identified, tetrachloroethane, dimer and higher telomer and 1,1,2,3,4,4-hexachlorobutane are consistent with the reaction sequence (8)-(10)



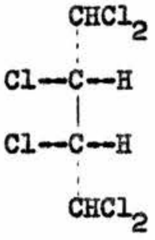
$$\begin{tikzcd}
\mathrm{Cl\cdot + CHCl = CHCl} \arrow[r] & \mathrm{CHCl_2\cdot CHCl\cdot} \arrow[r, "\mathrm{CCl_4}"] \arrow[d, "\mathrm{CHCl = CHCl}"] & \mathrm{CHCl_2\cdot CHCl_2 + CCl_3\cdot} & (8) \\
& \mathrm{CHCl_2\cdot CHCl\cdot CHCl\cdot CHCl\cdot} \arrow[r] \arrow[d, "\mathrm{CCl_4}"] & \mathrm{CHCl_2\cdot CHCl\cdot CH = CHCl + Cl\cdot} & (9) \\
& \mathrm{CHCl_2\cdot CHCl\cdot CHCl\cdot CHCl_2 + CCl_3\cdot} & & (10)
\end{tikzcd}$$

Trimer and higher polymers are then produced by reactions similar to (9). The dimer formed by reaction (9) is present as both *cis-* and *trans-* isomers[154] and the 1,1,2,3,4,4-hexachlorobutane was also isolated in two forms (a white crystalline/

crystalline solid and a clear liquid). These two products appear in the irradiations at both temperatures in equal G-values and also appear in the peroxide catalysed reaction in approximately the same proportion, relative to the dimer, as in the refluxing irradiation. This would explain their production via reaction (10) and not necessarily by a radical-radical combination (11)

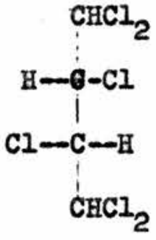
$$CHCl_2\cdot CHCl\cdot CHCl\cdot CHCl\cdot + Cl\cdot \rightarrow CHCl_2\cdot CHCl\cdot CHCl\cdot CHCl_2 \qquad (11)$$

The two isomers are evidently the <u>meso</u> and <u>racemic</u> forms since the product contains two similar asymmetric carbon atoms



$$\begin{array}{c} CHCl_2 \\ Cl-C-H \\ | \\ Cl-C-H \\ CHCl_2 \end{array}$$

meso



$$\begin{array}{c} CHCl_2 \\ H-C-Cl \\ | \\ Cl-C-H \\ CHCl_2 \end{array}$$

($\pm$) or racemic

In the bromotrichloromethane solution there are two different halogen atoms to be considered i.e. a chlorine atom from reaction (4) and a bromine atom from reaction (1). These atoms will attack the dichloroethylene double bond to give 1,2,2-trichloroethyl or 2-bromo-1,2-dichloroethyl radicals respectively which will both disappear by bromine abstraction to give 1-bromo-1,2,2-trichloroethane and 1,2-dibromo-1,2-dichloroethane, respectively. The production of the formed is equal to the tetrachloropropene value and indicates that all chlorine atoms disappear by reaction with dichloroethylene.

In the bromine atom attack on 1,2-dichloroethylene the reverse reaction is more important than for chlorine and this explains the much higher degree of isomerisation found in this solution compared with the carbon tetrachloride solution. The near independence on temperature of the dibromodichloroethane does not, therefore, necessarily mean that the reactions leading to its formation have zero activation energies. Other factors influencing its production are

the/

the difference, if any, in rates of decomposition of the bromotrichloroethyl radical at different temperatures and the varied availability of bromine atoms. This latter factor is dependent on the suppression of the back reaction (12)

$$Br\cdot + CCl_3\cdot \longrightarrow BrCCl_3 \qquad (12)$$

which, it was suggested, decreases in importance at the higher temperatures for the trichloroethylene-halomethane systems. Some of the bromine atoms must also disappear either by combination with each other or abstraction from bromotrichloromethane to give molecular bromine which was observed, especially in the high temperature irradiation. This then introduces the possibility of heterolytic bromine addition to the dichloroethylene as a source of the dibromodichloroethane.

The two solutions, bromotrichloromethane-dichloroethylene and carbon tetrachloride-dichloroethylene, in general exhibit the classical free radical reactions and furnish very little information regarding reactions peculiar to the radiolysis. This is especially true of the bromotrichloromethane solution where the ease of bromine abstraction gives rise to long radical chain processes which mask the minor radiolytic processes other than the actual breakdown of the halomethane itself by reaction (1).

APPENDIX TO SECTION III

Preparation of sym-heptachloropropane.[135]

$$CHCl = CCl_2 + CCl_4 \xrightarrow{AlCl_3} CCl_3{\cdot}CHCl{\cdot}CCl_3.$$

Trichloroethylene (33 ml.), carbon tetrachloride (80 ml) and crushed anhydrous aluminium chloride (5 gm) were stirred mechanically in a 500 ml. flask for 48 hours at 20°-30°C. The reaction mixture was poured onto ice, shaken, and the organic layer separated off. After several washings with water the organic layer was dried over calcium chloride and the unreacted materials distilled off. Fractionation under reduced pressure gave the sym-heptachloropropane 126°-132°C/20 mm. Yield 15 gm.

Attempted dechlorination of the above product to form 1,1,3,3,3-pentachloroprop-1-ene.

$$CCl_3{\cdot}CHCl{\cdot}CCl_3 \xrightarrow{Zn} CCl_2 = CHCCl_3$$

Following the method of Whilmore and Homeyer[136], zinc dust (3 gm) and 95% ethanol (15 ml.) were brought to the reflux temperature in a three-neck flask fitted with a condenser, dropping funnel and stirrer. To the refluxing mixture sym-heptachloropropane (10 gm) was added over a period of 45 minutes.

Removal of zinc by filtration and distillation of the ethanol left a heavy organic residue. Examination of this residue by G.L.C. revealed a main product higher boiling than the expected pentachloropropene and no product corresponding to the expected retention time of 1,1,3,3,3-pentachloropropene.

Trichloroacetyl peroxide initiated reaction of carbon tetrachloride with trichloroethylene.

To a solution of sodium chloride (20 g) in distilled water (100 ml) cooled to -20°C in an alcohol-water-cardice mixture, sodium peroxide (4.7 g) and trichloroacetyl chloride (18 g)(previously cooled to -15°C) were added. The mixture was stirred for 1 hour at -10° to - 15°C and a flocculent precipitate of trichloroacetyl peroxide was produced (ca. 60% yield). This was/

was extracted into carbon tetrachloride (200 ml) and dried over molecular sieve in a cold box. The molecular sieve was filtered off and trichloroethylene (20 ml) was added. The mixture was left at room temperature for two days and the products identified as stated previously (page 108) by gas chromatography.

Attempted preparation of 1,1,3,3,3-pentachloroprop-1-ene.

The production of this pentachloropropene was envisaged by the following sequence of reactions involving the use of triphenyl phosphine in carbon tetrachloride as a source of dichloromethylenetriphenylphosphorane[137]

$$CCl_4 + 2(C_6H_5)_3P \longrightarrow \underset{\text{I}}{(C_6H_5)_3\cdot PCl_2} + \underset{\text{II}}{(C_6H_5)_3P = CCl_2}$$

Subsequent reaction of I and II with chloral would then be expected to yield pentachloroethane and the required pentachloropropene.

$$\text{I} + CCl_3\cdot CHO \longrightarrow CCl_3\cdot CHCl_2 + (C_6H_5)_3PO$$

$$\text{II} + CCl_3\cdot CHO \longrightarrow CCl_3\cdot CH = CCl_2 + (C_6H_5)_3PO$$

Triphenyl phosphine (40 gm) and carbon tetrachloride (90 ml) were left to react overnight. Chloral (30 ml) was then added to this solution from a dropping funnel. The addition of chloral tended to cause heating and after all the chloral had been added a gelatinous precipitate had formed. The reaction mixture was treated with petrol-ether (60-80) and the precipitate filtered off. Reduction of the volume and examination by G.L.C. indicated a series of products of longer retention time, on a silicone elastomer column, than the irradiation product suspected to be 1,1,3,3,3-pentachloroprop-1-ene.

Preparation of 1,1,2,3-tetrachloropropane[138].

$$CH_2Cl_2 + CHCl = CHCl \xrightarrow{AlCl_3} CHCl_2\cdot CHCl\cdot CH_2Cl.$$

Dichloromethane (100 ml), 1,2-dichloroethylene (60 ml) and finely ground anhydrous/

anhydrous aluminium chloride (10 g) were stirred at room temperature for 48 hours. The solution was then poured onto ice water and the organic layer was washed and dried over calcium chloride. The unreacted material was distilled off at atmospheric pressure and fractionation at reduced pressure yielded the product boiling 76°C/14 mm.

Refractive index $n_D^{20} = 1.5000$

Lit. value for $CHCl_2 \cdot CHCl\ CH_2Cl$ $n_D^{20} = 1.5037$.

Preparation of 1,1,1,2,3-pentachloropropane.

The following sequence of reactions should yield the 1,1,1,2,3-pentachloropropane.

$$CH_2 = CH_2 + CCl_4 \longrightarrow CCl_3 \cdot CH_2 \cdot CH_2Cl \qquad (1)$$

$$CCl_3 \cdot CH_2 \cdot CH_2Cl \xrightarrow{-HCl} CCl_3 \cdot CH = CH_2 \qquad (2)$$

$$CCl_2 = CH \cdot CH_2Cl \xrightarrow{Cl_2} CCl_3 \cdot CHCl \cdot CH_2Cl \qquad (3)$$

Addition of carbon tetrachloride to ethylene-reaction (1)

The reaction was based on the method used by Joyce et al[139] inthe benzoyl peroxide initiated reaction but cobalt-60 gamma rays were used to initiate the chain reaction. The expected path of the reaction is:-

$$CCl_4 \rightsquigarrow CCl_3\cdot + Cl\cdot \qquad (1a)$$

$$CCl_3\cdot + CH_2 = CH_2 \rightarrow CCl_3 \cdot CH_2 \cdot CH_2\cdot \qquad (1b)$$

$$CCl_3 \cdot CH_2 \cdot CH_2\cdot + CCl_4 \rightarrow CCl_3 \cdot CH_2CH_2Cl + CCl_3\cdot \qquad (1c)$$

$$CCl_3 \cdot CH_2 \cdot CH_2 + CH_2 = CH_2 \rightarrow CCl_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2\cdot \qquad (1d)$$

$$CCl_3 \cdot (CH_2)_4\cdot + CCl_4 \rightarrow CCl_3 \cdot (CH_2)_4\ Cl + CCl_3\cdot \qquad (1e)$$

The competitive reactions (1c) and(1d) have been shown to depend on the ethylene concentration with reaction (1c) predominating at low concentrations.

In the present work, carbon tetrachloride, (2 1) was saturated with ethylene at atmospheric pressure and the saturation was maintained by having a steady flow of ethylene (10 mls/min) through the irradiation vessel. The

irradiation/

irradiation was carried out at an unmeasured dose rate and the reaction followed by testing samples on G.L.C. Only two products were observed and these could be separated by fractional distillation.

First fraction B.pt. = 62°C/30 mm.

Second fraction B.pt. = 96°-98°C/12mm.

These were concluded to be 1,1,1,3-tetrachloropropane and 1,1,1,5-pentachloro:propane respectively.

n_D^{20} = 1.4823 for first fraction. Lit.[139] for 1,1,1,3-tetrachloropropane = 1.4825

n_D^{20} = 1.4860 for second fraction Lit.[139] for 1,1,1,5-tetrachloropentane = 1.4859

In the above experiment the ratio of tetrachloropropane to tetrachloropentane was found to be 4:1. Another experiment conducted in a similar fashion with the carbon tetrachloride at its boiling point (78°C) produced the tetrachloropropane exclusively with a small percentage of hexachloroethane as the only other product.

<u>Dehydrochlorination of the tetrachloropropane</u>-reaction (2)

Dehydrochlorination was carried out with alcoholic potassium hydroxide as described by Nesmeyanov[140].

$$CCl_3 \cdot CH_2 \cdot CH_2\, Cl \xrightarrow{\text{Alc. KOH}} CCl_3 \cdot CH = CH_2$$

Potassium hydroxide (68 gm) was dissolved in absolute alcohol (240 ml) and this solution was added dropwise to vigorously stirred 1,1,1,3-tetrachloropropane (170 g). The reaction temperature was maintained at 25°C by controlled addition and occasional cooling. When all the alcoholic solution had been added the reaction mixture was added to twice its volume of water and the non-aqueous layer separated and dried over calcium chloride. Distillation yielded a product boiling 62°C/240 mm. The infrared spectrum indicated unsaturation and the refractive index corresponded to the literature value for 3,3,3-trichloroprop-1-ene

Found n_D^{20} = 1.4682 Literature[140] for 3,3,3-trichloropropene = 1.4680

Chlorination/

Chlorination of 3,3,3-trichloropropene - reaction (3)

$$CCl_3{\cdot}CH = CH_2 \xrightarrow{Cl_2} CCl_3{\cdot}CHCl{\cdot}CH_2Cl$$

Chlorine was passed into carbon tetrachloride (75 ml) until the gain in weight corresponded to 12 gm. The 3,3,3-trichloroprop-1-ene (30 gm) was then addedto this solution and left in the sunlight. Monitoring the reaction mixture by G.L.C. indicated a rapid chlorination, and distillation gave an 80% yield of product.

boiling point 65°-66°C/4mm.

Found $n_D^{20} = 1.5097$

Literature for 1,1,1,2,3-pentachloropropane $n_D^{20} = 1.5105$.

Action of anhydrous aluminium chloride on 3,3,3-trichloropropene.

$$CCl_3{\cdot}CH = CH_2 \xrightarrow{AlCl_3} CCl_2 = CH{\cdot}CH_2Cl$$

This reaction was used to prepare a sample of 1,1,2-trichloroprop-1-ene. The conversion was readily brought about at room temperature with catalytic quantities of the aluminium chloride.

Preparation of 1,1,2,2,3-pentachloropropane.

$$CH_2Cl{\cdot}CO{\cdot}CH_2Cl + PCl_5 \longrightarrow CH_2Cl{\cdot}CCl_2{\cdot}CH_2Cl + POCl_3$$

$$CH_2Cl{\cdot}CCl_2{\cdot}CH_2Cl \xrightarrow[KOH]{alc} CHCl = CCl{\cdot}CH_2Cl$$

$$CH_2Cl{\cdot}CCl = CHCl \xrightarrow{Cl_2} CH_2Cl{\cdot}CCl_2{\cdot}CHCl_2$$

Sym- dichloroacetone was dissolved in ether (600 ml) and the solution was added dropwise to phosphorus pentachloride (144 gm). The mixture was stirred continuously during addition, and further for a total period of 24 hours with the temperature maintained at 0°C. The ethereal solution was shaken with its own volume of water twice and then dried over calcium chloride. After removal of the ether the resulting organic compound (50 gm) was added to a solution of potassium/

potassium hydroxide (12.5 gm) in absolute alcohol (75 ml). This mixture was stirred at 25°C for 6 hours, poured into water (100 ml) and the separated organic layer extracted with water (2 x 50 ml) to remove any alcohol before finally drying over calcium chloride.

Chlorination

The above product (20 gm) was chlorinated without further purification, the chlorination being as described for the 3,3,3-trichloropropene. Distillation gave a product boiling 64°-66°C/4mm. with no unsaturation in the infrared spectrum.

Found $n_D^{20} = 1.5119$

Literature[141] for 1,1,2,2,3-pentachloropropane $n_D^{20} = 1.5122$

Preparation of 1,2-dibromo- 1,2-dichloroethane[142].

$$CHCl = CHCl + Br_2 \qquad CHClBr \cdot CHClBr$$

Bromine was added slowly at room temperature to a mixture of cis- and trans- dichloroethylene. Distillation gave a product boiling point 70°-72°C/10mm.

Found $n_D^{20} = 1.5669$

Literature[142] for 1,2-dibromo- 1,2-dichloroethane $n_D^{20} = 1.5672$.

Preparation of 1-bromo-1,2,3,3,3-pentachloropropane.

1-Bromo-3,3,3-trichloroprop-1-ene was prepared by the method of Heiba and Anderson[103] and the subsequent chlorination of this yielded the desired product

$$BrCCl_3 \rightsquigarrow Br\cdot + CCl_3\cdot$$

$$CCl_3\cdot + CHBr = CHBr \longrightarrow CCl_3\cdot CH = CHBr + Br\cdot$$

$$CCl_3\cdot CH = CHBr + Cl_2 \longrightarrow CCl_3\cdot CHCl\cdot CHClBr$$

1,2-Dibromoethylene (40 gm) and bromotrichloromethane (350 gm) were irradiated in a sealed vessel at an unmeasured dose rate. Inspection of the resultant irradiated solution by G.L.C. showed the main peaks corresponding to the expected products/

products, 1-bromo-3,3,3-trichloropropene and the high boiling product, sym- tetrabromoethane. After removal of the unreacted bromotrichloromethane the products were subjected to a reduced pressure fractional distillation using a 9" Vigreux column. The fraction boiling 70°-80°C/25mm. was collected and subjected to a further distillation. This second distillation gave a major fraction distilling at 74°-75°C/25mm. and a G.L.C. test indicated only one major compound which was used in the second stage without further purification.

Chlorination.

1-Bromo-3,3,3-trichloropropene (5 gm) was added to carbon tetrachloride (50 mls) saturated with chlorine. The mixture was irradiated by an incandescent lamp for fifteen minutes. The green colour of chlorine did not completely disappear but examination by G.L.C. showed the near complete removal of the bromotrichloropropene with the appearance of one new compound of longer retention time. Distillation yielded the product boiling point = 50°C/0.1mm. with a G.L.C. retention time identical with the 1:1 addition product of bromotrichloromethane-dichloroethylene formed in the greatest amount in the room temperature irradiation; the infrared spectrum was also identical with the stated addition product.

Attempted preparation of other Bromopentachloropropanes

Using the anhydrous aluminium halides as catalysts it was hoped to add a suitable halomethane to a chloroethylene to give the required compound. Two routes were investigated

(a) $CHCl = CHCl + CHCl_3 \xrightarrow{AlBr_3} CHCl_2 \cdot CHCl \cdot CCl_2Br$

(b) $CHCl = CHCl + BrCCl_3 \xrightarrow{AlCl_3} CCl_2Br \cdot CHCl \cdot CHCl_2$

The conditions for both experiments were similar to those used in the preparation of sym-heptachloropropane (page 153) The results of both experiments indicated a very small conversion by the above routes with the major product in (a) being asym-hexachloropropane and in (b) lower boiling unsaturated compounds. Investigation of the products formed, of similar retention times by G.L.C. to the 1:1 adducts of bromotrichloromethane and dichloroethylene, indicated a mixture of compounds in both (a) and (b).

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