IRRADIATION OF ORGANIC SYSTEMS WITH GAMMA RAYS

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TO

MY PARENTS

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INTRODUCTION.

The announcement by Roentgen in 1895 of the discovery of the so-called X- or Roentgen rays marked the beginning of a new era in the progress of science. Almost immediately it led to the discovery by Becquerel of penetrating radiation from the uranium mineral, pitchblende. This was followed two years later by the discovery of radium and polonium by the Curies, and subsequently by the rapid development of the subject of radioactivity by Rutherford, Soddy and many others, leading to the discovery of uranium fission in 1938.

Radiation chemistry is a rapidly expanding branch of chemistry, the development being due in part to the post-war availability and development of powerful radiation sources and in part to its many applications to problems in chemical, medical and industrial fields. Radiation chemistry is the study of the chemical effects produced in other compounds by high energy particles and radiations, including both radioactive emanations and the energetic particles of high voltage instruments and nuclear reactors; radiochemistry is the study of the radioactive elements themselves. The two subjects are therefore quite different but the former is largely dependent on the latter for its sources of energy.

The most commonly used ionising radiations are the very short wavelength electromagnetic radiations, gamma and X-rays, and the corpuscular radiations, electrons (beta rays), helium

nuclei (alpha rays), protons, neutrons and deuterons. Alpha, beta and gamma rays, neutrons and fission fragments are the natural emissions of radioactive decay while highly accelerated protons, deuterons, helium nuclei, fast electrons and X-rays can be artificially produced when required.

It is primarily due to the advance of nuclear technology in the past 15 years that radio-isotopes of many elements are available in sufficient quantity for application to chemical, medical and industrial research. They are produced either by isolation and subsequent purification from the waste products of atomic piles or are specially "tailored" by a radiochemical laboratory to meet specified requirements.

The uses of isotopes are many and varied. In the sphere of chemistry itself, the stable isotopes, deuterium and oxygen-18 and the beta-emitting isotopes, tritium, carbon-14, chlorine-36, etc., are used to yield information on reaction mechanisms; the beta-emitting isotopes, carbon-14, phosphorus-32 and sulphur-35 and nitrogen-15 (stable), afford insight into the metabolic processes of plants and living organisms. Radioactive iodine (I-131), phosphorus-32, caesium-137 (gamma emitter) are extensively used in medicine while iron-55 is used as a tracer to study frictional wear of metal surfaces. The electron-emitting isotope strontium-90 is employed in thickness gauges and cobalt-60 is widely used to radiograph metal castings for

detection of defects deep in the metal structure, the gamma rays possessing the required penetration.

Cobalt-60, the radiation source used in the work to be described in this thesis, is one of the more frequently used radio-isotopes in the study of the effects of ionising radiation on chemical systems. This isotope has a half-life of 5.3 years, emits gamma rays of energy 1.17 and 1.33 MeV[I] and beta rays of 0.31 MeV, but as the latter have little power of penetration, their effect can generally be ignored. The fact that the gamma rays are practically monoenergetic, is one important difference between the two types of photon radiation, since X-rays are usually produced with a range of energies. This arises because X-rays are extranuclear in origin, being produced in an X-ray tube by the rapid deceleration of electrons, which may be monoenergetic themselves, but as a large number of electronic transitions are usually involved, the resulting X-rays possess a range of energies. On the other hand, gamma rays are emitted from the nucleus and have very precise energy determined by the upper and lower states between which nuclear transitions occur. Cobalt-60, which is produced by the slow neutron bombardment of ordinary cobalt in an atomic pile, $^{59}Co(n,\gamma)^{60}Co$, has a higher neutron/proton ratio than is consistent with nuclear stability, and in an attempt to regain stability, ejection of a beta particle (electron) from the nucleus occurs, thereby lowering the ratio of neutrons to protons. This transformation, however,

leaves the nucleus in an excited state and resultant emission of gamma ray photons allows the daughter nucleus to return to the ground state, i.e.

$$^{60}_{27}Co \rightarrow {}^{60}_{28}Ni + {}^{0}_{-1}\beta + 2\gamma$$

Gamma rays are radiations of the same character as ultraviolet or visible light but of very much shorter wavelength and consequently the energy of their quanta is very much greater. Whereas in Photochemistry, only certain molecules may absorb photons of particular energy directly as the primary process, all molecules are susceptible to the effects of high energy radiation; however, the reactions induced by such radiation can be as specific as most chemical reactions because the initial energy is rapidly degraded and most of the chemical changes are brought about by the action of electrons of energy of 100eV or less. Many of the effects produced by such radiations are like those produced by the less energetic radiations of UV or visible light but the primary ionisation reaction of radiation chemistry and the production of fast electrons, produce chemical effects essentially different from those in photochemical reactions. Thus there are both differences and similarities between Photochemistry and Radiation Chemistry.

<u>The Interaction of Radiation with Matter.</u>

The absorption of high energy radiation by matter can occur by five processes.[2-5]

The most important process of energy absorption for the ^{60}Co γ-rays (1.17 and 1.33 MeV) is Compton Scattering. In Compton Scattering, photons, of energy range 0.5 to ca. 10 MeV, lose part of their energy by ejecting electrons from atoms; the deflected photons, now of reduced energy and longer wavelength, interact further by Compton Scattering or by photo-electric absorption, whilst the ejected electrons cause ionisation or excitation. This mode of energy absorption is the main process for materials of low atomic weight and depends on the electron density of the medium.

An important process at energies below 0.2 MeV is Photo-electric absorption in which the energy of the photon is used to eject a bound electron from an atom or molecule with a kinetic energy equal to that of the incident photon minus the binding energy of the electron. The atom is left in an excited state and regains the ground state by electron rearrangement and emission of X-rays characteristic of the atom involved. This effect is more important for elements of high atomic number; for example, the contribution to total energy absorption in the case of alkyl iodides is greater than in alkyl chlorides.

Pair production does not assume importance as a means of energy absorption until the energy of the incident photon is greater than 1.02 MeV and has little effect until very much higher energies are reached (50-100 MeV).

This effect involves the formation of a positron-electron pair by a photon of energy at least 1.02 MeV (equivalent to the rest masses of the two particles) whilst passing through the electric field of the nucleus. The electron and positron produced lose their energy by causing ionisation and excitation, the positron eventually combining with an electron, yielding two gamma ray photons, each of energy 0.51 MeV, travelling in opposite directions.

Two other processes of minor importance are

(a) Coherent Scattering, which occurs with low energy radiations, is the basis of X-ray crystallography but is unimportant in Radiation Chemistry because insufficient energy is transferred to the system to cause chemical change.

(b) Nuclear Disintegration occurs only with energies greater than 10 MeV, and is caused by the photon penetrating the nucleus, causing some neutron emission of short half-life.

Therefore it can be seen that, irrespective of the mode of primary interaction of gamma rays with matter, the result is the production of fast electrons within the system. These electrons are highly energetic, possessing in many cases nearly all the energy of the incident photon. Since chemical reaction requires only a few electron-volts per molecule for initiation, fast electrons are capable of activating a vast number of molecules. It is therefore not the initial act of the gamma ray that is directly responsible

for the chemical changes observed but rather the ejected fast electrons causing excitation and ionisation along their tracks. They interact with the outer electrons of atoms in molecules in a random manner, causing either excitation to a higher energy level or ejection to form positive ions. Some of these ejected electrons may have sufficient energy to cause further ionisation, etc., and are called Secondary electrons but as their kinetic energy becomes less (ca. 100 eV), they are termed "delta" rays. Finally, clusters of ions are produced by slow electrons (10 eV) in the immediate vicinity of the parent ion.

Excited molecules are either produced as described above or by recombination of positive ions with electrons, which is an important reaction in the liquid phase. The excitation is of the whole molecule and in large molecules, the point of subsequent reaction may be divorced from the site of energy absorption.

Excited molecules can dissociate into free radicals or yield molecular products by unimolecular decomposition. Generally, most of the chemical effects observed result from the formation of free radicals which may combine with one another or react with other molecules. Not all excited molecules yield free radicals; fluorescence, collisional deactivation and energy transfer being other methods of energy dissipation; similarly, positive ions can undergo dissociation, e.g.,

$$C_2H_6^+ \rightarrow C_2H_5^+ + H^\cdot$$

or enter into reactions with neutral molecules resulting in processes such as hydride ion transfer,

$$C_2H_5^+ + C_mH_n \longrightarrow C_2H_6 + C_mH_{n-1}^+$$

or carbon-carbon bond formation,

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

These ion-molecule reactions are very rapid and modern work has shown the importance of such mechanisms in the liquid phase [6,7], as well as in the gas phase,[8] where the ejected electron may escape more easily from the field of the positive ion.

G-values.

Quantitative results in Radiation chemistry are expressed in terms of G-values which refer to the number of molecules, either formed or decomposed, for every 100 eV of energy absorbed by the chemical system. Normally, G-values range between 0.05 to about 4, unless a chain reaction is involved when values may rise to tens of thousands. G-values are expressed thus, $G_{(C_2Cl_6)}$ or $G_{(-CCl_4)}$, indicating the yield of hexachloroethane produced while the negative sign in the subscript denotes destruction of carbon tetrachloride. It is therefore necessary to know the quantity of energy absorbed by a system and this is determined by the use of a dosimeter.

Dosimetry.

The units used in this work to measure absorbed dose are the Electron-volt (eV) and the Roentgen (r). The rate of energy

absorption, or dose rate, can be expressed either in roentgens or electron-volts per unit volume of absorbing medium per unit time i.e., r/ml/min or eV/ml/min. The roentgen is defined for gamma radiation as the radiation unit from which one ml. of water absorbs 0.98 rad,[9] the rad being equivalent to the absorption of 100 ergs/gm. Thus the roentgen equals 98 ergs/ml and since 1 eV = 1.602×10^{-12} ergs, 1 r = $98/1.602 \times 10^{-12}$ eV/ml.

Owing to the involved techniques of the physical measurement of absorbed energy, it has become standard practice in radiation chemistry to use, for dose-rate determination, a radiation-induced chemical reaction whose dependence on dose has been studied. An ideal chemical dosimeter should be easy to prepare and stable indefinitely under ordinary storage conditions. The concentration of radiolytic product should be proportional to radiation dose, independent of dose rate, radiation energy and temperature, nor should there be any post-irradiation change in the concentration of the product. The method of analysis should be simple and accurate throughout the range of product concentration corresponding to the dose range of the dosimeter.

The most frequently used and satisfactory chemical dosimeter is that based on the oxidation of aerated aqueous solutions of M/1000ferrous sulphate, 0.5 to 1.0 $\bar{N}$ with respect to sulphuric acid.[10,11] The chemical yield of this oxidation reaction has been accurately measured by spectrophotometric

methods, and the energy input has been measured by calorimetry[12,13] and ionisation chamber methods.[14] The results are in good agreement with a value of 15.5 ± 0.2 ferric ions produced per 100 eV absorbed in this system,[11] i.e., $G_{(Fe^{3+})} = 15.5 \pm 0.2$.

The ferrous sulphate or Fricke dosimeter has disadvantages under certain conditions. For total doses of less than 2,000 r, it is not sufficiently sensitive, while at doses greater than 50,000 r, air saturated solutions become depleted of oxygen in a closed system and the ferric yield falls. Organic impurities increase the value of $G_{(Fe^{3+})}$ even if present only in small amounts,[15] and care must be exercised to exclude organic material by the use of highly purified water ("triple-distilled water") or to inhibit production of organic peroxides, which subsequently cause oxidation of three ferrous ions per initial hydroxyl radical instead of one. This can be achieved by addition of chloride ions[15] in sufficient quantity to react with all free hydroxyl radicals produced by irradiation and yield an equivalent number of chlorine atoms, which are much less reactive towards organic molecules, but which will oxidise an equal number of ferrous ions. The stabilising effect of added chloride on ferrous sulphate solutions saturated with benzene used for dosimetry purposes has recently been demonstrated by Burton.[16]

Balkwell and Adams[17] describe a modification of the Fricke dosimeter which renders it four times more sensitive, combined with a slower auto-oxidation rate. The solution, which contains

1.32×10^{-3} M benzoic acid and 9.26×10^{-4} M ferrous ion in 1.0 $\bar{N}$ sulphuric acid, is claimed to be stable over a period of years, during which it shows no change in sensitivity or linearity of response.

Some physical changes, notably the colouration of certain glasses[18] or rigid polyvinyl films,[19] have also been considered as dosimeters, as well as many chemical reactions.[20-22] Recently techniques such as densitometry[23] and spectrophotofluorometry[24-25] have been applied to the measurement of high and low doses respectively and the gas chromatographic measurement of the hydrogen yield from methane has been used as a dosimeter[26] for gas phase irradiations.

In the present work, all dose rate determinations were carried out using the Fricke dosimeter. As has already been mentioned, absorption of energy from ^{60}Co gamma radiation takes place predominantly by Compton scattering. The energy absorption by any given system will, therefore, be proportional to its electron concentration and, consequently, a correction must be made for this when comparing the energy absorbed by a system with that absorbed by the ferrous sulphate solution under identical conditions.

The energy absorbed per unit volume (E ergs/cm^3) is related to the flux of radiation (I ergs/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. As this latter function is a constant for radiation of a given frequency and the geometry of the experimental and dose rate systems is identical, the ratio of the electron densities gives the ratio of energy absorption by the two systems.

Therefore:-

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

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

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

M = the molecular weight of the liquid,

N = Avogadro's Number

and $\sum Z$ = sum of the atomic numbers of each of the atoms in the molecule.

If two compounds, a and b, are irradiated in solution, the contribution to the electron density of the solution by the solute must be taken into account by the general equation:-

$$N_e(\text{sol.}) = \frac{V_a}{(V_a + V_b)} \cdot \frac{d_a}{(MW)_a} \cdot N \cdot \sum Z_a \cdot + \frac{V_a}{(V_a+V_b)} \cdot \frac{d_b}{(MW)_b} \cdot N \cdot \sum Z_b \cdot$$

where $\frac{V_a}{(V_a+V_b)}$ = the volume fraction of a in the solution.

The electron density of the ferrous solution is obtained by treating it as pure water with a density of 1.023 gms/cc.,

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

$$N_e \text{ (ferrous solution)} = 0.5675 \times N.$$

Experimental Determination of Dose Rate.

The reagents required for preparation of the ferrous sulphate dosimeter are:

(1) Analar Ferrous Ammonium Sulphate.

(2) Analar Sulphuric Acid.

(3) Pure water, free from organic impurities.

The water was purified by subjecting tap-water to a three-stage distillation process i.e., the water was distilled from an acid potassium dichromate solution, then from potassium carbonate solution and finally redistilled without any reagent present. The distillation apparatus was made of Pyrex glass throughout and the distilled water was stored in a silica glass vessel.

All Pyrex glass apparatus used in dosimetry and other radiation work was thoroughly cleaned in chromic acid, hot water, distilled water and finally triple-distilled water before being flame-dried on a vacuum line.

Solutions of M/1000 ferrous ammonium sulphate in 0.8$\bar{N}$ sulphuric acid were prepared with the pure water. The irradiation vessel, for which the dose-rate was required, was filled with this solution and placed in the identical position in the radiation chamber as was used for the experimental irradiation. Samples were then removed at intervals and the ferric ion concentration was measured spectrophotometrically with a Unicam SP 500 by comparing

the transmission of the irradiated sample with that of the original solution at 304 mμ. The molar extinction coefficient of the ferric ion in 0.8$\bar{N}$ sulphuric acid at this wavelength is accurately known (Table I(a)) and the concentration was calculated from the equation $\log {}^{I_o}/_{I} = e.c.d.$

where e = molar extinction coefficient.

c = concentration in moles per litre.

d = cell thickness in centimetres.

The figures in Table I(b), which are the results of a recent dose rate determination of the ^{60}Co source used in the present work, are shown on Graph I.

Calculation

$$\log {}^{I_o}/_{I} = e.c. \text{ for 1 cm. cells}$$

$$\therefore c = \log \frac{I_o}{I} / e \text{ moles/l. of ferric atoms}$$

The number of ferric atoms produced per ml.

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

From the graph, the value of $\log \frac{I_o}{I}$ per minute $= 1.346 \times 10^{-2}$ and the value of e at 24°C = 2213. In the reaction $Fe^{2+} \rightsquigarrow Fe^{3+}$, G = 15.5 atoms/100eV, hence

the energy absorption by the ferrous solution $= \frac{1.346 \times 10^{-2} \times 6.023 \times 10^{23} \times 10^{2}}{2213 \times 10^{3} \times 15.5}$ eV/ml/min.

i.e., Dose Rate = 2.36×10^{16} eV/ml./min.

Multiplication of the result by the factor $1.602 \times 10^{-12}/98$ converts the dose rate to roentgens per ml. per minute.

i.e., Dose Rate = 386 r/ml/min.

If S molecules of an organic product are formed per ml. per minute from the irradiation of the same vessel occupying the identical position on the source, then, by definition, the G-value for 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

$$2.36 \times 10^{16} \times \frac{N_e \text{ (organic system)}}{N_e \text{ (ferrous system)}} \text{ eV/ml./min.}$$

TABLE I(a).

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

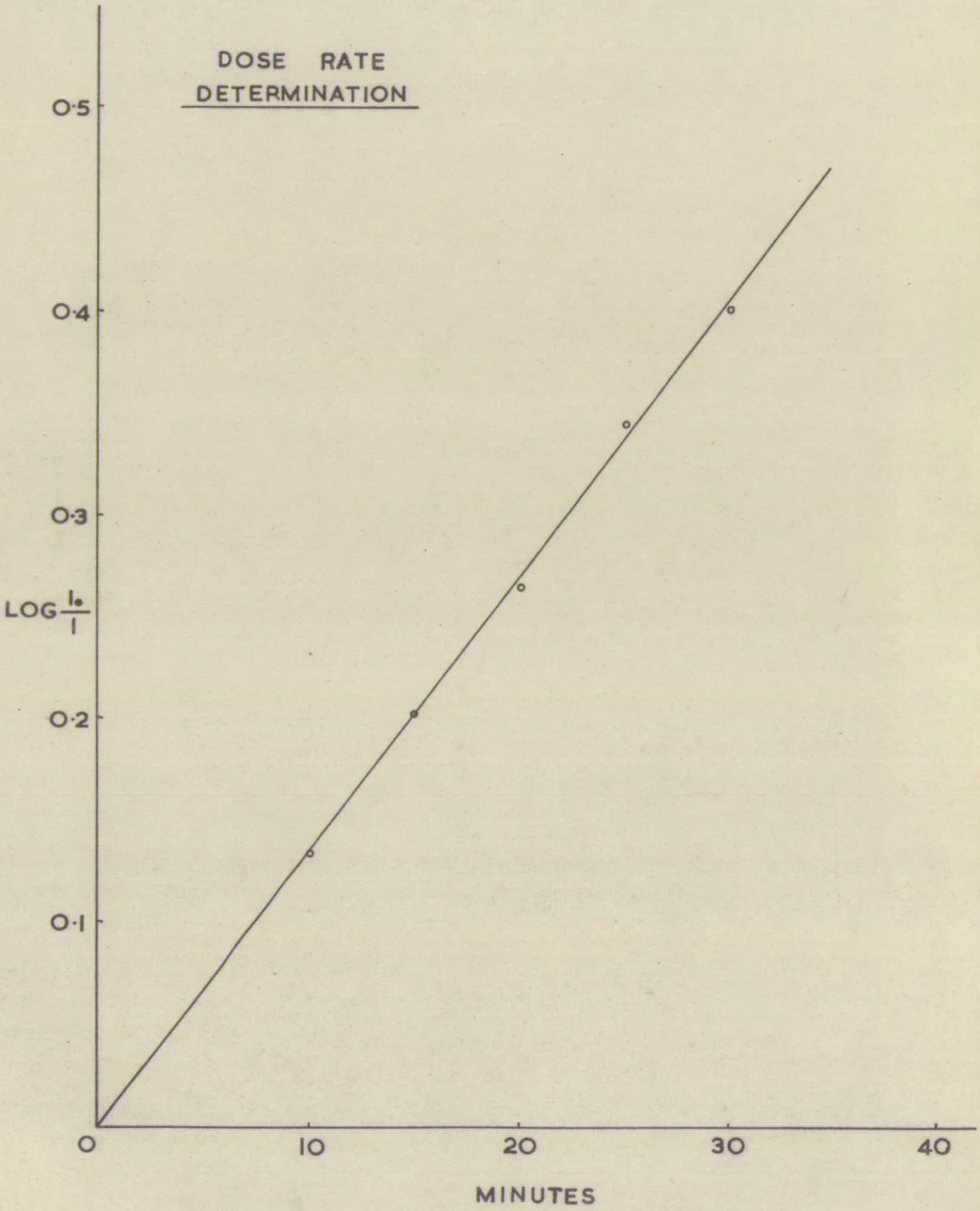
$T^{o}C$	ε
15	2074
16	2089
17	2104
18	2119
19	2135
20	2150
21	2165
22	2181
23	2197
24	2213
25	2229

TABLE I(b).

Dose Rate Determination.

Time in mins.	$\log I_o/I$	Temperature.	ε
10	0.134	$24^{o}C$	2213
15	0.202	24	2213
20	0.265	24	2213
25	0.346	24	2213
30	0.402	24	2213

GRAPH 1


DOSE RATE
DETERMINATION
0·5
0·4
0·3
LOG $\frac{I_0}{I}$
0·2
0·1
0
10
20
30
40
MINUTES

General Radiation Chemistry : some aspects.

Although the work to be described in this thesis pertains to non-aqueous organic systems only, a brief outline will be given of the irradiation of aqueous solutions.

It is well known that the radiolysis of pure water yields hydrogen and hydrogen peroxide, resulting from the production of H and OH radicals and the products from the irradiation of dilute aqueous organic solutions arise from the attack of these radicals on the organic molecules. It is not yet fully understood exactly how the radicals are produced, [27-29] but the net reaction can be expressed by

$$H_2O \longrightarrow H\cdot + \cdot OH.$$

The yield of the molecular products (hydrogen and hydrogen peroxide) in aqueous solutions depends largely on the efficiency of the radiation in causing ionisation along the tracks. Alpha particles, with a high value for linear energy transfer (LET), yield predominantly molecular products, because the radicals are produced in high concentration along the track facilitating dimerisation whereas with gamma radiation of low LET, the radicals can diffuse out of the tracks, probably encountering a solute molecule before dimerising, resulting in solute products being formed. For example, phenol is formed in the irradiation of an aqueous solution of benzene.[30]

Irradiation of dilute aqueous solutions of nitrobenzene,[31] chlorobenzene,[32] and benzoic acid,[33,34] results in the introduction

of a hydroxyl group into the aromatic nucleus to yield the three possible isomers, indicating that the attack is independent of the group already present and suggesting a free radical, rather than an ionic, mechanism. Daniels et al.,[35] noted the formation of mucondialdehyde from X-irradiation of aerated aqueous benzene. Aqueous solutions of phenol[36] differ from the aforementioned substituted benzenes on irradiation in that o-benzoquinone is formed as a primary product in acid solutions which are generally yellow in colour while alkaline solutions are red.

The irradiation of aqueous solutions of aliphatic hydrocarbons yields oxidation products as a result of attack by the H· and ·OH radicals produced from the water. In acid solution, methane[37] yields formaldehyde while in neutral solution methyl hydroperoxide is also formed; ethylene[38] forms acetaldehyde, formaldehyde, and glycolaldehyde, as well as polymeric material and in oxygenated aqueous solution acetylene[39] gives glyoxal with G = 8-10, indicating a chain reaction of short chain length.

Halogen compounds yield the corresponding acid when irradiated in aqueous or organic solvents. The production of hydrochloric acid from the X-irradiation of chloral hydrate[40] has a G in the range $(2\text{-}5) \times 10^2$ depending on dose rate, concentration, etc., indicating a chain reaction process, but with most halogen compounds G-values are low. The liberation of acid from aqueous chloride systems e.g., $CHCl_3/H_2O$, containing a suitable pH indicator can be used as a means of dosimetry where great accuracy is not required.

Aqueous solutions of alcohols, in the absence of oxygen, produce hydrogen, α-glycols and carbonyl compounds on irradiation. Ethyl alcohol undergoes hydrogen abstraction by the radicals produced from water, the resulting organic radicals dimerising to form glycol or disproportionating to form acetaldehyde. In the presence of oxygen, three times more acetaldehyde is formed than in degassed solutions.[41] Similarly, in the absence of oxygen, aqueous solutions of hydroxy-acids yield dimer as the principal organic product. In the presence of oxygen, dimer formation is reduced as in the case of the alcohols, with a corresponding increase in carbonyl formation.

The lower aldehydes are oxidised in deaerated aqueous solution to the corresponding acids; but acetone does not undergo this reaction unless oxygen is present.

The radiolysis of oxygen-free aqueous solutions of carboxylic acids exhibits the usual pattern of hydrogen abstraction by the free radicals produced from water followed by disproportionation of the organic radicals in the case of formic acid to yield CO_2 and H_2 or by dimerisation in the case of the higher acids. In the presence of oxygen, peroxide radicals are formed altering the reaction mechanism so that with formic acid, the net reaction becomes $HCOOH + O_2 \longrightarrow H_2O_2 + CO_2$ and in the case of acetic acid, along with hydrogen peroxide, glycollic acid $CH_2OH \cdot COOH$, glyoxylic acid $CHO \cdot COOH$, and oxalic acid $HOOC \cdot COOH$ are produced.

Esters liberate acid on irradiation unless they are unsaturated in which case polymer formation is the predominant process.

The study of the irradiation of naturally occurring compounds is one of the older fields of radiation chemistry, principally because of the use of radiation in radiotherapy and because of the need to know about the radiation hazards associated with the varying uses of atomic energy. The majority of the work has been carried out on aqueous solutions, either in the presence or absence of oxygen. For example, carbohydrates resemble the alcohols and hydroxy-acids in yielding carbonyl compounds, which may undergo further reaction, or dimerisation may occur in the absence of oxygen. Polysaccharides generally suffer degradation. Amino acids are deaminated, peptides undergo attack at the peptide link as well as at other points and proteins and enzymes lose their biological activity. Steroids are either oxidised or reduced at a few selected sites in the molecule, depending on the availability of molecular oxygen.

The Irradiation of Pure Organic Compounds.

The action of X-rays and alpha particles on hydrocarbons was studied in the early days of the subject by Lind and Bardwell.[42]

Although the products formed from the irradiation of methane have been known for a number of years, it is only recently with the elucidation of ion-molecule reactions that a reaction mechanism has been put forward in terms of the ions and free radicals known

to be formed.[43] The predominant ions found in the mass spectrum of methane are CH_4^+, CH_3^+ and CH_2^+. They react with methane thus

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

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

Neutralisation of CH_5^+ by an electron probably yields another methyl radical and a molecule of hydrogen. Iodine scavenging studies have confirmed that $\cdot CH_3$ is the main radical present, but small amounts of ethyl radicals have also been detected, produced presumably by neutralisation of $C_2H_5^+$, although normally this latter reaction yields ethylene and a hydrogen atom. The ethylene, hydrogen atoms and radicals undergo further reaction to yield the higher molecular weight products found.

Recently Manton and Tickner[44] concluded from a study of the radiolysis of methane using low energy electrons that, under these conditions, ions do not play a major part in the process and Yang and Manns[45] estimated the free radical contribution to the formation of C_2 and higher products to be at least 85%.

The radiation-induced polymerisation of acetylene[46] is believed to proceed by an ionic mechanism of the type

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

Polymer formation is the predominant process in the irradiation of alkenes. The yield of polymer from ethylene depends on the conditions of temperature and pressure during radiolysis, $G(-C_2H_4) \sim 100$ to 12,000 being recorded[47].

Isobutene, like ethylene, is polymerised by radiation in good yield and free radicals may play a part in the reaction when carried out at 0°C or above.[48] However, at -80°C, a temperature at which free radical propagation reactions are much reduced in rate, Davison et al.,[49] found liquid isobutene polymerised in better yield than at 0°C. In a recent review of the subject,[6] Charlesby has listed the salient features of the reaction:

(1) Initiation of polymerisation by radiation-produced ions.

(2) Propagation of polymer chains by a carbonium ion mechanism.

(3) Termination of chains by a unimolecular process.

(4) Termination of chains by a bimolecular process involving reaction with a radiation-produced inhibitor.

and (5) Degradation of polymer molecules by further radiation.

The polymerisation of many types of monomers, acrylates, methacrylates, styrene, acrylonitrile, vinyl compounds, etc., has been studied in detail. In most cases, the reactions proceed by means of a free radical induced chain reaction leading to high yields. Other applications of radiation to the field of polymers are, for example, formation of graft copolymers, the cross-linking of polythene and rubbers, both natural and synthetic, etc.. Cross-linked polythene is no longer soluble in organic solvents and at 120°C, instead of melting to form a viscous liquid, it merely softens and forms a rubber-like material.

The radiolysis of saturated hydrocarbons gives a large number of products in more or less comparable yields as well as numerous minor products. C-C fission and C-H fission are of comparable importance but Dewhurst[50] has shown that, in n-hexane, the ratio C-C to C-H scissions is greater than for random attack. This is consistent with the lower bond strength of a carbon-carbon bond; also tertiary C-C and C-H bonds are more readily broken than secondary, and secondary more so than primary. Most of the organic products are formed by reactions of free radicals in the system although some products may be formed directly by a unimolecular process and likewise a large part of the hydrogen formed is not produced from hydrogen atoms with thermal energies.

Aromatic compounds are very much more stable than aliphatic compounds to irradiation. In the radiolysis of liquid benzene, small yields of hydrogen and acetylene are noted, $G_{H_2} \sim 0.04$ and $G_{C_2H_2} \sim 0.01$, along with polymer formation $G_{-C_6H_6} = 0.9$. Schuler[51] reported that iodine has little effect on the yields of the two gaseous products from liquid benzene, suggesting that they are not formed by reactions of thermal hydrogen atoms or free radicals. However, mixtures of benzene and deuterobenzene on irradiation[52] yield HD and C_2HD as well as the isotopically pure gases, so these products cannot arise entirely from unimolecular processes.

Other aromatic hydrocarbons resemble benzene in giving low yields of gaseous products normally composed of hydrogen unless the parent hydrocarbon contains a side chain, for example ethyl benzene,

isopropylbenzene, etc., in which case methane is produced by fission of the C-C bond adjacent to the bond adjoining the aromatic ring.[53] However, toluene yields primarily hydrogen atoms and benzyl radicals.

Several reactions initiated by the beta decay of tritium have been studied recently.[54-56] Wexler et al.,[57] used a mass spectrometric technique to study the positively charged fragments resulting from the beta decay of tritium in o-, m-, p- and α- - labelled isomers of toluene. They found the mass spectra of the four isomers were very nearly the same, consisting of over 35 species, many of which were minor components. The results are interpreted as indicating that the influence of the position of the radioactive atom in the molecule on fragmentation following beta decay is obscured by secondary processes e.g., radiationless transition, hydrogen atom migration and rearrangement of the excited molecule-ion to yield the tropylium ion before break up.

As already mentioned, aromatic compounds are much more stable to irradiation than aliphatic compounds; benzene in the liquid phase is at least ten times more stable than other liquid hydrocarbons. This stability is believed[58] to be due to the excited species, $C_6H_6^+$, excited molecules and excited species formed by neutralisation of the ions, being highly resonance stabilised, insufficient energy being localised to cause decomposition before collisional deactivation or fluorescence dissipates the energy. The low product yields from substituted aromatic hydrocarbons are attributable, at least in part, to the

protective effect of the aromatic ring on the side chains which enables energy to be absorbed and dissipated again before appreciable decomposition occurs. This protective influence of the benzene ring has been demonstrated in the radiolysis of aromatic compounds in admixture with other compounds and results show that energy initially absorbed in one component can be transferred to the aromatic system and subsequently dissipated. For example, the hydrogen yield from the irradiation of cyclohexane-benzene solutions[59,60] is much less than from pure cyclohexane and much less than the yield expected from the percentage composition of the mixture if the radiolysis of the two components proceeded independently. Benzene has both lower ionisation and excitation potentials than cyclohexane and is able to protect the latter by "sponge-type" energy transfer[61] to itself before the cyclohexane has time to decompose. Since benzene is itself so resistant to radiation, most of the energy is disposed of without causing chemical change, although the very slightly increased yield of acetylene indicates some of the benzene is sacrificed in the process. In the cyclohexene-benzene system,[60] since benzene and cyclohexene have approximately equal ionisation potentials and the lowest excitation potential of the latter is above that of the former, it would appear that cyclohexene is a sacrificial protector for benzene owing to charge transfer, while benzene, because of excitation transfer, is a sponge-type protector for cyclohexene.

Chapiro et al.,[62] have recently provided evidence for energy transfer from a study of solutions of benzene/carbon tetrachloride, benzene/chloroform, etc., containing D.P.P.H. (diphenylpicryl-hydrazyl) as a radical scavenger.

The principal effect of radiation on primary and secondary alcohols is the loss of one of the hydrogen atoms on the α - carbon atom; this effect may also be accompanied by loss of a hydrogen atom from the hydroxyl group. The usual products are α- glycols, aldehydes, or ketones. Hydroxyacids react in a similar manner. Hummel, in the radiolysis of liquid methyl acetate[63] with gamma rays, found six gaseous and seventeen liquid products and stated that all bonds in the molecule appeared to be broken, except the carbonyl double bond.

The effect of radiation on alkyl halides, however, is more specific, as the predominant primary act of radiation is homolytic fission of the carbon-halogen bond.[64] This is consistent with the lower bond strengths of carbon-halogen bonds compared with carbon-carbon and carbon-hydrogen bonds, the weakest bond normally being the first to rupture. Chlorides yield hydrogen chloride while the corresponding hydrogen abstraction reaction by iodine atoms would be endothermic, as a result of which, they only combine with each other or other radicals; hence the use of iodine in radical scavenging studies. Alkyl halides frequently give isomeric halides in good yield on irradiation. Wiley[65] observed the chain isomerisation of n-propyl chloride to the more stable

isopropyl chloride occurred with a G $\sim$ 60 but was unable to detect the corresponding reaction for isopropyl chloride. Wilcox et al.,[64] reported the gamma radiation-induced isomerisation of n-butyl chloride to secondary butyl chloride also occurred with G = 60 while the rearrangement of isobutyl chloride to the tertiary isomer had G = 24; similarly, isobutyl bromide rearranges extensively to tertiary butyl bromide.[66]

Since the work to be described in this thesis deals with chlorinated compounds, either in the pure state (chloroform) or in admixture with hydrocarbons (carbon tetrachloride and benzene or cyclohexane), these topics will not be further discussed at this stage.

SECTION I

APPARATUS AND TECHNIQUES.

Cobalt-60 Source.

The radiation unit used in this work was similar in design to that described by Gibson and Pearce[67] and had been set up in conjunction with A.E.R.E. Harwell in 1954. In July 1957, two cobalt-60 sources were installed; a 140 curie vertically positioned source and a 64 curie horizontal source. The sources were in the form of ^{60}Co pellets contained in aluminium tubes which could be withdrawn electrically into a concrete shield, or propelled into the radiation chamber as required.

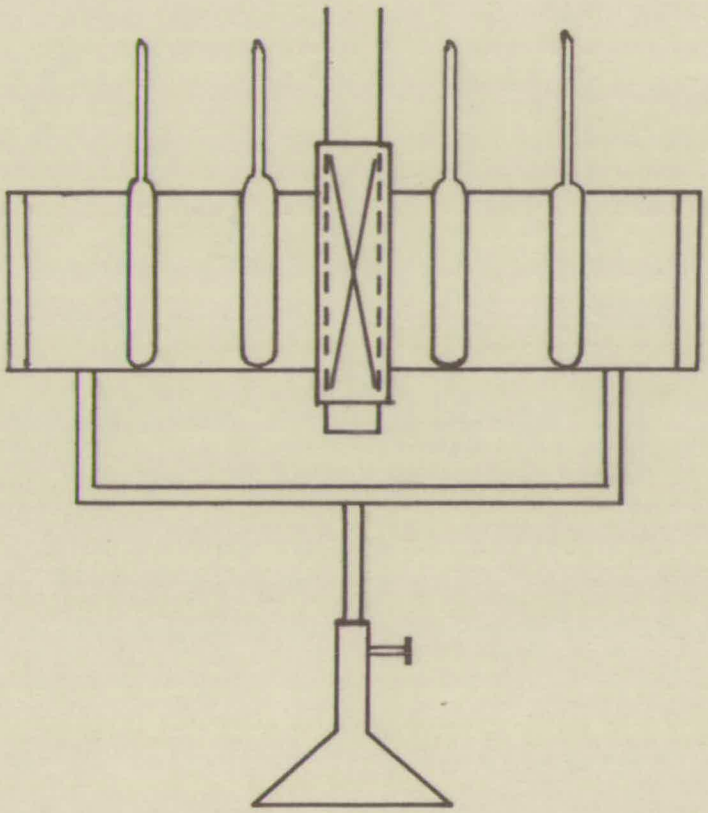
Solutions, for which no rigorous precautions were taken to exclude air, were irradiated in annular Pyrex glass vessels of capacities ranging from 50 mls to 2000 mls, fitted with Quickfit ground-glass stoppers. (Figures 1, (b) and (c))

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)). It was confirmed experimentally that each tube in the ring received the same dose. Dose rate determinations were carried out for each set of tubes, either before or after irradiation of the organic system, without altering the position of the metal ring on the source tube as this could have caused inaccurate dose rates to be recorded.

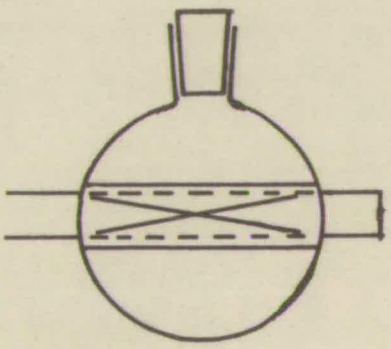
FIGURE 1

IRRADIATION VESSELS

1a METAL RING WITH TUBES

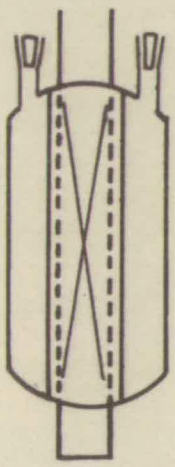


1b



HORIZONTAL SOURCE

1c



VERTICAL SOURCE

Preparation of de-aerated samples.

As already mentioned, glassware was cleaned with chromic acid for several days before being thoroughly rinsed and dried. The tubes for quantitative work were tested under vacuum for air leaks with an Edwards High Frequency Leak Detector. When filled, a tube was connected to an isolated part of the vacuum line by means of a cone and socket assembly. A Dewar flask containing liquid nitrogen was slowly raised underneath the tube in order to solidify the contents before opening the section to the oil diffusion pump. After solidification was complete, the air above the solid organic material was pumped off, the tube isolated again and the frozen solution melted by immersing the tube in a beaker of cold water. This last procedure was necessary to prevent expansion of the solid before liquefaction 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. As the solid melted, dissolved gas bubbled out into the dead space above the solution and the cycle of freezing, pumping and melting was repeated several times until degassing was complete, a Pirani gauge attached to the system giving an indication of the progress of the degassing procedure. The tube was sealed off under vacuum when no further degassing was detectable.

It was not feasible to use liquid nitrogen as freezing agent in all cases, especially in the case of cyclohexane or solutions containing a high percentage of cyclohexane, owing to the fact that the tubes cracked during the freezing process presumably due

to expansion of the solidifying solution. In such cases, a freezing mixture of crushed solid carbon dioxide and acetone was used successfully and, although degassing may not have been so complete, this did not affect the results of the irradiation, principally because all organic liquids were distilled in a stream of oxygen-free nitrogen prior to irradiation thereby reducing the oxygen content initially to a very low level before degassing took place.

Gas-Liquid Chromatography.

The low G-values of many reactions necessitates the use of a highly sensitive analytical technique and gas-liquid chromatography (G.L.C.) is ideal for the separation of complex mixtures whose components are present only in milligram quantities. Although a decade has not yet passed since James and Martin described their historic separation of fatty acids,[68] the potentialities of the technique are now so well known and several texts[69,70] have been published that only a short description of the analytical G.L.C. unit used in this work will be given.

The detectors used throughout were katharometers, shown diagrammatically in Figure 2 (a). The katharometer was in the form of a metal block, suitably drilled, with two stretched tungsten filaments fitted longitudinally in the gas streams, pure carrier gas only passing over the reference side and carrier gas and organic vapour passing over the other filament. The tungsten filaments were one-third sections of 100 watt electric light bulb

filaments supplied new by the courtesy of G.E.C. and were soldered to platinum wire to ensure good electrical contact. The platinum was then soldered to copper wire, hard brazing solder being used for all joins and borax as flux. The filaments formed two arms of a Wheatstone bridge network, Figure 2 (b), current to the bridge being supplied by 2-volt accumulators. The out of balance e.m.f. was measured on a 500 microvolt full scale deflection Sunvic recorder. The sensitivity of the detector was controlled by altering the bridge current by means of a variable resistance in series with the accumulators.

The katharometer block was buried in a lagged beaker of fine firebrick which was placed in a large beaker wound with resistance tape and heavily lagged with asbestos rope. The heater unit was insulated by mounting it in another lagged beaker in a box packed with mineral wool and asbestos waste. Current was supplied to the heating tape from a Claude-Lyons Variac Transformer whose input voltage was stabilised. As the katharometer unit was so heavily lagged to reduce heat loss and nullify external temperature changes, it required several hours to reach temperature equilibrium after any alteration was made in the voltage supplied to the heater. However, when equilibrium had been attained, the temperature of the detector was constant to $\pm 0.5^{\circ}C$ at $120^{\circ}C$.

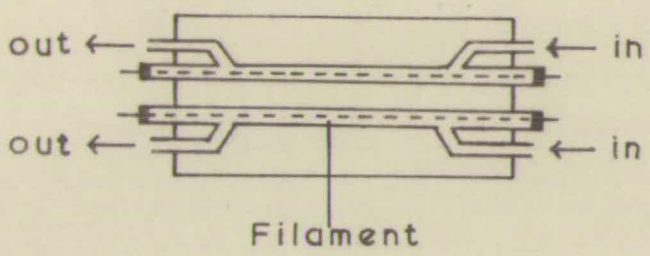
The chromatographic columns were Pyrex glass tubes of 5 mm internal diameter and 45 to 110 cms total length. They were maintained at steady temperatures inside thermally insulated heaters made from glass tubing wound with heating tape, current again being

supplied from an input-stabilised variac. Adequate temperature control was obtained in this way, $\pm 1^{\circ}C$ up to $150^{\circ}C$. For high temperature work, it was important to ensure that the exit tubes between the column heating jacket and the detection unit, as well as the katharometer itself, were maintained at a high temperature to prevent condensation of the organic vapour. Each unit required a buffered flow of hydrogen from a cylinder and this was achieved by means of a reducing valve, a needle valve, and a number of glass buffer vessels placed in series. A portion of the gas was allowed to escape through vertical columns of water which acted as safety valves and pressure regulators.

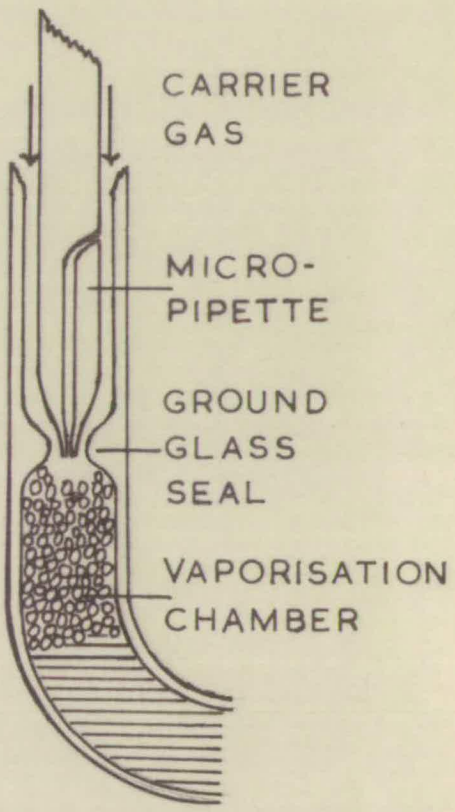
A sample injection system which introduces an accurately reproducible volume of liquid greatly facilitates quantitative work. The technique used in this case was based on the micro-pipettes now commonly used in gas chromatographic analysis and is shown in Figure 2 (c). The pipette consisted of a B10 Quickfit air leak joined to a short length of capillary tubing whose shaped tip had been ground into the constriction in the glass walls of the vaporisation chamber to form a gas-tight seal. The length of the pipette from the cone of the air leak to the ground-glass tip was such that when fitted in position there was free passage for the carrier gas. However, slight pressure was sufficient to depress the rubber connection causing the tip to seal off the gas flow, thereby forcing the carrier gas through the capillary and blowing the contents into the vaporisation chamber.

FIGURE 2

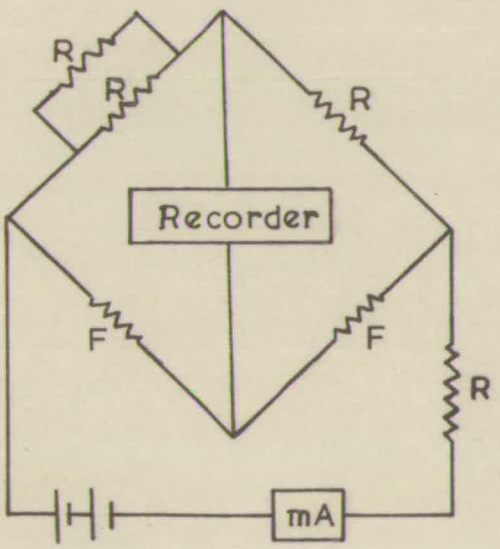
2a KATHAROMETER BLOCK



2c INJECTION SYSTEM



2b ELECTRICAL CIRCUIT



R: Variable resistance

F: Filament

A set of pipettes of capacities 6 µl, 15 µl and 27 µl were made and calibrated by calculating the volume occupied from the weight of distilled water required to fill the pipette at ambient temperature. It was found that the most suitable temperature for the vaporisation chamber was just below that temperature which would cause a blow-back through the capillary, resulting from too rapid vaporisation of the liquid. By this means sharp, symmetrical peaks could be produced for most compounds and by standardising the injection routine, results could be reproduced with an accuracy of 1% or better.

Various column packings were employed; the most frequently used stationary liquid phases were B.D.H. tricresyl phosphate, silicone elastomer (E 301, Griffin and George) and silicone fluid (M.S. 500, Hopkin and Williams). The tricresyl phosphate (T.C.P.) gave extremely good separations for most of the halogenated compounds but could not be employed above 160°C because of its tendency to volatilise from the column packing (column stripping). These oils, or solution of silicone elastomer in ethyl acetate, were absorbed on Johns-Manville celite (60-90 mesh), Gas Chromatography Ltd. G-cel (60-80 mesh) or crushed firebrick which had been elutriated with water to remove dust before drying and grading.

A Griffin and George Mark IIa G.P.C. unit was used for general qualitative analysis. This instrument was of conventional design employing katharometer detectors and a reduced outlet-pressure, and need not be described further.

Preparative scale Gas-Liquid Chromatography.

In addition to the analytical apparatus already described, a large scale G.L.C. unit was constructed. This was capable of separating 1.5 - 2 mls of mixtures, depending on the length of column used.

The injection system was able to vaporise a large sample and is shown in Figure 3 (a). By manipulation of the taps, the sample was transferred rapidly from the reservoir to the electrically heated vaporising chamber filled with Dixon stainless steel gauze rings.

The detector used was a katharometer of the same design as already described for the analytical columns. Early experiments, however, indicated that, used in this manner, it was unstable and insensitive. Both these defects were found to be due to the high gas flow rates employed (200 - 400 mls N_2/min), and were overcome by the introduction of a bypass system which allowed only a small fraction of the effluent gas stream to pass over the filament. The reference filament of the detector was sealed off and used merely as a fixed resistance. The rest of the electrical system was the same as shown in Figure 2 (b).

The recovery of the separated components of an injection was the most difficult problem encountered, owing to the presence of a large proportion of non-condensable gas. In the present work, the aim was to produce a pure sample of a desired component in a directly usable form and so adsorbents such as charcoal or

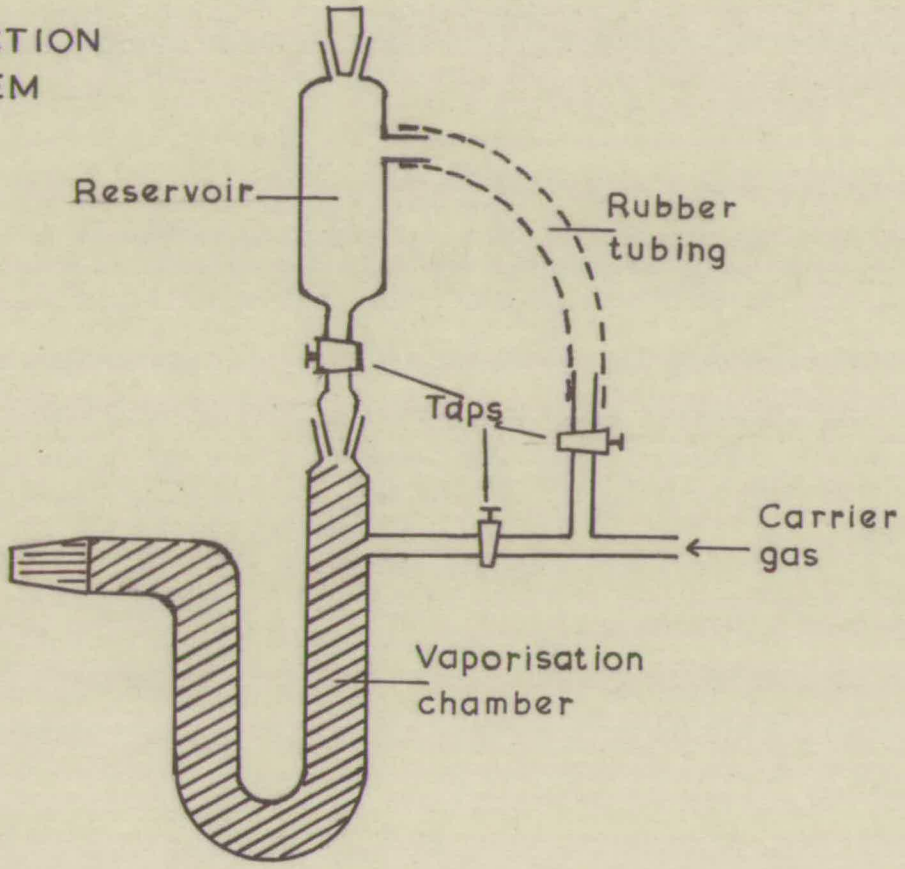
alumina were not employed. The major loss of material was due to fog formation and in an endeavour to precipitate and condense the fog, the traps were filled with glass helices and cooled in liquid nitrogen, but this generally led to blocking of the traps by solidified material. Various modifications were tried and the design finally used is shown in Figures 3 (b) and (c); the cooling agent was generally cardice/acetone although ice-water was found to be slightly more efficient for high boiling compounds. The first section of the trap, which had a well at the bottom, was empty and was connected to the second part, which was filled with glass helices, by a B7 cone and socket. Most of the vapour condensed in the first part, the liquid running into the well, while the remaining fog passed over into the second section where further condensation occurred, but rarely to such an extent as to cause a blockage. After a sufficient quantity of a component had accumulated from a series of injections, the helix packed section of the trap was heated electrically while passing a very slow stream of nitrogen through it in the reverse direction, thus sweeping the condensed liquid back into the first section of the trap which remained immersed in the freezing mixture. By this procedure about 75 to 80% recovery was achieved. The well at the bottom of the trap could then be removed by cutting the glass tube and the sample obtained for investigation.

It was soon realised that very long columns (8 feet x 25 mm i.d. or more) were unnecessary except for the most difficult separations, and the large gas flows and high temperatures necessary

FIGURE 3

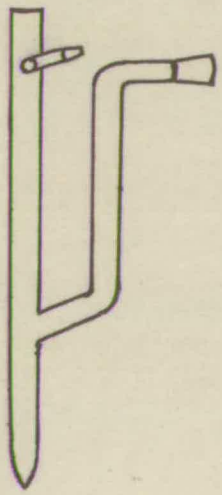
PREPARATIVE SCALE G.L.C.

3a INJECTION SYSTEM



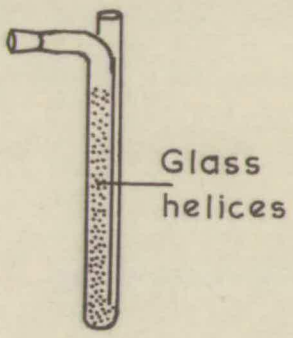
TRAPS

3b



First part

3c



Second part

to reduce retention times to reasonable periods caused serious column stripping. Shorter lengths of column proved to be highly successful for most separations provided that the internal diameter of the column was also reduced e.g., 3 foot length of column of 20 mm i.d. and 18 inch column of 15 mm i.d.. It was then found possible to operate at much lower temperatures, well below the boiling points of the injected compounds provided the vaporisation system was efficient and the exit tube and detector were hot enough to prevent condensation. Highly satisfactory separations were achieved for most mixtures, as many as four components being trapped out from each 1 ml injection of an irradiation residue.

During the latter part of the work, a Fraction Collector unit was obtained for the Griffin Mark IIa instrument. After modifications had been made to permit the changing of traps without releasing the vacuum throughout the whole system, this apparatus was used successfully for the isolation of the high boiling components produced in the irradiation of chloroform, as will be described in the next section.

The majority of Infrared Spectra were obtained with a Perkin-Elmer Infracord Spectrophotometer equipped with a sodium chloride prism and plates.

Refractive Indices were determined with an Abbe type Refractometer maintained at a constant temperature by water circulated from a thermostat tank.

Chemical Analyses were carried out by Messrs. Weiler and Strauss of Oxford.

SECTION II

THE IRRADIATION OF CHLOROFORM.

Introduction.

The decomposition of chloroform has been studied since 1848 and early workers, who examined the photochemical decomposition, reported the formation of chlorine, hydrogen chloride, carbonyl chloride and "other chlorine compounds"; in 1912, Baskerville[71] reviewed the field and drew attention to the marked influence of impurities (such as alcohol, water, and oxygen), temperature, and the colour of the glass of the reaction vessel used for the photolysis.

Since then, other workers,[72-74] studying the decomposition of chloroform induced by sunlight or ultraviolet light in the presence of air or oxygen, have reported the production of chlorine, hydrogen chloride, phosgene, water, carbon dioxide, hexachloroethane and various peroxides. More recently, the thermal decomposition has been studied by Russian workers[75] who found that hydrogen chloride and tetrachloroethylene were the principal products formed, along with small amounts of hexachloroethane and pentachloroethane. Semeluk and Bernstein[76] also studied the thermal decomposition at 500°C and concluded that the reaction leading to the major products proceeded by the following steps:

$$CHCl_3 \longrightarrow \cdot CHCl_2 + \cdot Cl$$

$$\cdot Cl + CHCl_3 \rightleftharpoons HCl + \cdot CCl_3$$

$$\cdot CCl_3 + \cdot Cl \longrightarrow CCl_4$$

$$\cdot CCl_3 \longrightarrow :CCl_2 + \cdot Cl$$

$$:CCl_2 + CHCl_3 \longrightarrow C_2Cl_4 + HCl$$

They inferred the C-Cl bond dissociation energy to be $\leqslant 72$ kcal./mole.

The radiation-induced decomposition of chloroform has been studied since 1917 when Kailan[77] first noted the formation of chlorine gas and hexachloroethane formed by the action of mixed β and γ radiation from radium. Cronheim and Gunther,[78] in 1930, irradiated dry oxygen-free chloroform with X-rays and observed that hydrogen chloride was a major product, the yield being proportional to the energy absorbed, and attributed its formation to a chain reaction of the type,

$$\cdot Cl + CHCl_3 \longrightarrow HCl + \cdot CCl_3$$

$$\cdot CCl_3 + CHCl_3 \longrightarrow \cdot Cl + CHCl_2\text{-}CCl_3$$

Halides such as chloroform are susceptible to oxidation and in 1953, Schulte et al.,[79] examined the chemical effects produced in chloroform, in the presence of oxygen, by gamma rays. They observed, as did earlier workers, that reproducible results could only be obtained if the chloroform was subjected to a rigorous purification by fuming sulphuric acid, since impurities have a pronounced effect on the radiolysis, a characteristic of chain reactions. Chloroform is oxidised by a chain mechanism to give a peroxide as the primary product,

$$CHCl_3 + O_2 \longrightarrow CCl_3OOH.$$

Other initial reactions result in the formation of small amounts of chlorine and phosgene. As the radiolysis proceeds, the peroxide and chlorine disappear to yield phosgene, hydrogen chloride and other products; Schulte suggested that the disappearance of the

chlorine could probably be accounted for by the thermal reaction

$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl.$$

In the absence of oxygen, diverse yields of hydrogen chloride and hexachloroethane have been reported and this will be commented on later.

During the study of the irradiation of chloroform containing the radical scavenger D.P.P.H., designed to yield information as to the number and nature of the radicals produced from chloroform, Prevot-Bernas et al.,[80] noted that the highly coloured D.P.P.H. continued to disappear after irradiation had ceased. This post-irradiation "after-effect", which is greater in oxygen-free solutions,[81] was originally attributed to a relatively slow reaction of hydrogen chloride with D.P.P.H., the hydrogen chloride being formed in the $CHCl_3$/D.P.P.H. solution by a single-step reaction such as $CHCl_3 \rightsquigarrow HCl + CCl_2^{++} + 2e$, since D.P.P.H. is an efficient chain terminator and would therefore inhibit production of hydrogen chloride by the chain mechanism suggested by Cronheim and Gunther.[78] However, later work[81] has shown that hydrogen chloride reacts rapidly with the radical scavenger, and further, since the effect is greater in oxygen-free solutions, peroxides cannot be responsible either; thus the cause of the after-effect is unknown, but may be due to some stable, long-lived free radicals or other irradiation products, which react slowly with D.P.P.H.

The gamma irradiation of pure chloroform has been studied previously in this department. Miller,[82] in 1958, carried out a qualitative and quantitative analysis of the products from chloroform

irradiated in the presence and absence of dissolved air. G.L.C. analysis of the first fraction of the distillate from a large volume of irradiated chloroform, showed the presence of dichloromethane and subsequent G.L.C. examination of the concentrated residue indicated tetrachloroethylene, sym-tetrachloroethane, pentachloroethane and hexachloroethane to be the main components accompanied by three minor peaks at greater elution times. He found that compounds such as heptachloropropane, hexachloropropene and hexachlorobutadiene appeared to have similar retention times to those of the minor products.

The quantitative results which were obtained, are listed in Table 2 and are included for reference purposes.

The object of the present work was to identify the higher boiling minor components detected in the residue of irradiated chloroform and, if possible, deduce the mechanism of their formation.

TABLE 2.

Radiolysis of Chloroform.

Quantitative Results obtained by Miller.

PRODUCT.	In the presence of dissolved air	In the absence of dissolved air
	G-value	G-value
HCl	5.82	4.34 4.21
CCl_4	0.1	-
CH_2Cl_2	1.16	1.32 1.38
sym-$C_2H_2Cl_4$	0.39	0.58 0.55
C_2HCl_5	0.77	0.94 0.99
C_2Cl_6	2.02	2.42 2.34
C_2Cl_4	0.10	0.11 0.14

The High Molecular Weight Components of Irradiated Chloroform.

The irradiation of 80 mls of deaerated chloroform in an evacuated sealed tube and subsequent G.L.C. analysis of the residue, concentrated by careful distillation, confirmed the production of the C_1 and C_2 chlorinated alkanes and tetrachloroethylene as previously reported. Examination at 170°C on a 3' G.L.C. column packed with 60-90 celite containing 30% (W/W) silicone elastomer E.301, revealed the presence of five other minor compounds with retention times greater than that of hexachloroethane. The first three compounds had retention times two to three times that of hexachloroethane while the last two poorly defined peaks were eluted after a considerably longer interval. From their behaviour under these conditions, they were believed to represent poly-chlorinated C_4 compounds, and because of the difficulty of dealing with compounds of such high boiling point on G.L.C., they were not investigated further; however, it has to be stressed that these compounds were formed only in very minor yields and therefore contribute little to the radiolysis of chloroform.

Since silicone elastomer (S.E.) is virtually a non-selective G.L.C. stationary phase material, compounds of a similar nature are generally eluted in order of increasing boiling point and on this basis, the boiling points of the first three minor components were estimated to be in the ranges 195°-200°C, 215°-225°C and 240°-250° respectively. The yield of the first compound was much smaller than the yields of the other two components of the mixture. Chlorinated propanes, whose boiling points

approximate to those estimated for the irradiation products, are the pentachloropropanes, hexachloropropanes and heptachloropropanes. The physical constants[83] of these compounds are listed in Table 3. From a consideration of the possible modes of formation of these compounds during the radiolysis of chloroform, the study of the isomers of the penta- and hexachloropropanes was confined to those possessing at least one chlorine atom on each carbon atom, as it was believed most unlikely that isomers containing methyl or methylene groups could be involved.

Comparison of injections of carbon tetrachloride solutions of asym-heptachloropropane, which was commercially available, with injections of the chloroform residue under identical conditions on a 3' S.E./celite column packing, showed exact agreement with the third component of the mixture. Later work, using a 2' length of column packed with 25% T.C.P. on graded firebrick, which was found to be a very selective stationary phase for chlorinated compounds, likewise gave exact agreement of retention times, thereby virtually proving the identity of the third component, although the possibility that the symmetrical isomer might behave in an identical manner on G.L.C., could not be ruled out.

The first approach to the problem was the syntheses of samples of sym-pentachloropropane and sym- and asym-hexachloropropanes and subsequent comparison of the prepared compounds with those produced by irradiation on G.L.C.
(For details of the syntheses, see the appendix to this Section.)

TABLE 3.

The Physical Constants of Penta-, Hexa- and Hepta-chloropropanes.

Formula.	Boiling Point.	Melting Point.	Refractive Index.
Penta-chloropropanes.			
$CHCl_2-CHCl-CHCl_2$	198°C		$n_D^{16.5} = 1.5131$
$CCl_3-CHCl-CH_2Cl$	192-3°C		
$CCl_3-CH_2-CHCl_2$	178-9°C		$n_D^{25} = 1.4977$
$CCl_3-CCl_2-CH_3$		179°C	
$CHCl_2-CCl_2-CH_2Cl$	191°C/755 mm		$n_D^{25} = 1.5098$
Hexa-chloropropanes.			
$CHCl_2-CCl_2-CHCl_2$	218.5°C		$n_D^{18} = 1.5262$
$CCl_3-CHCl-CHCl_2$	216°C		$n_D^{17} = 1.5250$
$CCl_3-CH_2-CCl_3$		102°C	
$CCl_3-CCl_2-CH_2Cl$			
Hepta-chloropropanes.			
$CCl_3-CCl_2-CHCl_2$	247-8°C	29-30.5°C	$n_D^{35} = 1.5401$
$CCl_3-CHCl-CCl_3$	249°C	11-11.5°C	$n_D^{21} = 1.5427$

Comparison of Polychloropropanes with irradiation products.

A comparison of injections of sym-pentachloropropane in chloroform solution with injections of the chloroform residue on a 3' S.E./celite column at 176°C, 3.4 l.N_2/hr. flow rate, showed agreement with the first small peak eluted after hexachloroethane; similarly, retention times corresponded using a 2' column of 25% T.C.P. at 157°C.

Injections of solutions of the synthesised hexachloropropane isomers under identical conditions showed that the peak representing the asymmetrical isomer was eluted fractionally faster than that for the symmetrical isomer, as would be expected from their boiling points of 216°C and 218°C respectively. When compared with the chromatogram of the irradiation residue, these isomers were found to correspond closely with the second of the high boiling components but because of the virtually identical retention times, it was not possible to decide which isomer was present in the residue. Analysis carried out using a T.C.P. column packing gave no further information.

These results indicated that the C_3 compounds produced in the radiolysis of chloroform were sym-pentachloropropane, either one or more of the hexachloropropanes and asym-heptachloropropane. In order to identify the isomers present, large volumes of chloroform were irradiated for long periods in the hope that a sufficient quantity of these minor constituents would be formed to enable them to be isolated in a pure state by

means of a large scale G.L.C. unit. This would permit comparison of their physical properties with those of authentic chlorinated propanes, purified likewise by the large scale G.L.C. unit.

The Irradiation of 4 litres of Pure Chloroform.

Chloroform supplied by T. & H. Smith, Ltd., contained 0.5 to 1% alcohol as stabiliser as well as about 0.5% dichloromethane. 500 ml batches were shaken vigorously with water three times to remove the alcohol, dried by shaking with several quantities of anhydrous calcium chloride and then subjected to a slow fractional distillation to remove the dichloromethane. Before irradiation, the purified chloroform was distilled in an atmosphere of oxygen-free nitrogen. The chloroform was irradiated in two batches in a 2 litre stoppered vessel, the first volume at a dose rate of approximately 280 r/ml/min. for a period of 840 hours equivalent to a total dose of 8.2×10^{20} eV/ml., and the second at 270 r/ml/min. for 1390 hours, a total dose of 1.3×10^{21} eV/ml.

After irradiation, unchanged chloroform in each sample was distilled off at atmospheric pressure until the volume was reduced to about 300 mls. During this process, copious quantities of dissolved hydrogen chloride and phosgene gases were evolved. The chloroform was colourless and remained so until the volume was reduced very much further, when slight discolouration occurred, in contrast to the behaviour of irradiated chloroform containing the alcohol stabiliser which becomes dark brown in colour on distillation and smells strongly of acetaldehyde.

Since the purpose of these irradiations was not to study the production of chlorinated methanes or ethanes, a detailed examination of these products was not undertaken, although their presence was noted by G.L.C. analysis. Residual chloroform and higher boiling compounds up to and including hexachloroethane were removed by distillation under reduced pressure, firstly by means of a water pump and subsequently by a rotary oil pump, lowering the pressure to 0.5 – 0.1 mm Hg. This permitted the distillation to proceed at temperatures not exceeding 60-65°C, thereby preventing any thermal decomposition of the products. A total of 47 gms. hexachloroethane were isolated from the two irradiations, this figure representing a minimum yield, since a small quantity remained dissolved in the residues.

Analysis of the residues by G.L.C. on both silicone elastomer and T.C.P. column packings revealed the presence of several peaks after that for residual hexachloroethane:

(a) a small double peak which corresponded to pentachloropropane,

(b) a double peak at the position for hexachloropropane,

and (c) a peak for heptachloropropane.

Both residues gave the same pattern of peaks and were combined. There was a very small peak between the hexachloropropane and heptachloropropane peaks in the residue of the second irradiation, but no attempt was made to isolate it.

As previously mentioned, a sample collection unit fitted to the Griffin Mark IIa Gas Chromatographic Apparatus was used for the isolation of these compounds. The effluent gas stream

from the column passed through a Y-junction and by fitting a 3-way T-junction tap to each of the side arms leading to the inlet side of a trap, it was possible to change traps, without altering the gas flow through the column, by sealing off the trap from the pump by the needle valve provided on the outlet side, closing the 3-way tap to the column on the inlet side, simultaneously allowing air to enter the trap by the third limb of the tap, provided there was free passage for the carrier gas through the other trap to the pump. The tubes connecting the column and traps were wound with heating tape, supplied with a low voltage from a variac transformer, and thermally insulated with asbestos rope. The traps were U-shaped with one limb extended forming a well, and liquid nitrogen was used as cooling agent. Trapping efficiency was about 50%. A soft glass column, 30" long and 15 mm. i.d., packed with 10% (W/W) T.C.P. on 60/80 celite was used for the separation at a temperature of 145°C and a flow rate of 4.5-5.0 l.N_2 per hour.

The residue was treated batchwise by injecting 0.5 ml. samples into the column; the unwanted components i.e. solvent and chlorinated ethanes, were trapped out in one trap and then the desired components in 3 separate traps. This 2 hour cycle of operations was repeated some 30 times, gradually building up the amount of each fraction. Once completed, G.L.C. analysis of the fractions, which were brown in colour, showed each to be contaminated with small amounts of the other components.

Accordingly, each fraction was passed through the column again to remove such contaminants and any of the stationary phase which may have volatilised from the column.

Heptachloropropane.

On re-injecting the third fraction (c), a white crystalline compound was obtained. Comparison of its infrared spectrum (in Nujol) with that of authentic asym-heptachloropropane (spectra 1a and 1b) showed the two to be identical. The melting point and refractive index of the compound were determined:-

Sample.	Melting Point.	Refractive Index.
Irradiation product.	28.0-29.0°C	$n_D^{35.2} = 1.5390$
asym-heptachloropropane	28.5-29.5°C	$n_D^{35.2} = 1.5392$
Mixed M.P.	28.0-29.0°C	
Lit. value	29.0-30.5°C	$n_D^{35} = 1.5401$

Thus, the third component of the residue was positively identified as asym-heptachloropropane, $CHCl_2-CCl_2-CCl_3$.

A carbon, hydrogen and chlorine analysis of the compound, however, was poor, the high percentage of C and H perhaps being caused by contamination of the solid with a trace of stationary phase material from the column.

	Analysis found	Analysis calculated for C_3HCl_7
%C	13.53	12.61
%H	0.55	0.35
%Cl	86.20	87.06
	100.28	100.02

Pentachloropropane.

The material of the first fraction isolated from the residue (a) was passed through the column again at a lower temperature, 120°C and with a flow rate of 4.0 l.N_2/hr., enabling two compounds to be isolated. Separation was incomplete and some mutual contamination occurred. The first of these compounds had a sweet smell and the strongest absorption in the infrared spectrum occurred at 1755 cm^{-1}, indicative of a carbonyl group. Absorptions in the carbon-halogen region were weak and poorly resolved. Insufficient sample was available for further examination, although an approximate value for its refractive index was obtained, $n_D^{19} = 1.505$, and it was concluded that the compound contained a keto group and was formed in the radiolysis of chloroform only in the presence of oxygen, as its production was not observed in the irradiation of deaerated chloroform.

The second component isolated from this fraction, although contaminated with the above compound, gave an entirely different spectrum (No. 2b) containing all the absorptions observed in the spectrum of sym-pentachloropropane, (No. 2a). The presence of a small quantity of the other compound is responsible for the absorption at 1750 cm^{-1} and the less sharply defined appearance of the peaks between 1300-1200 cm^{-1}. The refractive index was not obtained because of the lack of material but the similarity of the spectrum with that of authentic sym-pentachloropropane, taken into account with the identical behaviour of the compound

and the prepared sample on both T.C.P. and S.E. column packings, proved that sym-pentachloropropane is a product formed in small yield during the radiolysis of chloroform.

Hexachloropropane.

Qualitative analysis of the second fraction trapped from the residue (b) confirmed this fraction to be composed of two compounds which were partially separated. Almost complete separation was achieved with the large scale G.L.C. unit by using two 30" x 15 mm. i.d. columns packed with 25% (W/W) S.E. on 60/80 celite coupled together in series at a temperature of 160°C and a flow rate of 4.6 l.N_2/hr.. The liquid trapped out in each fraction was passed through the column again to achieve complete separation.

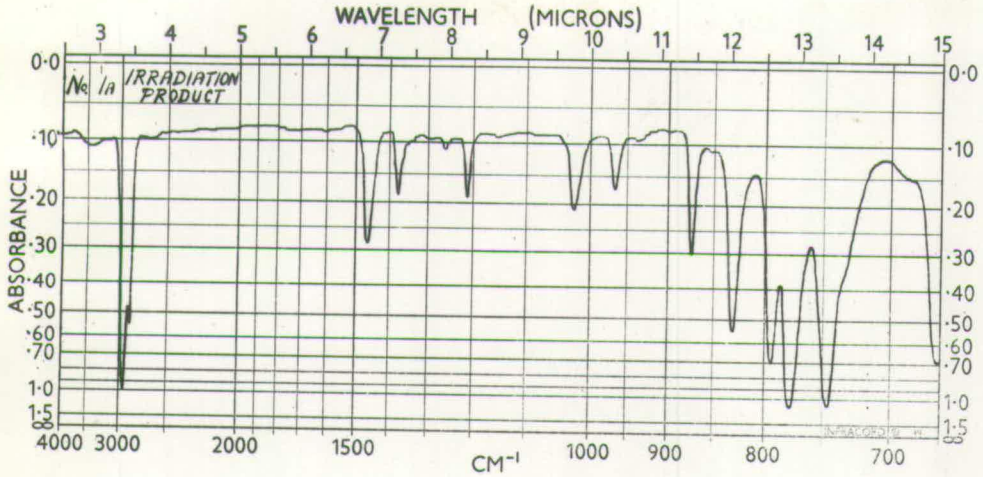
The infrared spectrum of the first fraction (No. 3c) contained all the major absorptions of both the sym- and asym-hexachloropropane isomers, (spectra Nos. 3a and 3b). The absorptions at 1560, 1750 and 1770 cm^{-1} are attributed to small amounts of impurities which were not separable by G.L.C. under the conditions employed, or were produced by thermal decomposition on the column.

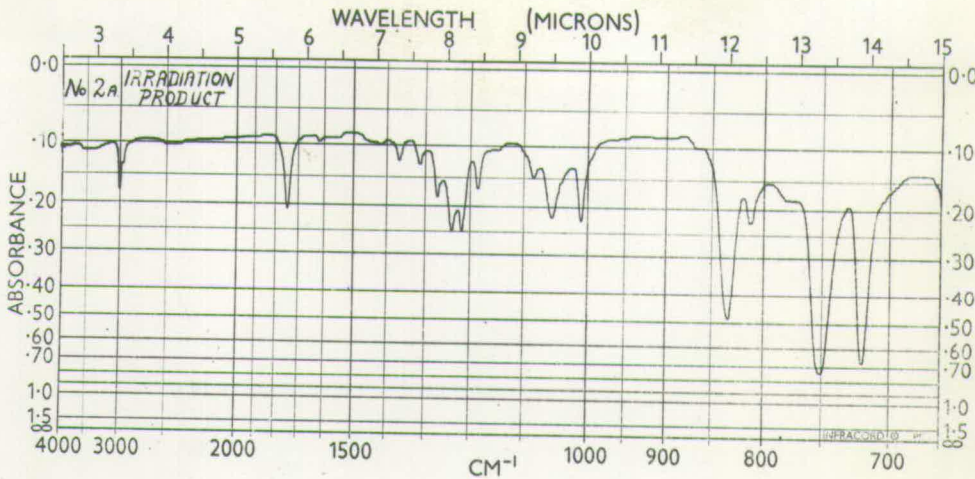
The spectrum of a 2:1 mixture of the sym- and asym- isomers (No. 3d) closely reproduced the spectrum of the irradiation products and from a consideration of the ratios of peaks in the superimposed spectra, the ratio of the amounts of the symmetrical and asymmetrical isomers formed by irradiation was estimated to be 3:1.

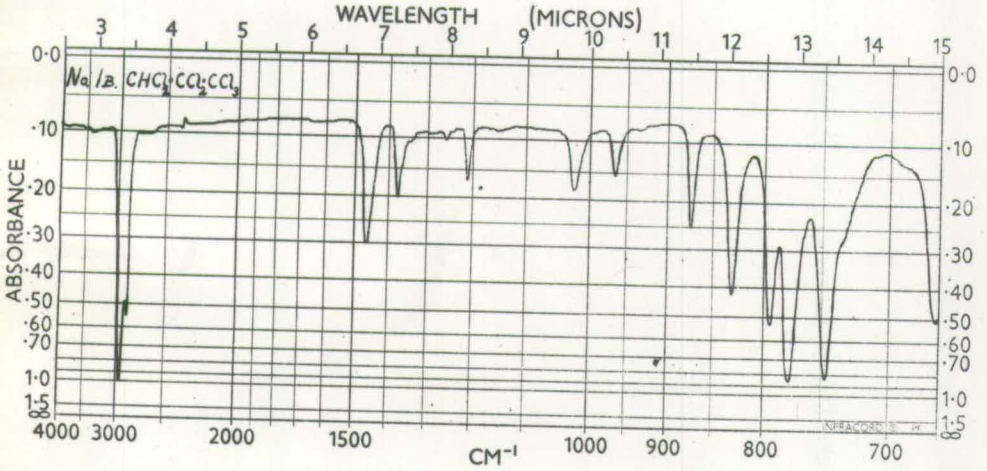
The spectrum of the second component isolated from this fraction showed C = C unsaturation at 1590 cm^{-1}, one type of C-H absorption at 3000 cm^{-1}, probably caused by a $-CHCl_2$ group, and intense C-Cl absorption between 940 and 720 cm^{-1}; no carbonyl absorption was detected.

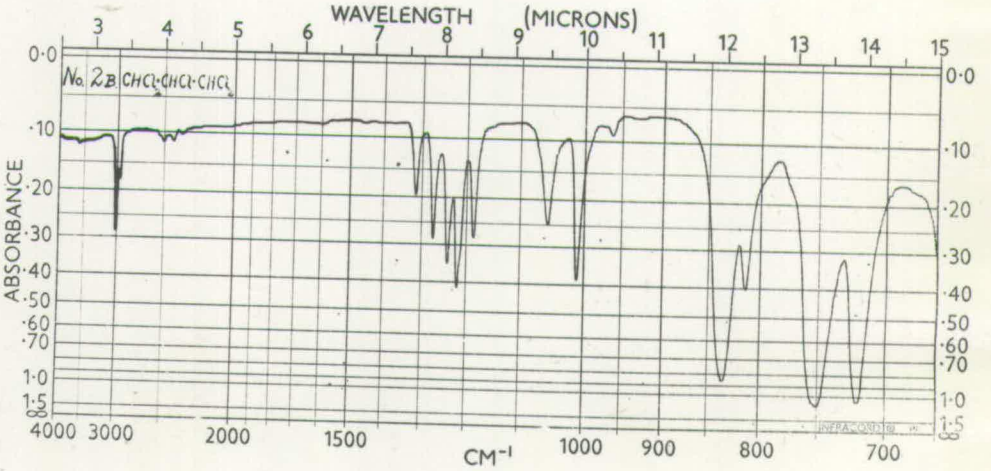
The results obtained show that 1,1,2,3,3-pentachloropropane, 1,1,1,2,3,3- and 1,1,2,2,3,3-hexachloropropane and 1,1,1,2,2,3,3-heptachloropropane are the major higher molecular weight products formed during the irradiation of chloroform, although the yields are very small in comparison with those of the C_2 products. The yields of the first two compounds were estimated to be approximately equal but smaller than the yields of the last two products.

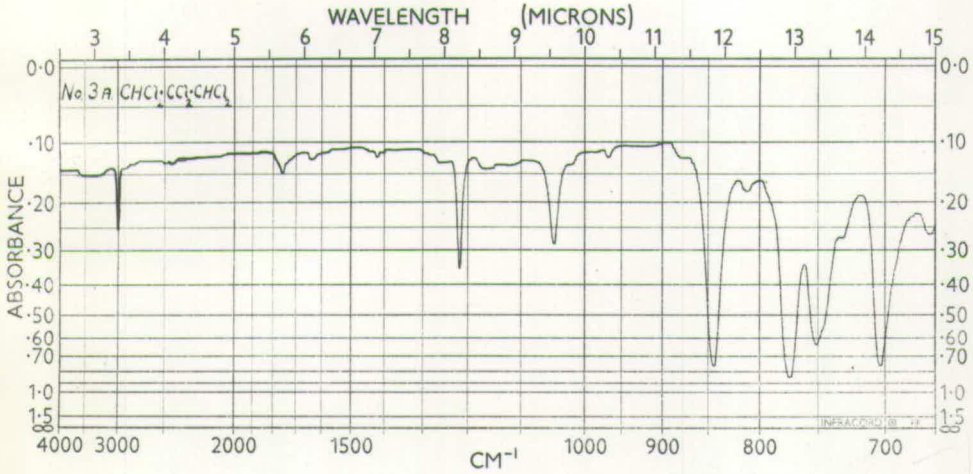
Before possible mechanisms leading to the formation of these compounds are discussed, the results of the irradiation of three tubes of deaerated chloroform, chloroform/10 mole % trichloroethylene, and chloroform/10 mole % tetrachloroethylene will be presented since they have a bearing on the mode of formation of the C_3 products.

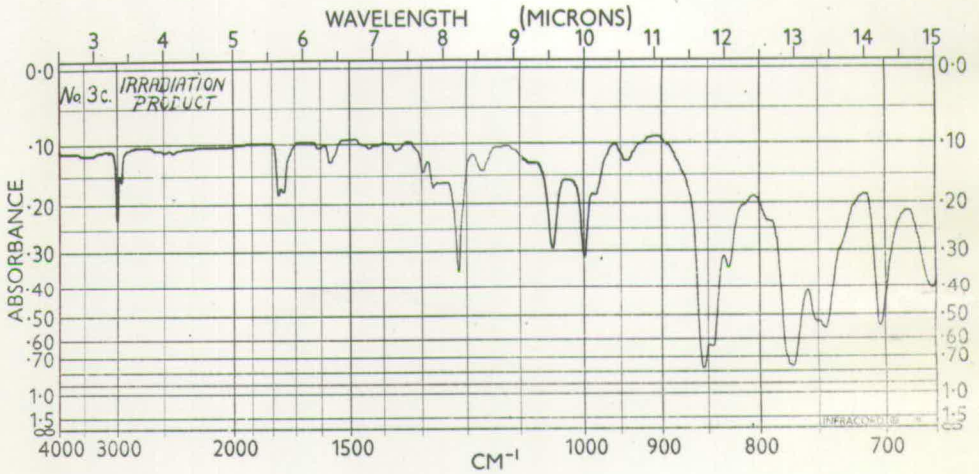

WAVELENGTH (MICRONS)
No. 1A IRRADIATION PRODUCT
ABSORBANCE
CM⁻¹

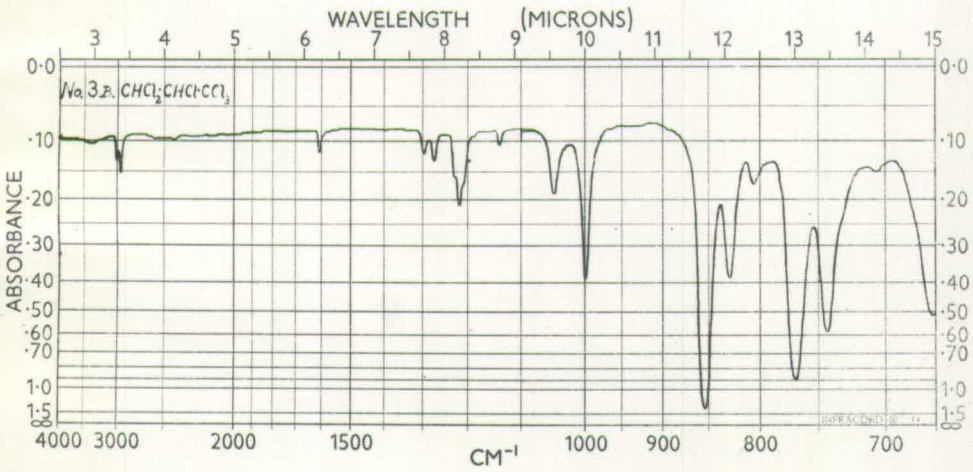

WAVELENGTH (MICRONS)
No. 2A IRRADIATION PRODUCT
ABSORBANCE
CM⁻¹

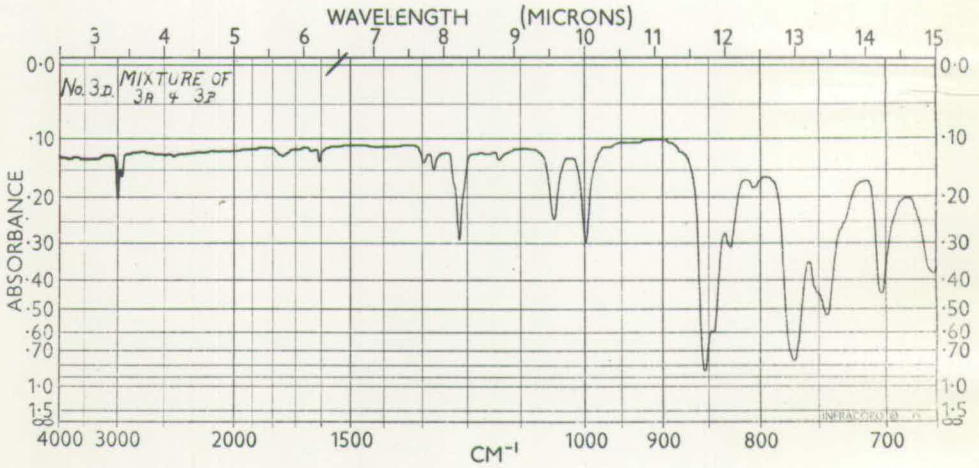

WAVELENGTH (MICRONS)
No. 1B CHCl₂·CCl₂·CCl₃
ABSORBANCE
CM⁻¹


WAVELENGTH (MICRONS)
No. 2B CHCl₂·CHCl·CHCl₂
ABSORBANCE
CM⁻¹


WAVELENGTH (MICRONS)
No. 3A. CHCl·CCl₂·CHCl₂
ABSORBANCE
CM⁻¹


WAVELENGTH (MICRONS)
No. 3C. IRRADIATION PRODUCT
ABSORBANCE
CM⁻¹


WAVELENGTH (MICRONS)
No. 3B. CHCl₂·CHCl·CCl₃
ABSORBANCE
CM⁻¹


WAVELENGTH (MICRONS)
No. 3D. MIXTURE OF 3A & 3B
ABSORBANCE
CM⁻¹

The Irradiation of Solutions of Chloroform + 10 mole % Trichloroethylene and Chloroform + 10 mole % Tetrachloroethylene.

The purpose of irradiating degassed solutions of trichloroethylene and tetrachloroethylene in chloroform, along with a tube of pure chloroform, was to evaluate the contribution of these chlorinated ethylenes towards the formation of the chlorinated propanes.

Preparation.

Chloroform was purified as already described. B.D.H. trichloroethylene and tetrachloroethylene were shaken several times with dilute hydrochloric acid to remove the basic stabiliser, twice with aqueous sodium carbonate solution, twice with water and dried with several portions of anhydrous sodium sulphate and calcium chloride, before being distilled under nitrogen. The first and last 10% portions were rejected.

10 m% solutions of each were prepared by mixing 10.2 mls $CCl_2 = CCl_2$ with 72 mls $CHCl_3$ and 9.0 mls $CHCl = CCl_2$ with 72 mls $CHCl_3$ prior to degassing and sealing off the tubes. The tubes were irradiated at a dose rate of 2.79×10^{16} eV/ml/min. for 336 hours.

Results.

Hydrogen Chloride.

The contents of each tube were poured into an accurately known excess of dilute standard sodium hydroxide ($\sim$ 0.1N) contained in a separating funnel and the stoppered vessel shaken for several

minutes to ensure complete neutralisation 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 deci-normal standard hydrochloric acid, using methyl red as indicator, permitted calculation of the amount of sodium hydroxide neutralised by the hydrogen chloride produced in the irradiation, and hence the yield of hydrogen chloride in terms of moles per ml. of irradiated material. This was the general procedure used for the determination of hydrogen chloride in all irradiations. The yields of hydrogen chloride for the three tubes are listed in Table 4.

Organic Products.

Measurement of the organic products which were less volatile than the starting materials was carried out by the following general procedure.

After removal of hydrogen chloride and drying with anhydrous calcium chloride, the organic liquid was transferred to a 250 ml. R.B. pyrex flask fitted with a 12" Widmer or Vigreux fractionating column. Unchanged starting materials were removed by slow fractional distillation until the volume was reduced to about 30 mls., when the residue was transferred to a 50 ml. flask fitted with a 6" fractionating column packed with $\frac{1}{4}$" glass helices and the distillation continued until the volume was reduced to less than 5 mls., in the case of chloroform and the chloroform-trichloro-ethylene solution, and 10 mls in the case of the chloroform-tetra-

chloroethylene solution. G.L.C. monitoring of the last few mls. of distillate showed that no loss of the lower boiling products occurred in this way.

The residues were carefully transferred to either 5 or 10 ml. graduated flasks and the fractionating columns and distillation flasks subjected to thorough, repeated, rinsing with small volumes of distillate, which were added to the residues to ensure complete transfer of products. The graduated flasks were made up to the mark with the appropriate distillate and stoppered with rubber bungs.

The amount of a compound present in 5 mls. of residue was calculated from G.L.C. analysis by comparing its peak height or peak area with those produced by a set of solutions containing known percentages or weights of the compound, determined immediately before injection of the residue. The standard solutions were prepared in graduated flasks using carbon tetrachloride or chloroform as solvent, and exactly reproducible injections of standards and residues could be made by means of the injection pipettes described in Section I, provided that the capillary of the pipette was flushed out with chloroform and blown dry before each injection. The pipettes were normally filled with chromic acid overnight. The temperature of the column was chosen, depending on the boiling point of the compound in question, so that the peak appeared 10 to 15 minutes after injection. For example, on a 3'6" S.E./celite column with a flow rate of 110 mls.H_2/min., sym-tetrachloroethane (b.p. 146°C) required a column temperature of 90°C, while 120°C was required for hexachloroethane (sublimes 185°C). Standards

containing a certain percentage of a compound produced the same peak height, within experimental error, independent of whether higher or lower boiling compounds were present, provided they were not present in excessive amounts and that the temperature of the injection point was sufficient to ensure rapid vaporisation.

The yields of sym-tetrachloroethane, pentachloroethane and hexachloroethane determined for the three irradiations are shown in Table 4.

Calculation of G-values.

The expression for the G-value is given by

$G = \frac{S \times 100}{E_{(abs)}}$ where S = the number of molecules formed during the absorption of $E_{(abs)}$ eV of energy

$$G = \frac{\text{moles/ml} \times 6.023 \times 10^{23} \times 10^{2}}{E_{(abs)}/\text{ml.}}$$

The total dose/ml = dose rate (eV/ml/min.) x minutes of irradiation.

= y eV/ml for ferrous sulphate solution.

$E_{(abs)}/\text{ml}$ = energy absorbed per ml by the organic solution $= y \times \frac{N_e(\text{organic})}{N_e(\text{ferrous})}$;

$N_e(\text{ferrous}) = 0.5675 \times N.$

The electron density, N_e, of the organic material:-

(a) For pure $CHCl_3$:- $N_e(CHCl_3) = \frac{1.4892}{119.4} \times 58 \times N$

$= 0.7235.N$ electrons/ml., since,

for $CHCl_3$, $d_4^{20} = 1.4892$, M.W. = 119.4, and $\Sigma Z = (6 + 1 + 3 \times 17 = 58)$

$\therefore$ the G-values for the products from pure chloroform are given by the expression:-

$$G = \frac{\text{moles/ml} \times 6.023 \times 10^{23} \times 10^{2} \times 0.5675}{2.787 \times 10^{16} \times 336 \times 60 \times 0.7235}$$

(b) For $CHCl_3$/10 m% $CHCl = CCl_2$ and $CHCl_3$/10 m% $CCl_2 = CCl_2$, the electron densities of the solutions were calculated to be 0.7223 x N and 0.7308 x N respectively, by assuming that ideal mixtures were formed and substituting the volumes used and the values, $d_4^{20} = 1.4680$, M.W. = 131.4 and $\sum Z = 64$ for trichloroethylene, and $d_4^{20} = 1.6228$, M.W. = 165.8 and $\sum Z = 80$ for tetrachloroethylene, along with those for chloroform, in the equation on p.12.

The G-values are listed in Table 4.

TABLE 4.

Radiolysis of Chloroform, Chloroform - 10m% Trichloroethylene and Chloroform - 10m% Tetrachloroethylene solutions

Dose Rate = 2.787×10^{16} eV/ml/min : Irradiation time = 336 hours.

PRODUCT	SYSTEM		
	$CHCl_3$	$CHCl_3$ + $CHCl{=}CCl_2$	$CHCl_3$ + $CCl_2{=}CCl_2$
Volume Irradiated	80.5 mls	80.0 mls	81.5 mls
HCl			
moles/ml x 10^5	6.97	4.50	4.38
G	5.86	3.79	3.65
$CHCl_2$-$CHCl_2$			
moles/ml x 10^6	6.61	8.19	6.29
G	0.56	0.69	0.52
$CHCl_2$-CCl_3			
moles/ml x 10^6	9.85	7.79	41.28
G	0.83	0.66	3.44
CCl_3-CCl_3			
moles/ml x 10^6	28.85	1.19	20.72
G	2.43	0.10	1.73

Examination of the High Boiling Residues.

The analysis of the compounds eluted after hexachloroethane was carried out on a 3'6" S.E./celite column at 133°C, and at a flow rate of 105 mls H_2 per minute. Injections of identical size were made of each of the three residues, contained in either 5 or 10 ml graduated flasks, by means of an injection pipette (p.32). By this method, the areas of the peaks in each residue could be compared directly, corrections being made for the volumes of the residues;

(1) Pure $CHCl_3$: after hexachloroethane, two minor peaks, corresponding to hexachloropropane(s) and heptachloropropane, in the ratio of 2:3, appeared at 27 minutes and 52 minutes.

(2) $CHCl_3/CHCl{=}CCl_2$: a major peak at 27 minutes, 23 times the area of the corresponding peak in the chloroform residue, followed by a second major peak, of equal area, at 41 minutes. No peak at 52 minutes.

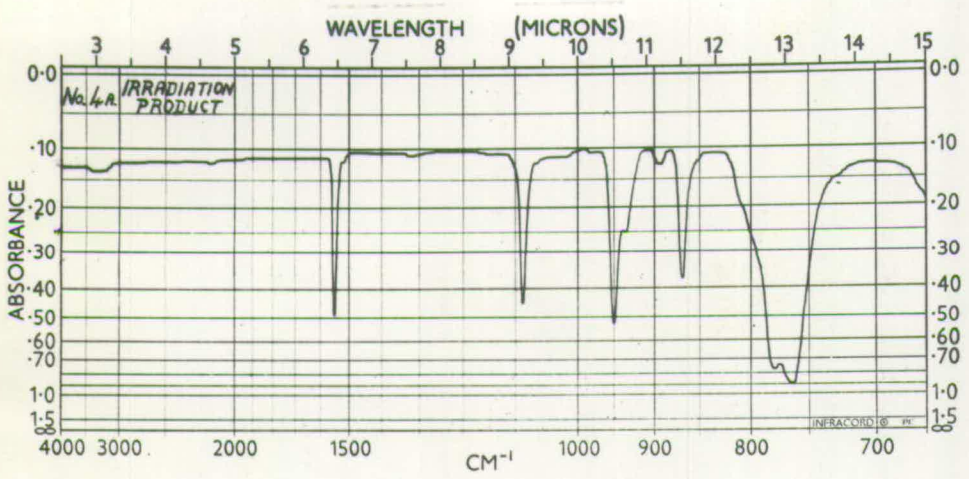
(3) $CHCl_3/CCl_2{=}CCl_2$: a major peak, at 22 minutes, with a shoulder on the tail of the peak, whose appearance was estimated to have occurred at 24-25 minutes; the area of the main peak was calculated to be almost exactly twice that of the major peaks in residue (2). A second small peak at 53 minutes, the ratio of these small peaks being 2:2.8, but increased in area by a factor of 6 compared with those in the pure chloroform residue.

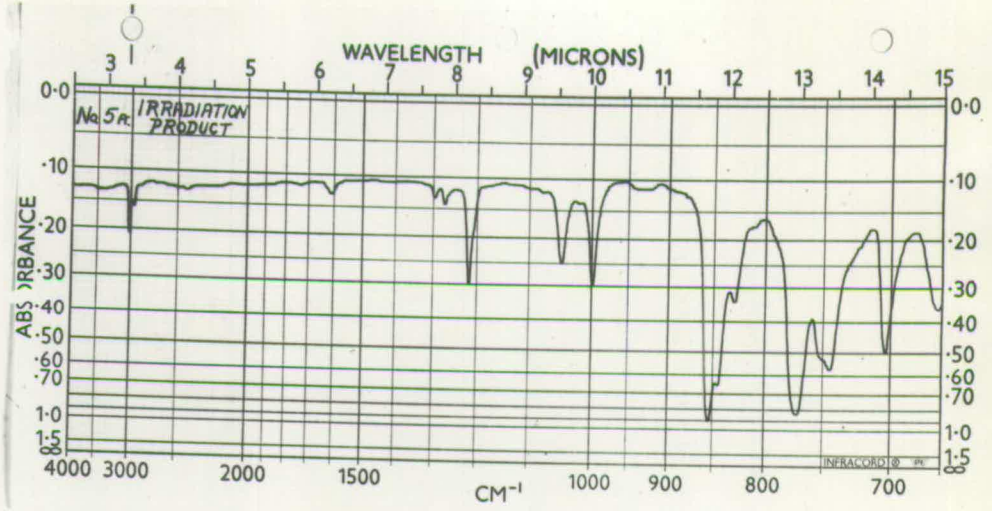
The peak appearing at 52 minutes was assumed to be asym-heptachloropropane. The major peak with retention time of 22 minutes in residue (3) agreed exactly with hexachloroprop-1-ene, and by comparison with standard solutions, was found to be present in 2.36% solution, giving a G-value of 1.71.

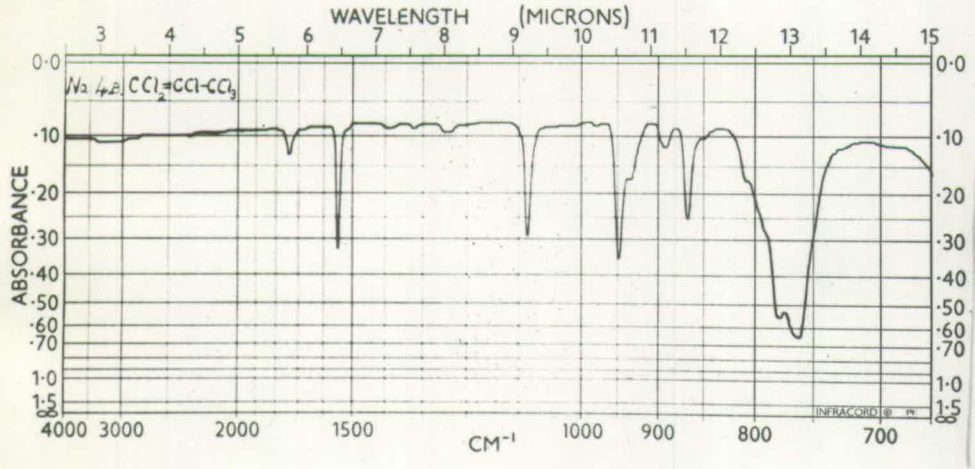
The identity of the major components in residue (2) and confirmation of the presence of hexachloroprop-1-ene in (3) was obtained by concentrating the residues to small volume and separating the desired components on an 18" x 15 mm. i.d. G.L.C. column packed with 25% S.E. on celite at 130°C, flow rate 250 mls N_2/min. Sufficient of each was procured only for infrared analysis.

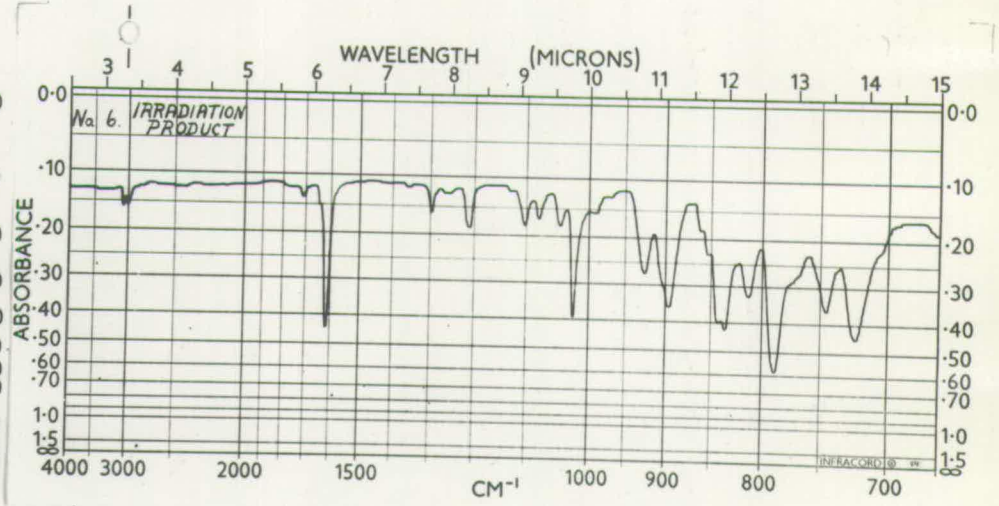
Comparison of the spectrum of the product (No. 4b) isolated from residue (3) with that of a pure sample of hexachloroprop-1-ene (No. 4a) proved the two to be identical. The spectrum (No. 5a) of the first major component of residue (2) was found to be identical with that of the sample of mixed hexachloropropane isomers isolated previously from the pure chloroform residue, i.e., both the sym- and asym- hexachloropropane isomers are produced in the same ratio as in pure chloroform, but in a yield increased by a factor of 23, in the chloroform solution containing 10 m% $CHCl=CCl_2$.

The second major component of the residue was shown to be the dimer of trichloroethylene by comparison of the infrared spectrum (No. 6) with that obtained for the trichloroethylene dimer by a previous worker in this department.[84]


WAVELENGTH (MICRONS)
No. 4 R. IRRADIATION PRODUCT
ABSORBANCE
CM⁻¹
INFRACORD


WAVELENGTH (MICRONS)
No. 5 R. IRRADIATION PRODUCT
ABSORBANCE
CM⁻¹
INFRACORD


WAVELENGTH (MICRONS)
No. 4 P. CCl2=CCl-CCl3
ABSORBANCE
CM⁻¹
INFRACORD


WAVELENGTH (MICRONS)
No. 6. IRRADIATION PRODUCT
ABSORBANCE
CM⁻¹
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Discussion.

It is now generally accepted that the first stage in the radiolytic decomposition of $CHCl_3$ is the homolytic fission of a carbon chlorine bond. Both excitation, and ionisation followed by recombination of ions forming an excited molecule, could lead to this result, which is consistent with the lower bond strength of the C-Cl bond. This may be followed by hydrogen abstraction by each of the free radicals and thereafter dimerisation reactions appear to be the predominant processes:-

$$CHCl_3 \rightsquigarrow \cdot CHCl_2 + \cdot Cl$$

$$\cdot CHCl_2 + CHCl_3 \longrightarrow CH_2Cl_2 + \cdot CCl_3$$

$$\cdot Cl + CHCl_3 \longrightarrow HCl + \cdot CCl_3$$

Some workers also suggest the reactions,

$$CHCl_3 \rightsquigarrow \cdot CCl_3 + \cdot H$$

$$\cdot H + CHCl_3 \longrightarrow HCl + \cdot CHCl_2$$

Then

$$2 \cdot CHCl_2 \longrightarrow CHCl_2\text{-}CHCl_2$$

$$2 \cdot CCl_3 \longrightarrow CCl_3\text{-}CCl_3$$

$$\cdot CHCl_2 + \cdot CCl_3 \longrightarrow CHCl_2\text{-}CCl_3$$

or

$$\cdot CHCl_2 + \cdot CCl_3 \longrightarrow CCl_2{=}CCl_2 + HCl$$

The last reaction could account for the formation of tetrachloroethylene but the following reaction would be expected to occur to some extent also,

$$\cdot CHCl_2 + \cdot CHCl_2 \longrightarrow CHCl{=}CCl_2 + HCl$$

However, no trichloroethylene has been detected, although this may be explained by its greater susceptibility to radical attack.

The formation of dichloromethylene radicals followed by dimerisation or reaction with a chloroform molecule, as suggested by Semeluk and Bernstein,[76] could also yield tetrachloroethylene, thus

$$CHCl_3 \rightsquigarrow :CCl_2 + HCl; \quad \cdot CCl_3 \longrightarrow :CCl_2 + \cdot Cl$$

$$2{:}CCl_2 \longrightarrow C_2Cl_4$$

$$:CCl_2 + CHCl_3 \longrightarrow C_2Cl_4 + HCl$$

It is now suggested that tetrachloroethylene is also formed as a secondary product from hexachloroethane by the reaction

$$CCl_3\text{-}CCl_3 \rightsquigarrow CCl_3\text{-}\dot{C}Cl_2 + \cdot Cl$$

$$CCl_3\text{-}\dot{C}Cl_2 \longrightarrow CCl_2{=}CCl_2 + \cdot Cl$$

$$\cdot Cl + CHCl_3 \longrightarrow HCl + \cdot CCl_3$$

This mechanism will be referred to again later.

$G_{(HCl)} = 5.86$ from the pure degassed chloroform is in good agreement with values found by Ottolenghi and Stein, G = 5.7,[85] by Hanrahan, G = 5.4,[86] and by Henglein, G = 5.4.[87] It is considerably greater than the value quoted by Miller, G = 4.3, but is half that reported by Johnston et al., who recently obtained G = 11.4[88] and 11.9.[89]

Ottolenghi and Stein observed that in the X-irradiation of chloroform, the $G_{(HCl)}$ did not remain constant with increase in total dose but showed a tendency to rise and suggested that the G-value obtained at a single total dose would be a function of the total dose. However, consideration of the other G-values reported above in relation to the total doses administered, does not confirm such a relationship.

The dose rates employed were similar, falling between 2.8 and 6.1 x 10^{16} eV/ml/min., with the exception of that used by Johnston which was approximately 30 x 10^{16} eV/ml/min. and that of Hanrahan which was 1.6 x 10^{18} eV/ml/min. and it would seem probable that the diversity of the results is caused by traces of impurities in the chloroform; it is interesting to note that chloroform purified by rigorous treatment with fuming sulphuric acid, etc.,[79] prior to distillation, apparently gave similar results to alcohol-free chloroform subjected only to distillation; the average $G_{(HCl)} = 5.7$[85] was virtually identical to the value obtained in this work with chloroform which was shaken with water to remove the stabiliser, prior to distillation.

Johnston et al., noted a marked increase in the yield of hydrogen chloride from chloroform irradiated at 70°C, a G = 31 being obtained, and attribute this to an increase in the abstraction reactions

$$\cdot Cl + CHCl_3 \longrightarrow HCl + \cdot CCl_3$$

$$\cdot H + CHCl_3 \longrightarrow HCl + \cdot CHCl_2$$

They also observed a slight increase in hydrogen chloride formation with added hexachloroethane at low doses but the yield fell below that for pure chloroform (11.9) as the dose increased. The initial increase is suggested to result from the reaction

$$H\cdot + CCl_3\text{-}CCl_3 \longrightarrow HCl + \cdot C_2Cl_5$$

There were three unidentified peaks on the chromatogram from the $CHCl_3/CHCl=CCl_2$ residue; the first, present in approximately half the yield of sym-tetrachloroethane, occurring between the peaks for sym-tetrachloroethane (b.p. 146°) and pentachloroethane (b.p. 161°), the other two small peaks appearing closely on either side of hexachloroethane. The former was not 1,1,1,2-tetrachloroethane, which is eluted before 1,1,2,2- tetrachloroethane (b.ps. 130° and 146° respectively) and the latter were attributed to isomers of pentachloropropane. An appreciable amount of high boiling material, in both the residues containing the chloroethylenes, was not eluted from the G.L.C. column, and was ascribed to polymer formation by the chloroethylenes. This is supported by the identification of the dimer of trichloroethylene. Reactions such as:

$$CHCl_3 \rightsquigarrow \cdot CHCl_2 + \cdot Cl$$

$$\cdot CHCl_2 + CHCl=CCl_2 \longrightarrow CHCl_2-CHCl-\dot{C}Cl_2$$

$$CHCl_2-CHCl-\dot{C}Cl_2 \longrightarrow CHCl_2-CH=CCl_2 + \cdot Cl$$

may be responsible for the production of the unidentified compound with boiling point between 146° and 161°C, since some tetrachloropropylenes boil in this temperature range. The intermediate C_3 radical could also attack a further trichloroethylene molecule, leading to the formation of high molecular weight compounds.

The G-values obtained in the present work for sym-tetrachloroethane and hexachloroethane agree exactly with those found by Miller, but there is a 10% difference in the yields of pentachloroethane.

The four-fold increase in the yield of pentachloroethane on addition of 10 m% tetrachloroethylene, accompanied by a decrease in the yield of hydrogen chloride, can be partly explained by the reaction

$$CCl_2{=}CCl_2 + \cdot Cl \longrightarrow \dot{C}Cl_2{-}CCl_3$$

followed by hydrogen abstraction

$$\dot{C}Cl_2{-}CCl_3 + CHCl_3 \longrightarrow CHCl_2{-}CCl_3 + \cdot CCl_3$$

occurring in preference to hydrogen abstraction by the chlorine atom. Also, the increased removal of chlorine atoms from the system, by addition to tetrachloroethylene, will reduce the back reaction

$$\cdot CHCl_2 + \cdot Cl \longrightarrow CHCl_3$$

resulting in a greater concentration of $\cdot CHCl_2$ radicals, free to combine with $\cdot CCl_3$ radicals, thereby increasing the pentachloroethane and decreasing the hexachloroethane yields. An increase in the yield of sym-tetrachloroethane might also have been expected, unless the rate of dimerisation of $\cdot CHCl_2$ radicals is already at a maximum in the spurs.

It is of interest to note that the main products formed in the irradiation of a solution of hexachloroethane in benzene (described in the Appendix to this Section), were found to be hydrogen chloride and tetrachloroethylene; no pentachloroethane was positively confirmed. This, therefore, would suggest that the pentachloroethyl radical eliminates a chlorine atom in preference to undergoing a hydrogen abstraction reaction. These results are supported by the observation of West and Schmerling[90]

that when hexachloroethane (in place of carbon tetrachloride) is used as the halogen donor in the peroxide initiated chain halogenation reaction of saturated hydrocarbons, a good yield of the alkyl halide is obtained, along with tetrachloroethylene and hydrogen chloride in place of the expected pentachloroethane. They also attribute this to a chlorine atom elimination reaction by the pentachloroethyl radical in preference to hydrogen abstraction.

The difference in the results in this case can be explained by assuming that the combination of a tetrachloroethylene molecule and an energetic chlorine atom produces an energetic or "hot" pentachloroethyl radical which is capable of abstracting a hydrogen atom whereas the same radical, formed from hexachloroethane by the loss of a chlorine atom, may be energetically incapable of abstracting a hydrogen atom and subsequently eliminates a chlorine atom. On the other hand, the fate of the pentachloroethyl radical may depend on the concentration of tetrachloroethylene present. If the equilibrium

$$\cdot CCl_2\text{-}CCl_3 \rightleftharpoons CCl_2{=}CCl_2 + \cdot Cl$$

exists, a high concentration of tetrachloroethylene, as in the 10 mole% solution in chloroform will favour the formation of the radical, which may then abstract a hydrogen atom to form pentachloroethane, while a low concentration of tetrachloroethylene will promote decomposition of the radical.

The decrease in the yield of hexachloroethane in the chloroform-tetrachloroethylene system can be attributed to

scavenging of $\cdot CCl_3$ radicals by tetrachloroethylene with the formation of hexachloropropene

$$CCl_2{=}CCl_2 + \cdot CCl_3 \longrightarrow \dot{C}Cl_2{-}CCl_2{-}CCl_3$$

$$\dot{C}Cl_2{-}CCl_2{-}CCl_3 \longrightarrow CCl_2{=}CCl{-}CCl_3 + \cdot Cl$$

Since no hexachloropropene was observed in the residue of 2 litre irradiation of pure chloroform, nor any substantial increase in the yields of hexa- and heptachloropropanes in the tetrachloroethylene-chloroform solution it would appear that tetrachloroethylene contributes little to the formation of the C_3 products. However, the six-fold increase in the yields of hexachloropropane and heptachloropropane is probably due to reactions such as

$$CCl_2{=}CCl_2 + \cdot CHCl_2 \longrightarrow \dot{C}Cl_2{-}CCl_2{-}CHCl_2$$

$$\dot{C}Cl_2{-}CCl_2{-}CHCl_2 + CHCl_3 \longrightarrow CHCl_2{-}CCl_2{-}CHCl_2 + \cdot CCl_3$$

$$\text{and } \dot{C}Cl_2{-}CCl_2{-}CHCl_2 + \cdot Cl \longrightarrow CCl_3{-}CCl_2{-}CHCl_2$$

The addition of 10 m% trichloroethylene to chloroform, in contrast, increases the yield of the hexachloropropane isomers 23 times relative to pure chloroform, but does not alter the ratio in which they are formed. This would suggest that trichloroethylene is an important precursor in the formation of these compounds, as illustrated in reactions (b), (f) and (h) in the following scheme:

I (a) $Cl_2C{=}CHCl + \cdot Cl \longrightarrow \dot{C}Cl_2{-}CHCl_2$

(b) $\dot{C}Cl_2{-}CHCl_2 + \cdot CHCl_2 \longrightarrow CHCl_2{-}CCl_2{-}CHCl_2$

(c) $\dot{C}Cl_2{-}CHCl_2 + \cdot CCl_3 \longrightarrow CCl_3{-}CCl_2{-}CHCl_2$

(d) $Cl_2C{=}CHCl + \cdot CHCl_2 \longrightarrow \dot{C}Cl_2{-}CHCl{-}CHCl_2$

(e) $\dot{C}Cl_2{-}CHCl{-}CHCl_2 + \cdot H \longrightarrow CHCl_2{-}CHCl{-}CHCl_2$

(f) $\dot{C}Cl_2{-}CHCl{-}CHCl_2 + \cdot Cl \longrightarrow CCl_3{-}CHCl{-}CHCl_2$

(g) $Cl_2C{=}CHCl + \cdot CCl_3 \longrightarrow \dot{C}Cl_2{-}CHCl{-}CCl_3$

(h) $\dot{C}Cl_2{-}CHCl{-}CCl_3 + \cdot H \longrightarrow CHCl_2{-}CHCl{-}CCl_3$

(i) $\dot{C}Cl_2{-}CHCl{-}CCl_3 + \cdot Cl \longrightarrow CCl_3{-}CHCl{-}CCl_3$

Reactions involving addition to the other carbon atom of the trichloroethylene molecule are considered to be sterically unfavourable and would also result in the formation of an electronically less stable radical.

All the products formed in this reaction scheme, with the exception of the last one, have been identified in the residue from pure irradiated chloroform. However, no trace of heptachloropropane was found in the tube of chloroform containing the added trichloroethylene.

This fact, viewed in the light of the very low yield of hexachloroethane from this system, would suggest that reactions involving $\cdot CCl_3$ radicals have been almost completely suppressed.

It would appear that trichloroethylene, at the concentration employed, is effectively preventing hydrogen abstraction reactions by combining with the free radicals, although radical combination reactions are probably still operative;

$$Cl_2C{=}CHCl + \cdot Cl \longrightarrow \cdot CCl_2{-}CHCl_2 \qquad (A)\ \text{(reaction I (a))}$$

$$Cl_2C{=}CHCl + \cdot CHCl_2 \longrightarrow \cdot CCl_2{-}CHCl{-}CHCl_2 \qquad (B)\ \text{(reaction I (d))}$$

Radical (A) would then be the source of pentachloroethane

$$\cdot CCl_2{-}CHCl_2 + \cdot Cl \longrightarrow CCl_3{-}CHCl_2$$

and sym-hexachloropropane

$$\cdot CCl_2{-}CHCl_2 + \cdot CHCl_2 \longrightarrow CHCl_2{-}CCl_2{-}CHCl_2 \quad \text{(reaction I (b))}$$

Radical (B) would be the source of asym-hexachloropropane

$$\cdot CCl_2{-}CHCl{-}CHCl_2 + \cdot Cl \longrightarrow CCl_3{-}CHCl{-}CHCl_2 \quad \text{(reaction I (f))}$$

Combination of this radical with $\cdot CHCl_2$ would give a higher boiling product.

The reason for the rise in the yield of sym-tetrachloroethane is not clear, nor is the mechanism for the formation of the hydrogen chloride; if hydrogen abstraction reactions are suppressed, then the residual yield of hydrogen chloride (G = 3.79) must be due to a "molecular" reaction or perhaps an ion-molecule mechanism. For example,

$$CHCl_3 \rightsquigarrow HCl + :CCl_2$$

$$:CCl_2 + CHCl_3 \longrightarrow C_2Cl_4 + HCl,$$

which is similar to the mechanism suggested by Semeluk and Bernstein to explain the results of the thermal decomposition of chloroform.[76] Unfortunately, no information is available concerning the yield of tetrachloroethylene, to qualify this suggestion. The dichloromethylene radicals might alternatively have been expected to add to trichloroethylene forming pentachlorocyclopropane with a G-value

equivalent to that of the hydrogen chloride, but this was not found to be the case.

To summarise, the products of the chloroform-trichloroethylene system can be explained by the reactions outlined in Scheme I, omitting those reactions involving trichloromethyl radicals.

In pure chloroform, the concentration of trichloroethylene, formed by the reaction,

$$2 \cdot CHCl_2 \longrightarrow ClCH{=}CCl_2 + HCl,$$

must be very much less and insufficient to prevent hydrogen abstractions; therefore $\cdot CCl_3$ radicals are present and asym-heptachloropropane can arise by reaction I (c)

$$\cdot CCl_2{-}CHCl_2 + \cdot CCl_3 \longrightarrow CCl_3{-}CCl_2{-}CHCl_2$$

Pentachloropropane can be formed by reaction I (e), i.e.,

$$\cdot CCl_2{-}CHCl{-}CHCl_2 + CHCl_3 \longrightarrow CHCl_2{-}CHCl{-}CHCl_2 + \cdot CCl_3$$

Trichloroethylene, at this very low concentration, must be a poor scavenger for $\cdot CCl_3$ radicals, otherwise sym-heptachloropropane would be produced by reactions I (g) and I (i). There is evidence to support this assumption in that even 10 m% trichloroethylene was unable to completely inhibit the formation of hexachloroethane (G = 0.1). This being the case, reaction I (h) can also be discounted, leading to the conclusion that reactions I (g), (h) and (i) occur neither in the irradiation of pure chloroform nor chloroform-trichloroethylene solution.

The two hexachloropropanes would still be produced by reactions I (a) and I (b) and I (d) and I (f). The ratio of the two would then be independent of the ratio of the concentrations of ·Cl and $\cdot CHCl_2$ radicals and, providing neither radical (A) nor (B), is used up preferentially in some competing reaction in either the pure chloroform system or the chloroform-trichloroethylene system, then the ratio of the hexachloropropanes should be the same in both systems. Competing addition reactions involving these radicals appear to occur in the chloroform system but probably affect both radicals to a similar extent; for example, parallel to the formation of heptachloropropane (reaction I(c))

$$\cdot CCl_2\text{-}CHCl_2 + \cdot CCl_3 \longrightarrow CCl_3\text{-}CCl_2\text{-}CHCl_2,$$

the reaction

$$\cdot CCl_2\text{-}CHCl\text{-}CHCl_2 + \cdot CCl_3 \longrightarrow CCl_3\text{-}CCl_2\text{-}CHCl\text{-}CHCl_2$$

probably also occurs and may be responsible for some of the very high boiling material produced.

The foregoing reaction mechanism, although not perfect, succeeds in explaining most of the observed facts, especially the identical ratio of the hexachloropropane isomers, produced in different total yields, in the two systems.

Other possible mechanisms examined were less successful in explaining the experimental results. For example, the formation of the chlorinated propanes, identified in the irradiation of pure chloroform, can be explained neatly by the following mechanism, based on combination reactions of the main radicals

known to be present in the system during irradiation:-

II (a) $\cdot CHCl_2 + \cdot CHCl_2 \longrightarrow CHCl_2\text{-}\dot{C}HCl + \cdot Cl$

$$CHCl_2\text{-}\dot{C}HCl \begin{cases} \xrightarrow{\cdot CHCl_2} CHCl_2\text{-}CHCl\text{-}CHCl_2 \\ \xrightarrow{\cdot CCl_3} CHCl_2\text{-}CHCl\text{-}CCl_3 \end{cases}$$

II (b) $\cdot CHCl_2 + \cdot CCl_3 \longrightarrow CHCl_2\text{-}\dot{C}Cl_2 + \cdot Cl$

$$CHCl_2\text{-}\dot{C}Cl_2 \begin{cases} \xrightarrow{\cdot CHCl_2} CHCl_2\text{-}CCl_2\text{-}CHCl_2 \\ \xrightarrow{\cdot CCl_3} CHCl_2\text{-}CCl_2\text{-}CCl_3 \end{cases}$$

These reactions lead to the production of all the isolated and identified products. II (a) leads to the formation of sym-pentachloropropane and asym-hexachloropropane, both of which were produced in smaller yield than sym-hexachloropropane and asym-heptachloropropane, formed in roughly equivalent yield by route II (b).

This mechanism satisfactorily accounts for the results of the radiolysis of pure chloroform but does not explain why the hexachloropropanes should be so much increased by the addition of trichloroethylene or why they are produced in almost exactly the same ratio as in pure chloroform. However, the intermediate radical formed in II (b), $CHCl_2\text{-}\dot{C}Cl_2$, is radical (A), formed from trichloroethylene by chlorine atom addition i.e.,

$$CHCl{=}CCl_2 + \cdot Cl \longrightarrow CHCl_2\text{-}\dot{C}Cl_2 \quad \text{(reaction I (a))}$$

and it was thought that an intramolecular migration of a chlorine atom might occur, forming the radical $\dot{C}HCl\text{-}CCl_3$, (C) and establishing the equilibrium

$$(A)\ CHCl_2\text{-}\dot{C}Cl_2 \rightleftharpoons \dot{C}HCl\text{-}CCl_3\ (C)$$

Radical (C) is that which would be formed by addition of the chlorine atom to the other carbon atom of trichloroethylene.

Evidence for such intramolecular halogen shifts in chlorinated and brominated alkanes has been reported by several workers.[65,91,92]

Addition of $\cdot CHCl_2$ to the isomeric radicals would lead to the formation of sym- and asym-hexachloropropanes in a fixed ratio depending on the position of equilibrium,

$$\begin{array}{ccc} CHCl_2\text{-}\dot{C}Cl_2 & \rightleftharpoons & \dot{C}HCl\text{-}CCl_3 \\ \downarrow \cdot CHCl_2 & & \downarrow \cdot CHCl_2 \\ CHCl_2\text{-}CCl_2\text{-}CHCl_2 & & CHCl_2\text{-}CHCl\text{-}CCl_3 \end{array}$$

Therefore, if this halogen transfer can occur once the radical $CHCl_2\text{-}\dot{C}Cl_2$ has been formed, the symmetrical and asymmetrical isomers of hexachloropropane can be formed in both these systems in the same ratio, but by initially different mechanisms.

However, radical (C) of the equilibrium, on addition of a $\cdot CCl_3$ radical, in the pure chloroform system, would produce sym-heptachloropropane, which was not found;

$$\begin{array}{ccccc} (A) & CHCl_2\text{-}\dot{C}Cl_2 & \rightleftharpoons & \dot{C}HCl\text{-}CCl_3 & (C) \\ & \downarrow \cdot CCl_3 & & \downarrow \cdot CCl_3 & \\ & CHCl_2\text{-}CCl_2\text{-}CCl_3 & & CCl_3\text{-}CHCl\text{-}CCl_3 & \end{array}$$

In the radiolysis of $CHCl_3/CHCl{=}CCl_2$, no peak was observed for heptachloropropane, but this is explicable because very few $\cdot CCl_3$ radicals are present, hence addition to these isomeric radicals would be negligible.

If the halogen transfer reaction is applied to the intermediate radical, $CHCl_2$-$\dot{C}HCl$, formed in II (a), the same radical is produced and hence only the two products already noted can be formed by addition of a $\cdot CHCl_2$ or $\cdot CCl_3$ radical, but the product from the latter is asym-hexachloropropane which would therefore mean that more of this isomer should be formed in the irradiation of pure chloroform than in the chloroform-trichloroethylene system, in which there is no comparable reaction.

None of these mechanisms accounts for all the observed facts in an entirely satisfactory manner. The mechanism suggested, based on the scavenging action of trichloroethylene preventing hydrogen abstraction reactions, explains satisfactorily the equal ratios of the hexachloropropane isomers produced in the chloroform and chloroform-trichloroethylene systems, and the presence of the other observed products, with the exception of the increased yield of sym-tetrachloroethane and the mode of formation of the hydrogen chloride. The defects of the other mechanisms have been discussed and it is possible that some non-specific type of reaction, perhaps involving an ion-molecule mechanism, is responsible for the formation of the C_3 compounds.

APPENDIX

TO

SECTION II.

The Formation of Tetrachloroethylene.

It was suggested on p.60 that tetrachloroethylene might be formed as a secondary product from hexachloroethane.

Evidence in support of this mechanism was obtained from the irradiation of solid, deaerated hexachloroethane and a solution of hexachloroethane in benzene. Neither chlorine nor tetrachloroethylene, the products of the pyrolysis of hexachloroethane, were found in the former, although what was believed to be a trace of carbon tetrachloride was detected. The examination was carried out by dissolving the solid hexachloroethane in ether and then slowly removing it by crystallisation, and studying the residue by G.L.C. These findings have been substantiated recently by Johnston et al.,[89] and although the results cannot be extrapolated directly to the liquid phase, it would suggest that tetrachloroethylene is not formed by a "molecular" mechanism.

The irradiation of a saturated solution of hexachloroethane in benzene gave tetrachloroethylene as the major organic product, hydrogen chloride and a small amount of chlorobenzene, along with a very small yield of carbon tetrachloride; no chloroform, or benzotrichloride were detected but perhaps a trace of pentachloroethane, although this could not be confirmed.

Formation of tetrachloroethylene in this system, virtually devoid of $\cdot CCl_3$ radicals, can occur by:-

$$CCl_3\text{-}CCl_3 \rightsquigarrow CCl_3\text{-}\dot{C}Cl_2 + \cdot Cl$$

$$CCl_3\text{-}\dot{C}Cl_2 \longrightarrow CCl_2{=}CCl_2 + \cdot Cl$$

$$\cdot Cl + C_6H_6 \longrightarrow HCl + \cdot C_6H_5$$

or

$$C_6H_6 \rightsquigarrow \cdot C_6H_5 + \cdot H$$

$$\cdot H + CCl_3\text{-}CCl_3 \longrightarrow HCl + \cdot CCl_2\text{-}CCl_3$$

followed by

$$\cdot CCl_2\text{-}CCl_3 \longrightarrow CCl_2{=}CCl_2 + \cdot Cl$$

$$\cdot C_6H_5 + \cdot Cl \longrightarrow C_6H_5Cl$$

$$C_6H_6 + \cdot CCl_2\text{-}CCl_3 \longrightarrow CHCl_2\text{-}CCl_3 \text{ (trace?)} + \cdot C_6H_5$$

$$\cdot C_6H_5 + C_6H_6 \longrightarrow \text{polymer products.}$$

The preferential formation of tetrachloroethylene in systems containing the pentachloroethyl radical formed from hexachloroethane has already been discussed (p. 63) and it is believed that at least part of the tetrachloroethylene formed in the chloroform system, as well as in the benzene-carbon tetrachloride and cyclohexane-carbon tetrachloride systems, (to be described), occurs by this chlorine elimination reaction:

$$\cdot CCl_2\text{-}CCl_3 \longrightarrow CCl_2{=}CCl_2 + \cdot Cl$$

$$\cdot Cl + RH \longrightarrow HCl + R$$

The formation of the pentachloroethyl radical itself can occur either by radiolytic decomposition of hexachloroethane or chlorine abstraction by another free radical,

$$CCl_3\text{-}CCl_3 \rightsquigarrow CCl_3\text{-}\dot{C}Cl_2 + \cdot Cl$$

or

$$R\cdot + CCl_3\text{-}CCl_3 \longrightarrow RCl + \dot{C}Cl_2\text{-}CCl_3$$

where

$$R\cdot = \cdot H\ ,\ \cdot C_6H_5 \text{ or } \cdot C_6H_{11}$$

Thus, in systems where hexachloroethane is produced in some quantity, tetrachloroethylene is probably formed, at least in part, as a secondary product.

The presence of the small amount of carbon tetrachloride was proved by concentrating it, by distillation, in a small volume of benzene and obtaining its characteristic infrared absorptions in the 800–750 cm^{-1} region, compensating for the spectrum of benzene by means of a variable path length cell placed in the twin beam of the instrument. A sample of benzene with added carbon tetrachloride gave an identical absorption spectrum.

The formation of carbon tetrachloride must occur by homolytic fission of the C–C bond,

$$CCl_3\text{-}CCl_3 \longrightarrow \cdot CCl_3 + \cdot CCl_3$$

followed by $$\cdot Cl + \cdot CCl_3 \longrightarrow CCl_4$$

or $$\cdot Cl + CCl_3\text{-}CCl_3 \longrightarrow CCl_4 + \cdot CCl_3$$

or $$\cdot CCl_3 + CCl_3\text{-}CCl_3 \longrightarrow CCl_4 + \cdot CCl_2\text{-}CCl_3$$

The absence of chloroform and benzotrichloride suggests that few $\cdot CCl_3$ radicals are formed and the reactions producing these radicals cannot be of importance.

The Preparation of 1,1,2,3,3-Pentachloropropane.

$$CHCl{=}CHCl + CHCl_3 \xrightarrow{AlCl_3} CHCl_2{-}CHCl{-}CHCl_2$$

The method[93] used was based on the reaction noted by Prins[83c] in 1914, and required mixing 90 gms. of dry 1,2-dichloroethylene with 225 gms. dry chloroform in a flask fitted with a reflux water condenser and electrical stirrer. 22 gms. of anhydrous, pulverised aluminium chloride in 15 mls chloroform, mixed with 90 gms. of sand, which had been washed with concentrated hydrochloric acid and water and dried over a Meker burner, were added to the reaction vessel and stirred while being gently heated on an isomantle to the boiling point. The mixture became black and viscous, accompanied by the evolution of much hydrogen chloride. The reaction was continued for 5 hours and after treatment with water and sodium carbonate, followed by removal of sodium aluminate, the organic liquid was separated and dried. Unreacted chloroform and dichloroethylene were distilled off and the residual higher boiling material subjected to fractional distillation under reduced pressure. The middle fraction boiled at 83.5°C/45 mm. and was almost pure by G.L.C. Yield 86 gms.

Purification.

Two 0.5 ml injections of the sym-pentachloropropane were passed through the G.L.C. column at a temperature of 130°C, 5.0 l N_2/hr.. The infrared spectrum was recorded (No. 2a) and

the refractive index was determined but was found to be slightly high when compared with the literature value:

value obtained, $n_D^{16.5} = 1.5142$; lit. value, $n_D^{16.5} = 1.5131$

The I.R. spectrum (No. 2a) shows absorptions for two types of C-H bond at 3010 cm^{-1} and 2960 cm^{-1}, the former twice as intense as the latter, which is consistent with the structure

$$CHCl_2-CHCl-CHCl_2$$

The intense bonds between 850 and 700 cm^{-1} are caused by C-Cl absorptions.

The Preparation of 1,1,2,2,3,3-Hexachloropropane.

This isomer of hexachloropropane[83] was prepared by dehydrochlorination of sym-pentachloropropane to 1,2,3,3-tetrachloroprop-1-ene, followed by chlorination of the double bond:

$$CHCl_2-CHCl-CHCl_2 + KOH\ (alc.) \longrightarrow CHCl=CCl-CHCl_2 + KCl + H_2O$$

$$CHCl=CCl-CHCl_2 + Cl_2 \longrightarrow CHCl_2-CCl_2-CHCl_2$$

(a) Preparation of 1,2,3,3-tetrachloroprop-1-ene[94].

21 gms. of potassium hydroxide (pellets) were refluxed in 200 mls alcohol until dissolved. After cooling, 81 gms. of pentachloropropane were added dropwise, the vigorous reaction being moderated by cooling in water. The mixture was refluxed at the boiling point for four hours and allowed to stand overnight.

After filtration of the solid potassium chloride and washing with water, the organic liquid was separated and dried with anhydrous calcium chloride. Examination by G.L.C. showed that about 30% reaction had occurred and that cis and trans isomers were formed. The alcoholic potassium hydroxide treatment was repeated and after working up, distillation yielded 15 gms. of the colourless tetrachloropropylene, containing a small quantity of the starting material. A considerable amount of unidentified high boiling material had also been formed.

(b) Chlorination.

Double the requisite amount of chlorine gas for 12 gms. tetrachloropropylene was absorbed in 150 mls. carbon tetrachloride.

The solution was illuminated with an Ozira lamp (rich in blue light), while a solution of the tetrachloropropylene in 10 mls carbon tetrachloride was added slowly with stirring, the reaction vessel being cooled in iced water. However, it was found that only a slow reaction occurred until the chlorination was carried out at room temperature in daylight.

The course of the reaction was followed by G.L.C., the double peak for the tetrachloropropylene isomers diminishing in size, while two new peaks, representing compounds of higher boiling point increased steadily, the second of these being approximately one-tenth the size of the first and of greater retention time.

The bulk of the carbon tetrachloride was distilled off leaving a colourless liquid with a camphor-like smell, containing small quantities of residual carbon tetrachloride, tetrachloropropylene, the major product of the reaction $CHCl_2-CCl_2-CHCl_2$, and a higher boiling component.

Purification: see p.81.

The Preparation of 1,1,1,2,3,3-Hexachloropropane.

Prins[83c] suggested two reactions:

(a) $$CHCl=CHCl + CCl_4 \xrightarrow{AlCl_3} CCl_3-CHCl-CHCl_2$$

(b) $$CHCl=CCl_2 + CHCl_3 \xrightarrow{AlCl_3} CHCl_2-CHCl-CCl_3$$

Reaction (a) was attempted because there should theoretically be only one product. This was found to be the case but its boiling point, as determined by Siwoloboff's micro-method, was found to be 260°-262°C and a carbon, hydrogen and chlorine analysis indicated a structure $C_6H_5Cl_8$ instead of a formula $C_3H_2Cl_6$ and boiling point of 216°C.

Reaction (b): 98.6 gms. trichloroethylene were added slowly with stirring to a mixture of 135 gms. chloroform (50% excess) and 22 gms. pulverised aluminium chloride. Gentle heating started the reaction which proceeded quietly for four hours, the solution turning a purple-red colour. After filtration and treatment with sodium carbonate solution, during which the colour

disappeared, the organic layer was removed, dried and excess chloroform distilled off under reduced pressure.

The residue was fractionated under reduced pressure into three fractions, the middle one, boiling at 86°/0.1 mm, was found to consist of three components, the second of which was present in greatest amount and believed to be the desired compound.

Purification.

G.L.C. analysis of the prepared isomers showed each to be accompanied by other higher or lower boiling impurities. Several 0.5 to 0.75 ml injections of each mixture were put through the column and the appropriate peak trapped out in each case, until 0.4 ml samples were built up. Each sample was passed through the column again before recording its physical properties. The infrared spectra, Nos. 3a and 3b, show a strong resemblance. The major C-Cl absorptions occurring between 900-700 cm^{-1} show a similar pattern but the maxima are slightly displaced either to higher or lower wavelengths; the asymmetrical isomer has a strong absorption at 1000 cm^{-1} while the symmetrical isomer absorbs strongly at 704 cm^{-1}, both of which are characteristic of the isomer concerned. The sym-isomer shows a single absorption at 3010 cm^{-1} characteristic of the C-H stretching in the group $-CHCl_2$ and the asym-isomer possesses absorptions at 3010 and 2960 cm^{-1} (cf. sym-pentachloropropane), consistent with a structure $CHCl_2-CHCl-CCl_3$. The refractive indices were:-

sym-hexachloropropane.	asym-hexachloropropane.
$n_D^{18} = 1.5267$	$n_D^{17} = 1.5282$
lit. value $n_D^{18} = 1.5262$	lit. value $n_D^{17} = 1.5250$

Agreement is less satisfactory in the second case.

SECTION III, IV and V.

The Irradiation of Mixtures of Hydrocarbons and Carbon Tetrachloride

SECTION III: Benzene and Carbon Tetrachloride

Appendix: Benzene-Chloroform and Benzene-Dichloromethane

SECTION IV: Cyclohexane and Carbon Tetrachloride

SECTION V:

(a) Acetylene and Carbon Tetrachloride

(b) Methylcyclopentane and Carbon Tetrachloride

Introduction.

The main features of the radiolysis of hydrocarbons have already been outlined in the General Introduction.

The radiation chemistry of aromatic hydrocarbons is distinguished by low yields of products, such as gases and polymer, and by the fact that the yield of polymer is about 10 times the yield of hydrogen, whereas in the irradiation of most saturated hydrocarbons, the yield of hydrogen is 2-3 times that of polymer. A characteristic feature of aromatic compounds is their relative stability to radiation and when mixed with other compounds, they sometimes appear to dissipate energy initially absorbed by these compounds thereby affording them a certain degree of protection. This stability of aromatic compounds does not, however, extend to resistance to attack by free radicals, for example, those formed in irradiated carbon tetrachloride.

Benzene resembles unsaturated aliphatic hydrocarbons in forming "polymer" on irradiation. This polymer, which is a viscous, yellow liquid and the main product of the radiolysis, contains aliphatic double bonds and increases in molecular weight as irradiation proceeds. Various workers[95, 96] have found $G(C_6H_6 \longrightarrow \text{polymer}) = 0.75\text{-}0.93$. Recently Gordon and colleagues[96] examined the composition of the polymer and found that the initial product contains diphenyl, phenylcyclohexene, phenylcyclohexadiene and bicyclic compounds in which neither ring is aromatic, hydro-

genated terphenyls and other polymeric material. There was no evidence of cyclic compounds with non-cyclic substituents.

The relatively high yield of polymer products is attributed to the preferential addition of hydrogen atoms and phenyl radicals to surrounding benzene molecules, rather than to dimerisation or hydrogen abstraction reactions yielding molecular hydrogen and other products. This is supported by the work of Burton and Lipsky,[61] who found that the radical yield in benzene was ~ 0.75, indicating that dissociative split into radical pairs does occur to a considerable extent, i.e.,

$$C_6H_6 \rightsquigarrow C_6H_6^{\ddagger} \longrightarrow \cdot C_6H_5 + \cdot H$$

and by evidence obtained from the radiolysis of aqueous solutions of benzene-d_6 or benzene in D_2O,[97] in which only a trace of HD is found, suggesting that the majority of hydrogen atoms produced in the radiolysis disappear almost entirely by immediate addition to surrounding benzene molecules,

$$H\cdot + C_6H_6 \longrightarrow \cdot C_6H_7$$

and not by dimerisation or the abstraction reactions,

$$H\cdot + C_6H_6 \longrightarrow H_2 + \cdot C_6H_5$$

$$\text{or } D\cdot + C_6H_6 \longrightarrow HD + \cdot C_6H_5, \text{ etc.}$$

Phenyl radicals, intermediate radical species and excited benzene molecules are also believed to be removed by a similar reaction to that outlined for the hydrogen atoms. Such scavenging processes by the benzene account satisfactorily for the partially hydrogenated nature of the polymer products; however, molecular

hydrogen is produced in the radiolysis of benzene in yields which are about 10% of the radical yields and if secondary reactions of hydrogen atoms are not responsible for the formation of the gaseous hydrogen, then non-radical processes such as,

$$C_6H_6^{**} \longrightarrow R' + H_2$$

$$\text{or } C_6H_6^{**} + C_6H_6 \longrightarrow R'' + H_2$$

must be important contributors.

Schuler[51] reached the same conclusion from studies on the irradiation of benzene containing 0.02 to 0.04 M iodine in which it was found that the yield of hydrogen was the same as that from pure benzene. Similarly, when oxygen is used as scavenger, only organic radicals, and not hydrogen atoms, are available for reaction with the added solute.

The radiation chemistry of cyclohexane is complex, despite the formation of only three major products. Although studied for many years, during the last decade intense interest has been shown in its irradiation and it is now one of the most widely studied organic compounds in radiation chemistry. In a recent paper,[98] Freeman has included a comprehensive list of previous publications on the radiolysis of cyclohexane.

The yield of hydrogen from pure cyclohexane (G = 5.5-5.8) is very sensitive to the presence of small quantities of solutes. As described earlier, Schoepfle and Fellows,[59] found that the hydrogen yield from cyclohexane containing benzene was appreciably

less than expected. This was the first indication that protection of one compound by another could occur and has been attributed to energy transfer from the cyclohexane to the benzene.

The effect of iodine on cyclohexane radiolysis is in some respects similar to the action of benzene.[99,100] At 10^{-3} M solute, $G_{(H_2)}$ = 5.3 and 4.7 for benzene and iodine respectively. With an increase in the concentration of the solutes, $G_{(H_2)}$ continues to fall rapidly and in the case of iodine at 10^{-2} M a minimum value of 3.8 is reached. If benzene, $\backsim 10^{-2}$ M, is added to cyclohexane containing this concentration of iodine, $G_{(H_2)}$ is found to increase at first, reaching a maximum of about 4.0 at a concentration of benzene = 10^{-2} M, and then rapidly decrease to 0.5 or less as 100% benzene is approached. The yields of cyclohexene, G = 2.28-2.50, and dicyclohexyl, G = 1.2-1.6, decrease rapidly at first with increase in benzene concentration and then more slowly;[98] the presence of quinone[101,102] likewise causes a decrease in the yields of hydrogen (to 2.1) and dicyclohexyl but not in cyclohexene. MacLachlan[103] found $G_{(C_6H_{10})}$ = 2.3 is reduced to 1.1 by 0.02 M iodine; similarly, 0.1 M benzyl chloride causes the same effect (G = 1.0) but the reduction is not linear with solute concentration, again a rapid decrease being followed by a slow decrease indicating at least two different processes leading to formation of cyclohexene.

From early work, Manion and Burton[60] concluded that the protective effect of benzene was due to energy transfer processes (sponge-type protection). Burton et al.[99] explained the results of the cyclohexane-benzene-iodine system on the basis that iodine acts not only as a radical scavenger but can prevent chemical reactions by interfering in the decomposition process of the excited species present. When cyclohexane is excited to a singlet state, then the reaction is

$$C_6H_{12}^{*} \longrightarrow \cdot C_6H_{11} + \cdot H$$

but if it is in a triplet state then

$$C_6H_{12}^{*} \longrightarrow C_6H_{10} + H_2$$

occurs. Iodine, in pure cyclohexane, promotes an internal conversion from triplet state to ground state and therefore suppresses the second reaction. Benzene, at low concentrations induces at least one reaction by which the singlet state is produced in cyclohexane instead of the triplet state. Therefore, in cyclohexane containing both iodine and benzene, the yield of hydrogen rises but as the concentration of benzene increases, the first reaction is also suppressed and the yield decreases.

Recently Freeman[98] has shown, by a complete study of all the products from the cyclohexane-benzene system and a steady-state treatment of the possible kinetic scheme, that the effect of benzene is two-fold, depending on concentration. At low benzene concentrations, where the electron fraction of the benzene is less than 0.05, rapid scavenging and/or energy transfer occurs

with a certain fraction of the hydrogen atoms and/or the excited cyclohexane species. At higher benzene concentrations, energy transfer protection seems to be the major effect of the benzene.

Further, the same author[104] has shown that two distinct reactive species appear to be important in the gamma radiolysis of cyclohexane (cf.Burton); one is C_6H_{12}'' (G = 3.0) and is subject to energy transfer protection by benzene, while the other C_6H_{12}' (G = 2.4) is not. It also appears that C_6H_{12}' decomposes to produce "cold" hydrogen atoms that can be scavenged by benzene

$$C_6H_{12}' \longrightarrow \cdot C_6H_{11} + \cdot H \text{ (cold)}$$

whereas C_6H_{12}'' decomposes to produce "hot" hydrogen atoms that cannot be scavenged by benzene

$$C_6H_{12}'' \longrightarrow \cdot C_6H_{11} + \cdot H \text{ (hot)}$$

or decomposes directly to produce molecular hydrogen

$$C_6H_{12}'' \longrightarrow C_6H_{10} + H_2$$

The rapid decrease in the hydrogen yield on addition of small amounts of benzene is attributed to the scavenging of the "cold" hydrogen atoms by benzene. The slower decrease at higher concentrations is due mainly to energy transfer protection of the species C_6H_{12}''. The same effects are produced when cyclohexene is used as scavenger.

The presence of quinone scarcely affects the yield of cyclohexene. Apparently it, unlike oxygen, is unable to interfere with the formation of this product, which may be produced, at least partly ($G < 1.0$), by the elimination of molecular hydrogen.[105]

The remainder of the cyclohexene is produced by a bimolecular process, probably the disproportionation of cyclohexyl radicals,

$$2 \cdot C_6H_{11} \longrightarrow C_6H_{10} + C_6H_{12}.$$

The yield of cyclohexene drops sharply with increase in cyclohexene concentration, so, either as a result of prolonged irradiation of cyclohexane or the irradiation of solutions of cyclohexene in cyclohexane, a steady state is reached where $G_{(C_6H_{10})} = 0$. Cyclohexene acts as a scavenger and in these scavenging reactions, destroys itself as well as its own precursors.

From the study of the effects of added solutes on the radiolysis of cyclohexane and from the radiolysis of cyclohexane and cyclohexane-d_{12} mixtures,[106] it would appear that up to about 25% of the reaction occurs by decomposition of excited cyclohexane molecules into hydrogen and cyclohexene. Benzene reduces the total yield of hydrogen isotopes without changing their ratio, supporting the view that it decreases both radical and non-radical processes.

Products of radical reactions account for 35-40% of the total and by inference, some undefined processes must be responsible for the remaining 30-35% of the products.

The radiation-induced chlorination of benzene appears to have been first carried out by Alyea[107] in 1930. He observed the formation of hexachlorocyclohexane from benzene saturated with chlorine gas exposed to α-radiation from radon. The same

system has been studied more recently and G-values in the order of thousands, referring to molecules reacted, have been reported. The product contains isomers of hexachlorocyclohexane and when the reaction is initiated by ultraviolet light the ratio of the isomers depends on the conditions under which the chlorination is carried out.[108] When carried out in carbon tetrachloride as solvent, the chlorination reaction is very much slower.

Kharasch[109] observed that carbon tetrachloride could be used as a radical chlorinating agent. In 1945, he reported the formation of 1,1,1,3-tetrachlorononane from octene-1 and carbon tetrachloride in the presence of peroxide initiators.

Zimin et al.,[110] in 1955, irradiated benzene and carbon tetrachloride solution with gamma rays and reported the formation of benzotrichloride, occurring in maximum yield, G = 0.45, in equimolar mixture; (compare with Table 6). The reactions were interpreted in terms of a free radical mechanism.

Benzene-carbon tetrafluoride mixtures have also been irradiated.[111] The main products detected were hydrogen fluoride, trifluoromethane, fluorobenzene and benzotrifluoride; the mechanism is unknown but is believed not to be free radical in nature.

In a recent paper, Chapiro et al.[112] describe the results obtained from a study of the gamma irradiation of benzene-chloroform and benzene-carbon tetrachloride solutions, each over the whole composition range and containing the radical scavenger

D.P.P.H. In the latter case, they found the free radical yield, G_R, was at a maximum in pure carbon tetrachloride ($\sim$20), the curve dropping sharply, as the amount of benzene increased, to form a S-shaped line, with the point of inflection at approximately equimolar composition, and after the slight rise in yield again towards higher benzene concentrations, a final rapid decrease in yield as the concentration of carbon tetrachloride decreased to zero. A similar curve was obtained with the benzene-chloroform solutions. The yields of radicals from the components of the mixture are not independent additive functions and the behaviour observed is attributed to the benzene exerting a protective effect, and the halogen compound, a sensitising action, on the system.

The present work carried out on the gamma irradiation of the benzene-carbon tetrachloride system is described in Section III.

It has been shown that the hydrogen atoms of cyclohexane are 6-7 x 10^2 more reactive to t-butoxy radicals than those of benzene[113] and 11 times more reactive than those of toluene towards chlorine atoms.[114]

The vapour phase chlorination of cyclohexane in sunlight has been studied by Nekrasova[115] who observed a 40% yield of the monochloro-compound but a slightly smaller yield (30%) when the reaction was carried out in the liquid phase at room temperature using an incandescent lamp. The formation of polychlorinated compounds was also noted.

In the presence of a catalytic amount of a decomposing organic peroxide, straight chain, cyclic or branched, saturated hydrocarbons and carbon tetrachloride undergo a hydrogen-halogen exchange chain-reaction yielding the monochloroalkane and chloroform.[90] Recently, DeTar and Wells[116] observed that, on producing hexyl radicals in the presence of cyclohexane and carbon tetrachloride as hydrogen and halogen donors, a reaction occurred in which the yields of chlorocyclohexane and chloroform were approximately equal and up to 20 times greater than the yield of n-hexyl chloride. Substituting benzene as hydrogen donor, neither chlorobenzene nor chloroform were formed. Similar behaviour is found in the gamma irradiation of cyclohexane-carbon tetrachloride solutions, described in Section IV.

Little work appears to have been carried out on the irradiation of mixtures of cyclohexane and chlorinated compounds. Swallow[117] found that the addition of 0.23 M hydrogen chloride to cyclohexane produced 25% more hydrogen than in pure cyclohexane and nearly 50% more free radicals. Chlorocyclohexane was formed as a major product. A similar effect is obtained using ultraviolet light instead of high energy radiation, suggesting that excited cyclohexane molecules may be transferring energy to the hydrogen chloride.

Forrestal and Hamill[118] have very recently irradiated cyclohexane-chloroform solutions over the whole range of concentrations and found that $G_{(HCl)}$ increases with halide concentration.

SECTION III.

THE IRRADIATION OF BENZENE-CARBON TETRACHLORIDE SOLUTIONS.

This system has been studied previously in the department by Miller[82] who carried out a qualitative analysis of the products formed in bulk irradiations of aerated equimolar benzene-carbon tetrachloride solutions and carbon tetrachloride containing 5% benzene by volume.

The compounds reported as being detected and identified in the equimolar solution were:-

(1) hydrogen chloride
(2) chloroform
(3) chlorobenzene
(4) hexachloroethane
(5) benzal chloride
(6) benzotrichloride
(7) diphenyl
(8) possibly tetrachlorocyclohexene
(9) hexachlorocyclohexane

The presence of much higher boiling material was noted.

The same compounds were detected in the 5% benzene solution, with the exception of chlorobenzene and benzal chloride; benzotrichloride and diphenyl, which were claimed to be major products in the equimolar solution, were reported as minor products in the latter solution, the major products now being hexachloroethane and higher boiling material. The identification of the products listed above was based on gas chromatographic procedures and comparison of the infrared spectra of product mixtures with synthetic mixtures or published data, except in the case of hexachloroethane which was isolated in a pure state. Quantitative data were obtained for the hydrogen chloride and chloroform in

the equimolar solution, $G_{(HCl)}$ = 3.1 and 3.8 and $G_{(CHCl_3)}$ = 0.4 and 0.5 being reported and $G_{(HCl)}$ = 2.1 in the case of the 5% benzene solution.

The object of the present work was to obtain G-values for all the identifiable products in solutions ranging in composition from 100% benzene to 100% carbon tetrachloride.

A set of sealed tubes of degassed benzene-carbon tetrachloride solutions were prepared, using B.D.H. Analar Benzene and May and Baker R-quality Carbon Tetrachloride "purified" by procedures previously used in the department i.e., shaking the benzene with concentrated sulphuric acid, water and then drying before distillation; fractional distillation of the P_2O_5-dried carbon tetrachloride.

The tubes were irradiated for 336 hours at a dose rate of 2.96×10^{16} eV/ml./min.

During the G.L.C.analysis of the concentrated residues, a peak was observed on the chromatogram that could not be attributed to any of the expected products. It appeared after tetrachloroethylene and chlorobenzene on a silicone elastomer column packing but between them on T.C.P.. G.L.C. comparison with C_8 hydrocarbons, such as styrene, ethyl benzene and o-xylene, which might have been formed by a reaction of a C_2 fragment and a benzene molecule, showed that none of these compounds were responsible. The halogen compound formed by the reaction of carbon tetrachloride and acetylene under the action of gamma rays

was likewise found to differ from the unidentified compound. (Details of this irradiation are given in Section V).

Further examination of the starting materials on a more sensitive G.L.C. unit revealed the presence of an impurity in the benzene which appeared to correspond to cyclohexane. The monochloro-compounds which might be expected as products from the irradiation of cyclohexane in carbon tetrachloride, include chlorocyclohexane and 1-chlorohexane, whose boiling points of 143° and 133°C respectively, are in the correct temperature range to result in their retention times being similar to those of chlorobenzene and the unidentified compound. However, comparison of the unknown compound with chlorocyclohexane (available commercially) and 1-chlorohexane (prepared by the action of phosphorus pentachloride on n-hexyl alcohol) on the two types of column packings employed, proved it to be different.

The marked influence of impurities on the radiolysis of organic systems is well known and the presence of a non-aromatic hydrocarbon in a medium containing only benzene as hydrogen donor would be expected to greatly facilitate hydrogen abstraction reactions resulting in an increase in the yield of hydrogen chloride and other products. The determination of the yields of chlorobenzene, hexachloroethane and benzotrichloride was, however, carried out for all the solutions, by procedures similar to those described in Section II (p.53) and the results are presented in the Appendix to this Section, since they cannot be

considered as representative of the benzene-carbon tetrachloride system. A comparison of these results with those presented in Table 6, obtained using absolutely pure materials, shows that the yield of hydrogen chloride was, in fact, almost twice that formed in the pure system and that the yields of the other compounds had been enhanced, as expected. The presence of the impurity explains the high results obtained by Miller for the yields of hydrogen chloride formed in the bulk irradiations.

The Irradiation of 2 litres Equimolar Benzene-Carbon Tetrachloride Solution.

In an attempt to further the identification of the unknown compound, 2 litres of equimolar solution were prepared and irradiated for 672 hours at a dose rate of 290 r/ml./min.

After irradiation, the solution was pale yellow with a pungent smell of hydrogen chloride. As the unchanged benzene and carbon tetrachloride were removed, accompanied by much hydrogen chloride, the solution became an intense golden yellow colour, finally yielding about 20 mls of brown residue, containing the same products as before.

By careful fractional distillation under reduced pressure, such that the oil bath temperature did not exceed 60°C, this first residue, after removal of further benzene and carbon tetrachloride, was divided into fractions, containing principally,

(a) Chlorobenzene and the unidentified compound

(b) Hexachloroethane

(c) Hexachloroethane and benzotrichloride

(d) Benzotrichloride and higher boiling material.

The unidentified compound in Fraction (a), of total volume 2 mls, was separated from the other components by means of the large scale G.L.C. unit, using the 3' column packed with 25% S.E. on 60-90 mesh firebrick, at a temperature of 48°C and nitrogen flow rate of 480 mls/min.

The compound was colourless and had a sweet smell similar to that of n-octane. The refractive index, at 25°C, was 1.4220. The Beilstein Halogen test indicated the presence of chlorine. The absorption maxima of the infrared spectrum are listed in Table 5, along with those of chlorocyclohexane and 1-chlorohexane included for comparison.

The compound is fully saturated. The absorptions noted at 1440 and 1380 cm^{-1} are attributed by Bellamy[119] to the $C-CH_3$ group and the absorption at 810 cm^{-1}, assuming it to be due to a C-Cl bond absorption, is higher than normal for a monochloro-compound (750-700 cm^{-1}), although in the spectra of some tertiary halides, chlorinated aromatics and dichloroethylene, absorption bands often appear between 800 and 900 cm^{-1}.

The $-(CH_2)_n-$ group ($n \geqslant 4$) appears to be absent as it absorbs strongly in the 750-720 cm^{-1} region, thus indicating a cyclic structure. The intense absorption at 1017 cm^{-1} is characteristic

TABLE 5.

Infrared Spectra.

s = strong, s-m = strong to medium, m = medium

m-w = medium to weak, w = weak.

Chlorocyclohexane	Irradiation Product	1-chlorohexane
		2975 s
2965 s		
	2945 s	2950 s
2880 s-m	2875 s-m	2880 s
1465 s-m	1460 s	1465 s-m
1453 s-m		1450 s-m
1440 s-m	1440 m	1435 m
	1430 m-w	
	1380 m	1380 m
1353 m-w		
1340 m-w	1340 w	1340 w
		1320 m-w
	1310 m-w	1310 m
	1290 m-w	1290 m
1270 s-m	1275 m-w	
1262 s-m		1265 m-w
	1257 m	
1215 s-m		
	1145 m-w	
1095 m-w	1090 m-w	
	1065 m-w	
1012 m-w	1017 s	
990 s-m		
	925 w	
887 s		
865 m-w		
855 m		
815 s		
808 m-w	810 s-m	
		755 s-m
727 s	* 725 m-w	
		720 m-w
675 m		
	* 650 m-w	

* poorly defined

of the cyclohexane ring structure and that at 1257 cm^{-1} can also be attributed to it; however, many cyclobutane and cyclopentane derivatives are also known to absorb in the region 1000-960 cm^{-1}, generally displaying a wide variation in the position of the band, and it might be that in this case, some interaction has raised the frequency of the absorption.

It would appear, therefore, that the compound is saturated, contains chlorine, a methyl group and probably has a cyclic structure. The results of two carbon and hydrogen analyses are shown below, but little further information is obtained since the analyses could equally correspond to the structure $C_6H_{11}Cl$ or $C_6H_{13}Cl$:-

Found:-

%C = 60.67	%H = 10.80	%Cl = 28.53
= 60.55	= 10.63	= 28.82

Calculated for a C_6-monochlorocycloalkane:-

%C = 60.76	%H = 9.34	%Cl = 29.89

Calculated for a C_6-monochloroalkane:-

%C = 59.75	%H = 10.86	%Cl = 29.40.

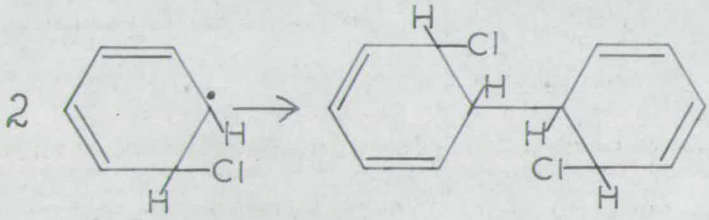
A preliminary irradiation of cyclohexane in carbon tetrachloride showed that no rearrangement reaction took place and only one monochloro-compound was formed, the expected chlorocyclohexane.

Despite the apparent non-agreement of the impurity in the benzene with methylcyclopentane on G.L.C., the presence of the methyl group prompted the irradiation of methylcyclopentane in carbon tetrachloride solution, details of which are described in Section V, but again no solution to the problem was forthcoming.

The identity of the impurity and its monochloro-derivative remain unsolved at present and perhaps the simplest way of tackling the problem would be to concentrate the impurity in a small volume of benzene by freezing (as described later) and isolate a pure sample by large scale G.L.C.

Fraction (d) of the residue.

An examination of this fraction, containing some benzotrichloride and the higher boiling products, showed that diphenyl, which was previously reported as a major product along with benzotrichloride in irradiated equimolar benzene-carbon tetrachloride solution, was barely detectable. Diphenyl could be formed during radiolysis either by dimerisation of phenyl radicals, phenyl radical attack on a benzene molecule followed by elimination of a hydrogen atom, or by dimerisation of chlorocyclohexadienyl radicals,



Subsequent heating of the C_{12} compound would probably be sufficient to cause elimination of a molecule of hydrogen chloride from each ring, with formation of diphenyl. This reaction would be expected

to proceed fairly readily since dehydrochlorination would restore aromatic character to the rings.

In order to discover whether diphenyl is a primary product of irradiation or produced by thermal decomposition during concentration of the residue, 5 mls of the residue were refluxed on an oil bath for periods of 20 or 30 minutes at increasing temperatures, 3-drop injections of the residue being made on a suitable G.L.C. column at the end of each period:

Period of Heating.	Temperature.	Peak.
20 minutes	100°C	Small, poorly defined.
20 "	140°C	no increase in size.
30 "	160°C	" "
30 "	175-180°C	" "
30 "	200-210°C	" "

In this way, diphenyl was shown not to be a product of a thermal decomposition reaction, and on further concentration of the 5 ml residue to approximately 1 ml, a larger peak was obtained which corresponded exactly with authentic diphenyl. Therefore, diphenyl is a primary product of the irradiation of an equimolar benzene-carbon tetrachloride solution, but is formed in extremely small yield, contrary to previous belief, and is detectable only after concentration of the residue to small volume.

The Irradiation of Degassed Solutions of Benzene and Carbon Tetrachloride.

Purification.

(1) Benzene:- B.D.H. Benzene for Molecular Weight Determinations was shown by G.L.C. analysis on a T.C.P. column at 70°C, to contain a trace of the unidentified impurity. It was found that the compound could be removed by freezing a volume of benzene (F.P. 5.5°C) slowly in an ice-salt freezing mixture to about four-fifths solid, decanting the residual liquid, melting the frozen benzene and repeating the cycle of freezing, decanting and melting four times. The course of the purification was followed by G.L.C. and by observing the rise in the freezing point on a Beckmann Thermometer at each stage until it became constant. The purified benzene was then dried for several days with anhydrous calcium chloride and sodium sulphate before being distilled in a stream of oxygen-free nitrogen, the first and last 10% portions being discarded.

Refractive index, $n_D^{20} = 1.5010$; (lit. value, $n_D^{20} = 1.5011$)

(2) Carbon Tetrachloride:- May and Baker R-quality carbon tetrachloride contained traces of dichloromethane and chloroform which were removed by slow fractional distillation, using a 4', 20 mm diameter column packed with Stedman stainless steel gauze rings, surrounded by an electrically heated jacket. The rate of distillation was controlled by an adjustable take-off head and the distillate was monitored by G.L.C. at 50°C. The purification

of 1500 mls carbon tetrachloride normally required 30-36 hours distillation at a take-off rate of approximately 5 mls per hour. A typical G.L.C. chart showing the change in composition of the distillate is shown in Figure 4; (full-scale deflection = 500 μV). The purified material was then stored over anhydrous calcium chloride and finally distilled rapidly in an atmosphere of nitrogen before use. Phosphorus pentoxide was not used as a drying agent as it was found that hydrogen chloride was formed after standing for a few days.

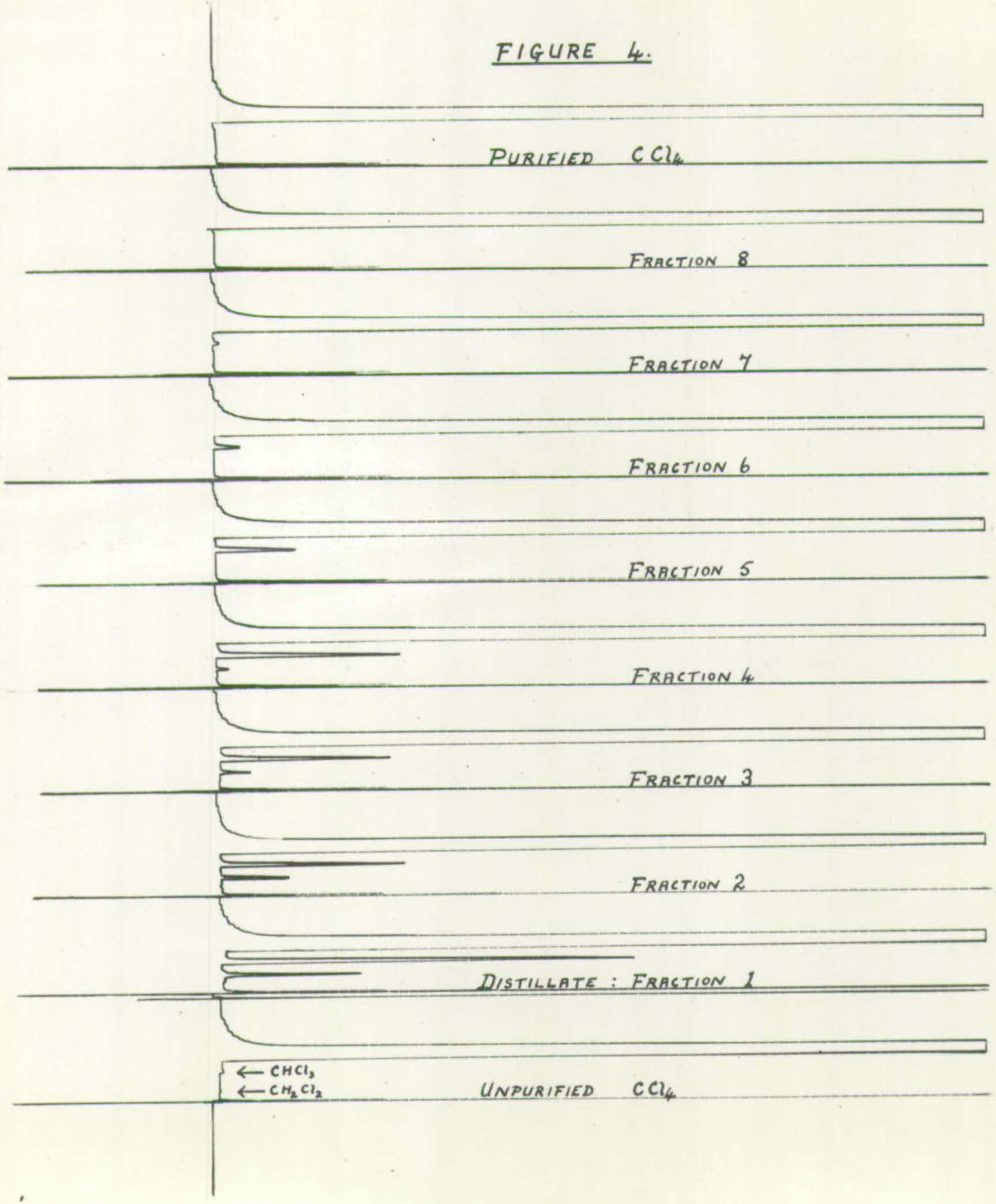
Refractive index, $n_D^{20} = 1.4602$; lit. value, $n_D^{20} = 1.4602$-4

The preparation of the tubes and the degassing procedure have already been described.

After irradiation, the yield of chloroform in a tube was measured as soon as it was opened by making a direct injection of the solution by means of the 27 μl pipette on the 3'6" S.E./Celite column at 50°C, immediately before determining the hydrogen chloride. Although small peaks were produced, this method was adopted in preference to attempting to concentrate the chloroform (after removal of the hydrogen chloride) by fractional distillation using the 4' Stedman ring column, since only 75-80% recovery was achieved with trial solutions of chloroform in carbon tetrachloride, presumably due to the volatile nature of chloroform.

The hydrogen chloride and other organic products were determined by the general methods described in Section II pp. 52-54, 5 ml graduated flasks being used for the residues. A 3'6" column

FIGURE 4.


PURIFIED CCl_4
FRACTION 8
FRACTION 7
FRACTION 6
FRACTION 5
FRACTION 4
FRACTION 3
FRACTION 2
DISTILLATE : FRACTION 1
← $CHCl_3$
← CH_2Cl_2
UNPURIFIED CCl_4

of 30% W/W silicone elastomer on celite (60-90 mesh) was used at suitable temperatures for the measurement of all the products, except diphenyl which was measured on a similar 2' column at 140°C, 115 mls H_2/min. flow rate.

The electron density of benzene, $N_e(C_6H_6) = \frac{0.8790}{78.10} \times N \times 42 = \underline{0.4726 \times N}$

and of carbon tetrachloride, $N_e(CCl_4) = \frac{1.5940}{153.8} \times N \times 74 = \underline{0.7670 \times N}$

The electron density of each solution was calculated by use of the equation on p. 12. For an equimolar solution of benzene and carbon tetrachloride, $N_e = 0.6261 \times N$, and hence the energy absorbed per ml. per minute by the organic solution, i.e., the rate of absorption of energy by the organic solution

= dose rate, as measured by the Fricke dosimeter, $\times \frac{0.6261 \times N}{0.5675 \times N}$

= dose rate x 1.104 eV/ml/min.

Similarly, the dose rate conversion factor for a solution containing 20 m% benzene - 80 m% carbon tetrachloride is 1.254.

The yields and G-values obtained from the irradiation of a set of tubes of different molar composition, all irradiated for the same period, are detailed in Table 6 and Graphs 2,2a and 3, followed, in Tables 7 and 8 and Graphs 4, 5 and 6, by those for two sets of tubes, of equimolar and 20 m% C_6H_6/80 m% CCl_4 composition respectively, the tubes of which received progressively increasing doses.

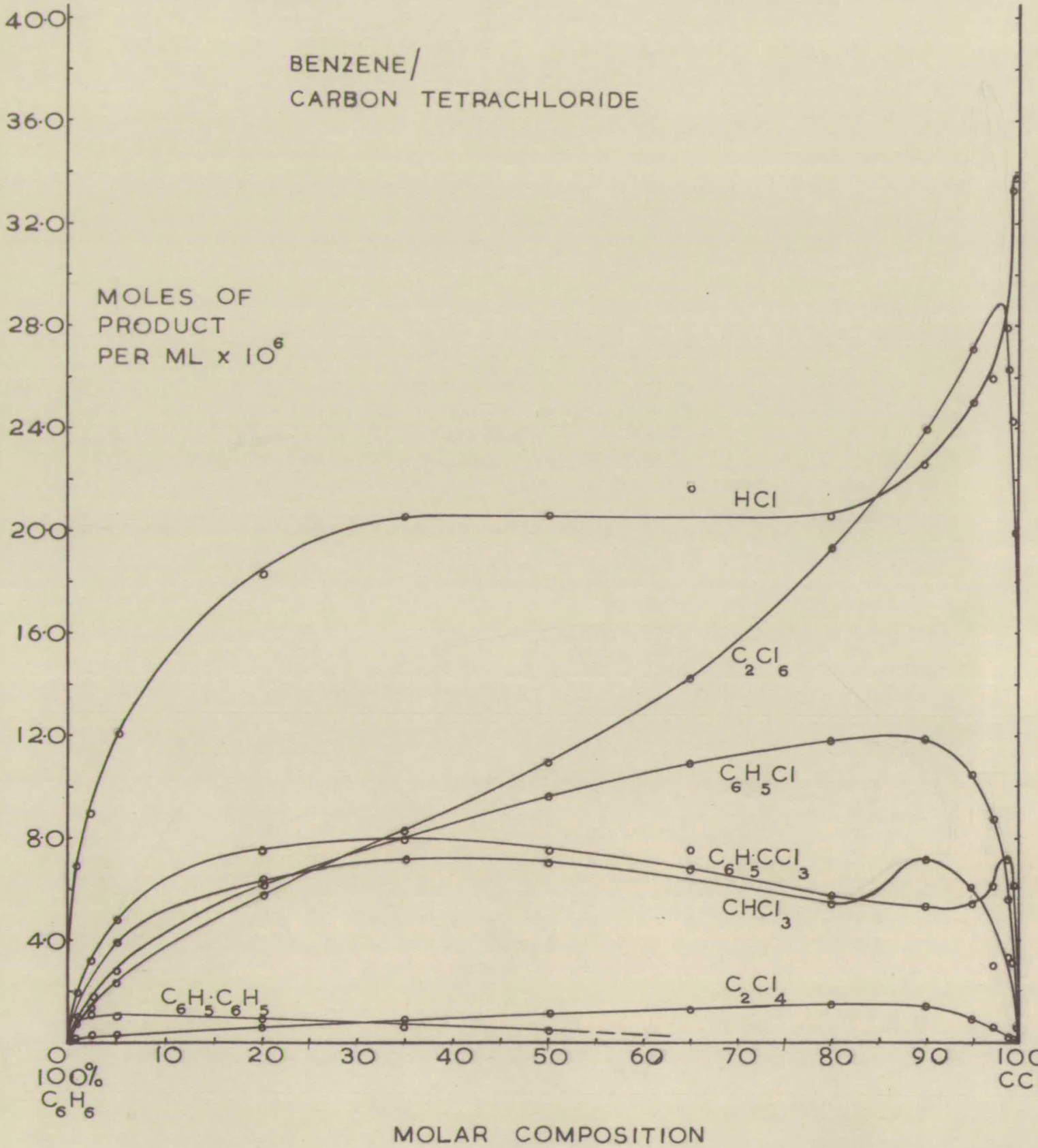
TABLE 6

RESULTS FROM THE IRRADIATION OF BENZENE-CARBON TETRACHLORIDE SOLUTIONS

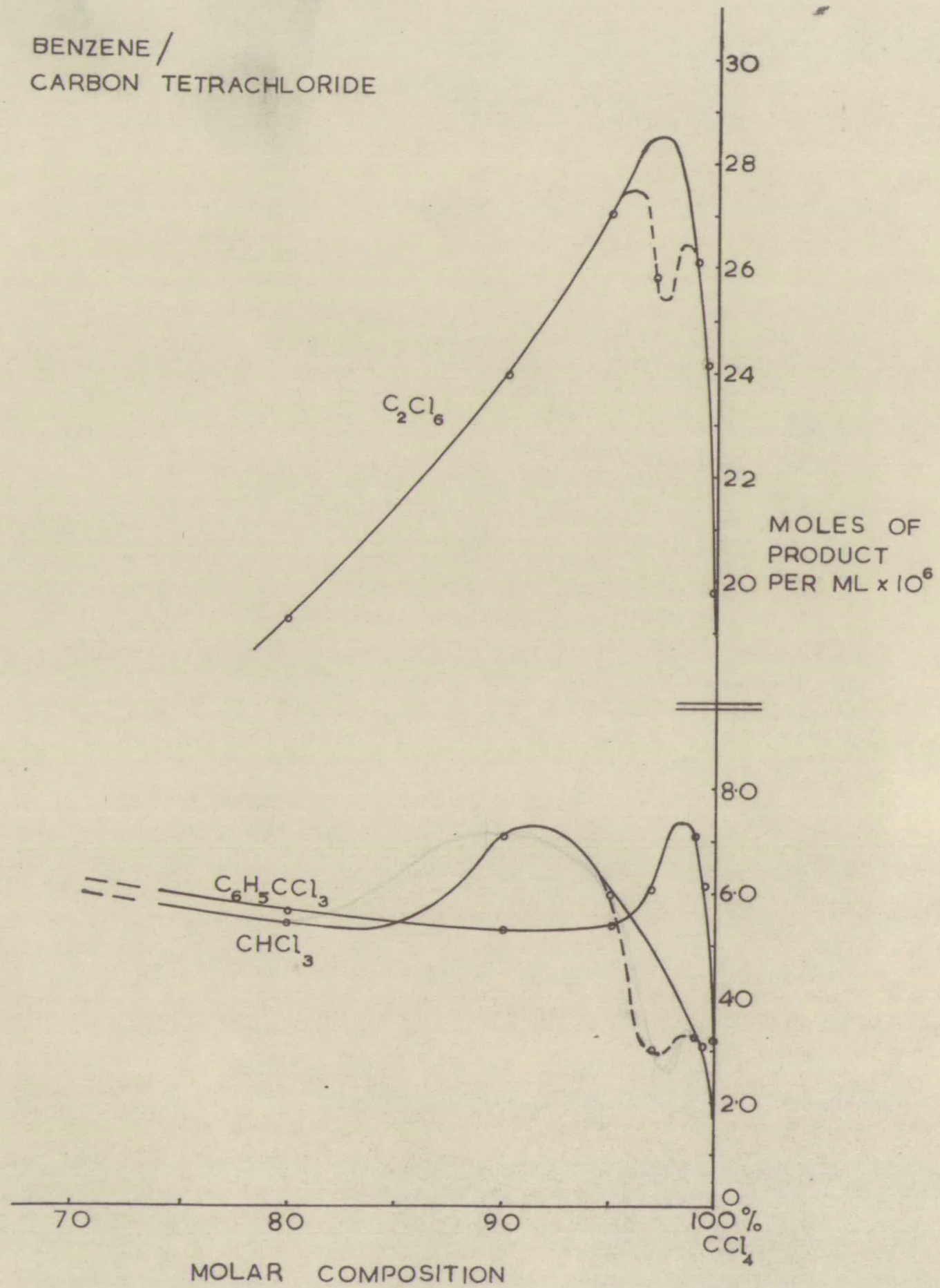
DOSE RATE = 2.82×10^{16} eV/ml/min.; IRRADIATION TIME = 336 Hours

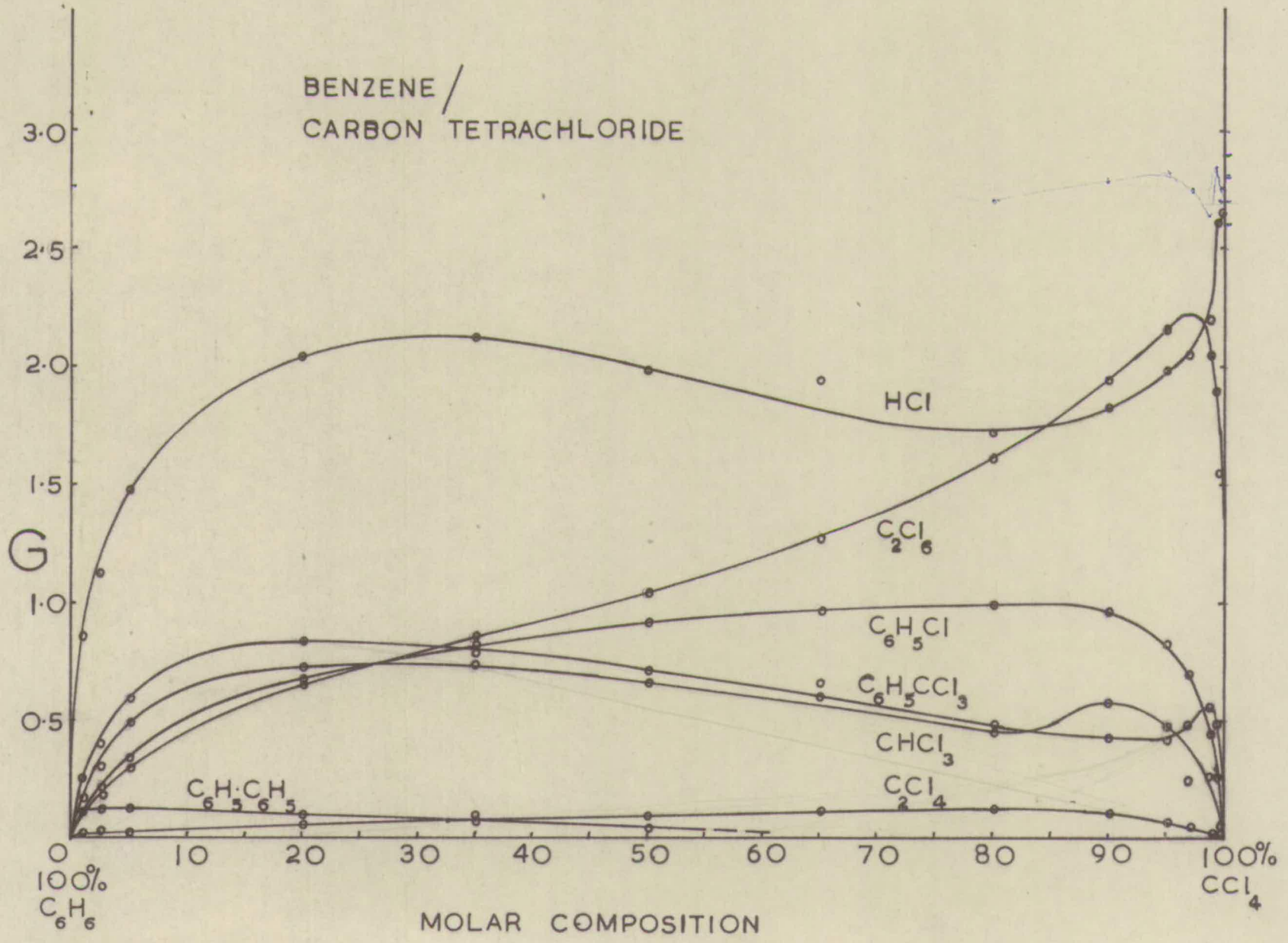
Mole % CCl_4	VOL. IRR.	HCl		$CHCl_3$		$CCl_2=CCl_2$		C_6H_5Cl		C_2Cl_6		$C_6H_5CCl_3$		$C_6H_5-C_6H_5$	
		Moles/ml $\times 10^5$	G	Moles/ml $\times 10^6$	G	Moles/ml $\times 10^6$	G	Moles/ml $\times 10^6$	G	Moles/ml $\times 10^6$	G	Moles/ml $\times 10^6$	G	Moles/ml $\times 10^6$	G
1.0	82	0.68	0.86			0.14	0.02	0.78	0.10	0.77	0.10	1.97	0.25	0.91	0.12
2.5	84	0.90	1.12			0.19	0.02	1.76	0.22	1.41	0.18	3.13	0.39	1.00	0.13
5.0	83	1.20	1.48	3.91	0.48	0.24	0.03	2.78	0.34	2.34	0.29	4.78	0.59	1.05	0.13
20	82.5	1.82	2.04	6.20	0.70	0.57	0.06	6.07	0.68	5.73	0.64	7.36	0.83	0.93	0.10
35	82	2.05	2.12	7.03	0.73	0.83	0.09	7.85	0.81	8.16	0.85	7.88	0.82	0.72	0.07
50	80	2.06	1.98	6.99	0.67	1.08	0.10	9.58	0.92	10.90	1.05	7.46	0.72	0.54	0.05
65	81	2.17	1.95	7.45	0.67	1.33	0.12	10.80	0.97	14.08	1.26	6.80	0.61		
80	83	2.04	1.72	5.39	0.46	1.46	0.12	11.66	0.99	19.23	1.26	5.67	0.48		
90	81	2.25	1.83	7.09	0.58	1.38	0.11	11.82	0.96	23.93	1.95	5.29	0.43		
95	84	2.50	1.99	5.98	0.48	0.90	0.07	10.41	0.83	27.05	2.16	5.39	0.43		
97	80.5	2.59	2.05	2.99	0.24	0.62	0.05	8.73	0.69	25.86	2.05	6.06	0.48		
99.0	81.5	2.78	2.19	3.30	0.26	0.19	0.02	5.55	0.44	26.16	2.06	7.11	0.56		
99.50	79.5	3.33	2.61	3.12	0.25	0.15	0.01	3.09	0.24	24.19	1.90	6.14	0.48		
99.95	83	3.38	2.65			0.10	0.01	0.59	0.05	19.79	1.55	3.13	0.25		

GRAPH 2


BENZENE/
CARBON TETRACHLORIDE
MOLES OF PRODUCT PER ML x 10^6
40·0
36·0
32·0
28·0
24·0
20·0
16·0
12·0
8·0
4·0
HCl
C2Cl6
C6H5Cl
C6H5CCl3
CHCl3
C2Cl4
C6H5·C6H5
0
10
20
30
40
50
60
70
80
90
100%
100% C6H6
CCl4
MOLAR COMPOSITION

GRAPH 2a


BENZENE /
CARBON TETRACHLORIDE
30
28
26
24
22
20
8·0
6·0
40
2·0
0
C_2Cl_6
$C_6H_5CCl_3$
$CHCl_3$
MOLES OF PRODUCT PER ML x 10^6
70
80
90
100 % CCl_4
MOLAR COMPOSITION


BENZENE /
CARBON TETRACHLORIDE
3·0
2·5
2·0
1·5
1·0
0·5
G
HCl
C_2Cl_6
C_6H_5Cl
$C_6H_5CCl_3$
$CHCl_3$
CCl_4
$C_6H_5C_6H_5$
0
100%
C_6H_6
10
20
30
40
50
60
70
80
90
100%
CCl_4
MOLAR COMPOSITION

GRAPH 3

TABLE 7

RESULTS FROM THE IRRADIATION OF EQUIMOLAR BENZENE-CARBON TETRACHLORIDE SOLUTIONS

DOSE RATE = 2.821×10^{16} eV/ml/min.; CONVERSION FACTOR = 1.104; DOSE RATE ABS. by ORG. SOLUTION = 3.113×10^{16} eV/ml/min.

VOL. IRR.	TIME HOURS	DOSE ABS. by SOLN.: eV/ml	HCl		C_6H_5Cl		C_2Cl_6		$C_6H_5CCl_3$	
			moles/ml $\times 10^5$	G	moles/ml $\times 10^6$	G	moles/ml $\times 10^6$	G	moles/ml $\times 10^6$	G
80	96	1.79×10^{20}	0.61	2.07	2.52	0.85	3.27	1.10	2.06	0.69
82	144	2.69×10^{20}	0.90	2.02	4.02	0.90	4.94	1.11	3.13	0.70
84	240	4.48×10^{20}	1.46	1.96	6.73	0.91	7.97	1.07	5.31	0.71
83.5	336	6.28×10^{20}	2.04	1.96	9.30	0.89	10.95	1.05	7.27	0.70
78	480	8.97×10^{20}	2.82	1.90	13.68	0.92	15.64	1.05	10.62	0.71
$G_{(initial)}$				2.08		0.90		1.12		0.70

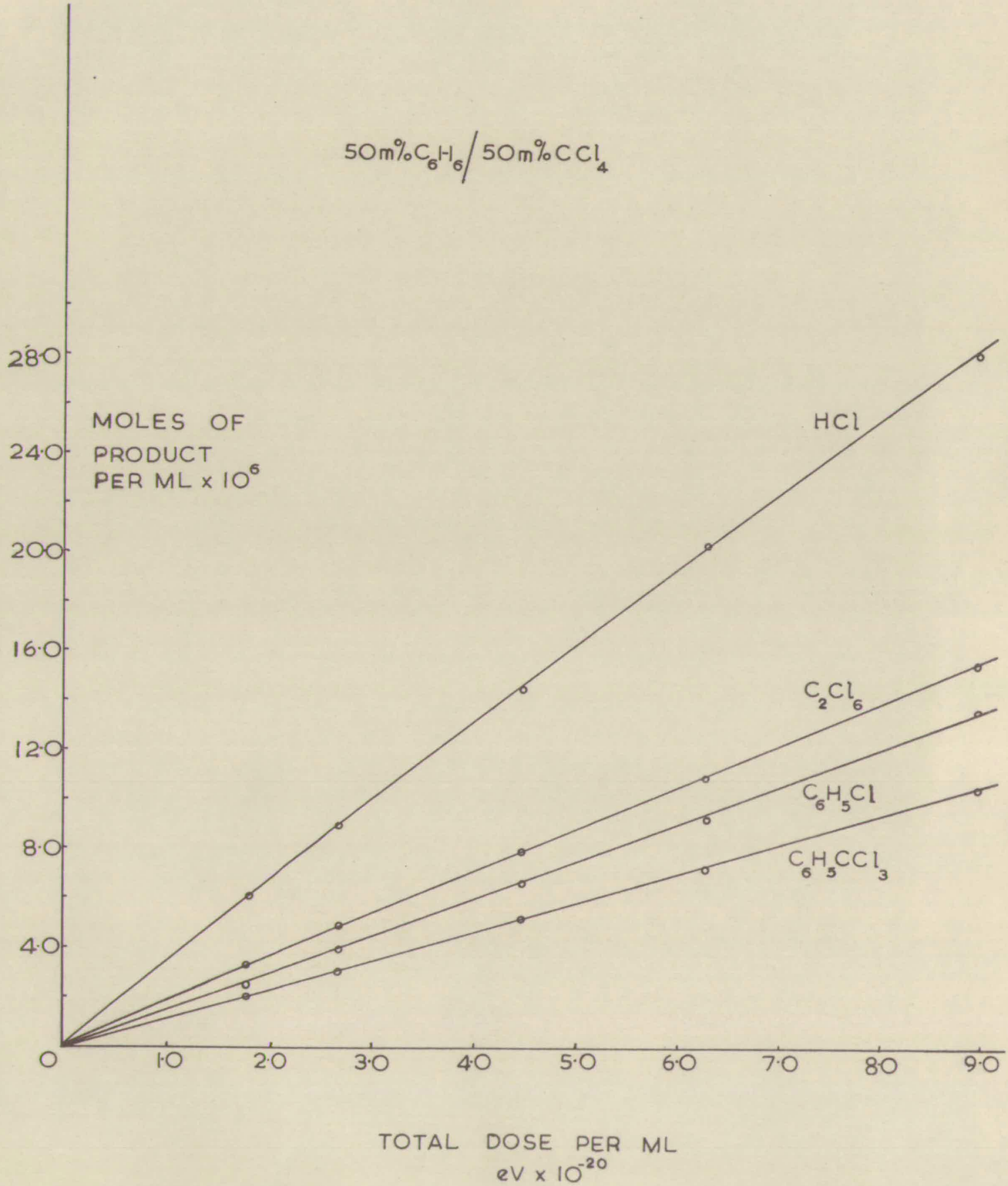
TABLE 8

RESULTS FROM THE IRRADIATION OF 20 mole% BENZENE - 80 mole% CARBON TETRACHLORIDE SOLUTIONS

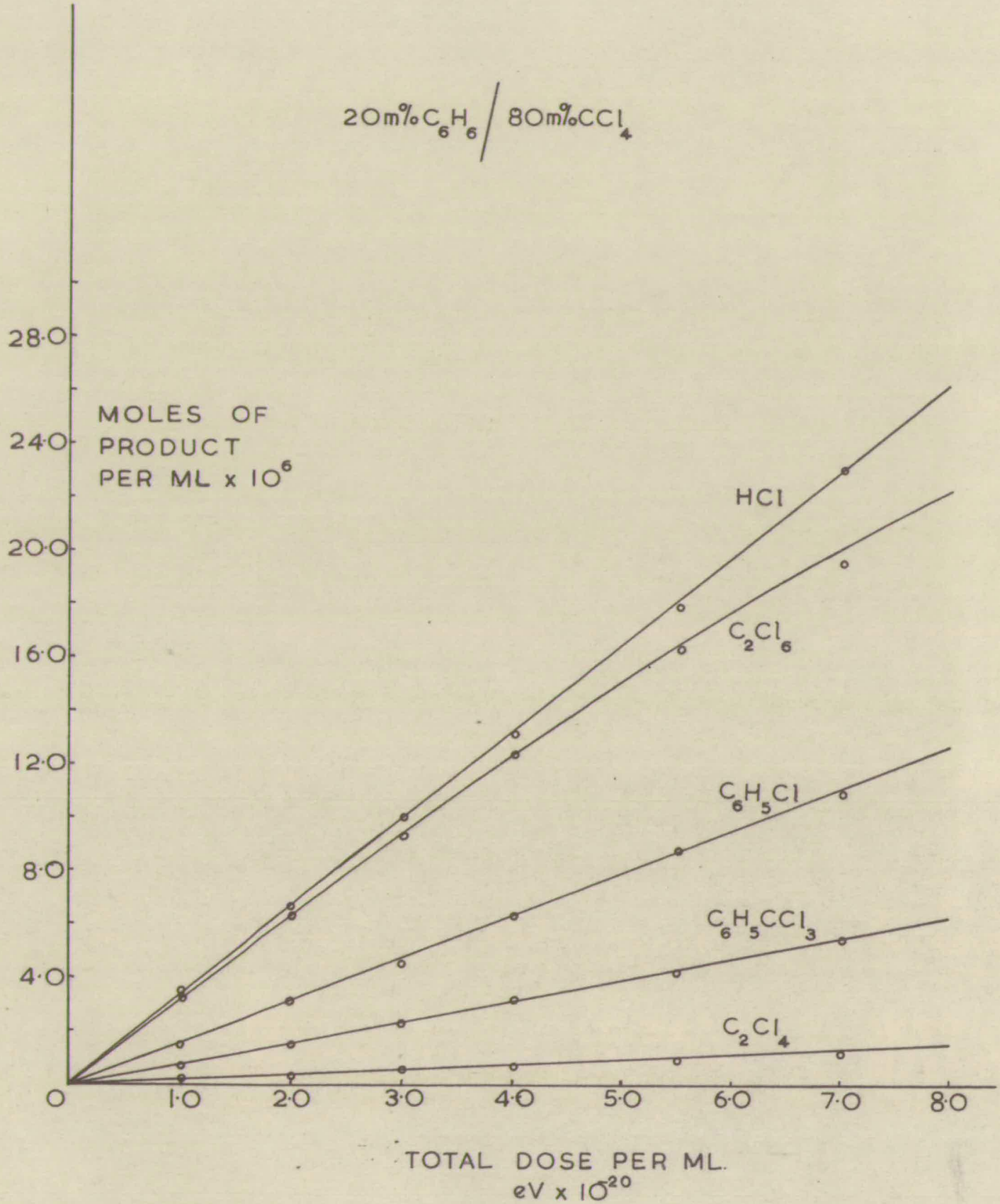
DOSE RATE = 2.787×10^{16} eV/ml/min.; CONVERSION FACTOR = 1.254; DOSE RATE (ORG. SOLUTION) = 3.494×10^{16} eV/ml/min.

VOL. IRR.	TIME HOURS	DOSE ABS. by SOLN.; eV/ml.	HCl		C_2Cl_4		C_6H_5Cl		C_2Cl_6		$C_6H_5CCl_3$	
			moles/ml $\times 10^5$	G	moles/ml $\times 10^6$	G	moles/ml $\times 10^6$	G	moles/ml $\times 10^6$	G	moles/ml $\times 10^6$	G
78	48	1.007×10^{20}	0.36	2.17	0.16	0.09	1.58	0.94	3.25	1.94	0.68	0.40
84	96	2.013×10^{20}	0.68	2.02	0.35	0.11	3.10	0.93	6.43	1.92	1.50	0.45
83	144	3.019×10^{20}	1.01	2.01	0.59	0.12	4.56	0.91	9.31	1.86	2.41	0.48
82	192	4.025×10^{20}	1.31	1.96	0.78	0.12	6.35	0.95	12.41	1.86	3.25	0.49
83.5	264	5.535×10^{20}	1.79	1.94	1.00	0.11	8.89	0.97	16.44	1.79	4.33	0.47
80	336	7.044×10^{20}	2.32	1.98	1.29	0.11	10.93	0.93	19.63	1.68	5.53	0.47
$G_{(initial)}$				2.07		0.11		0.94		1.98		0.47

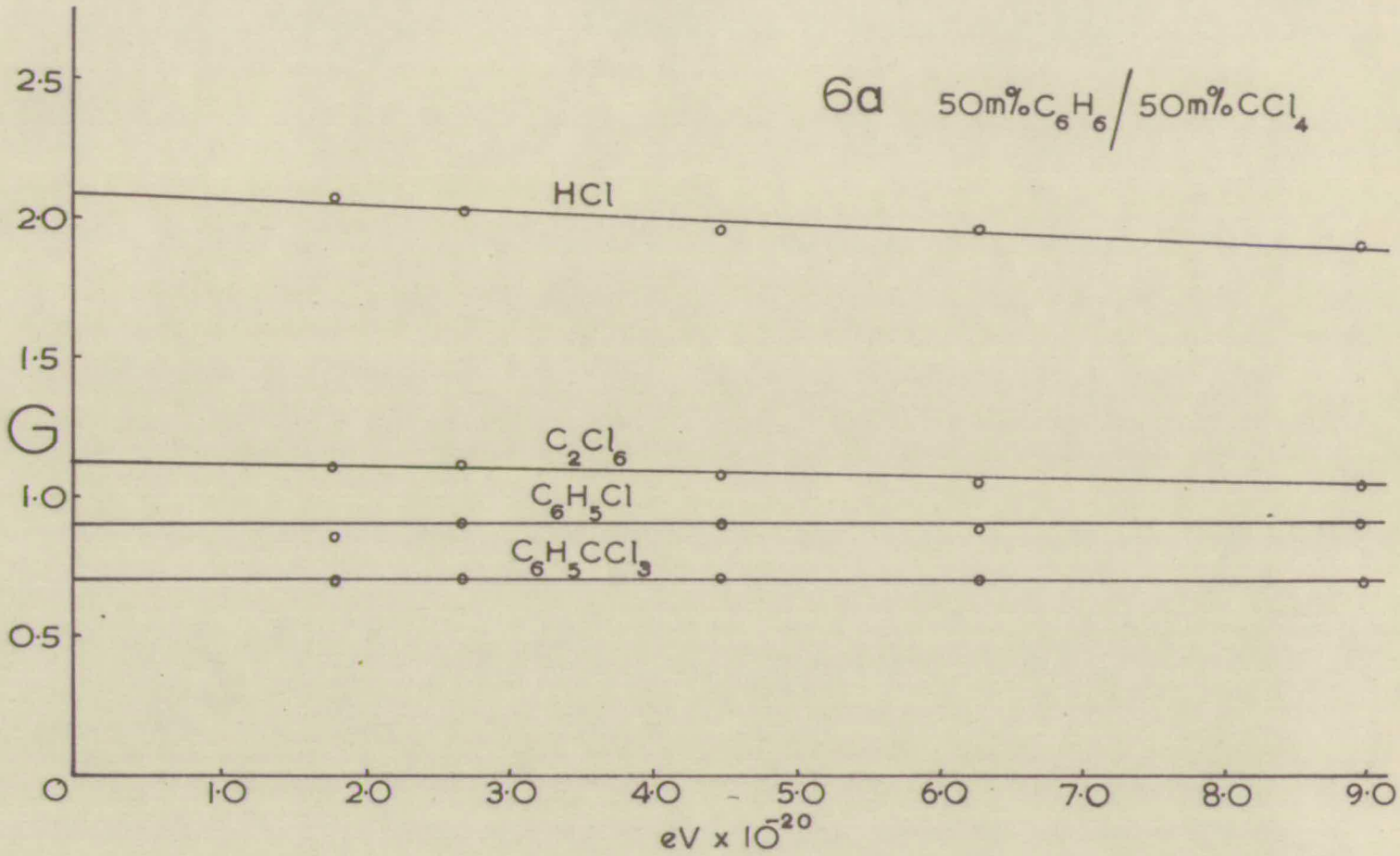
GRAPH 4

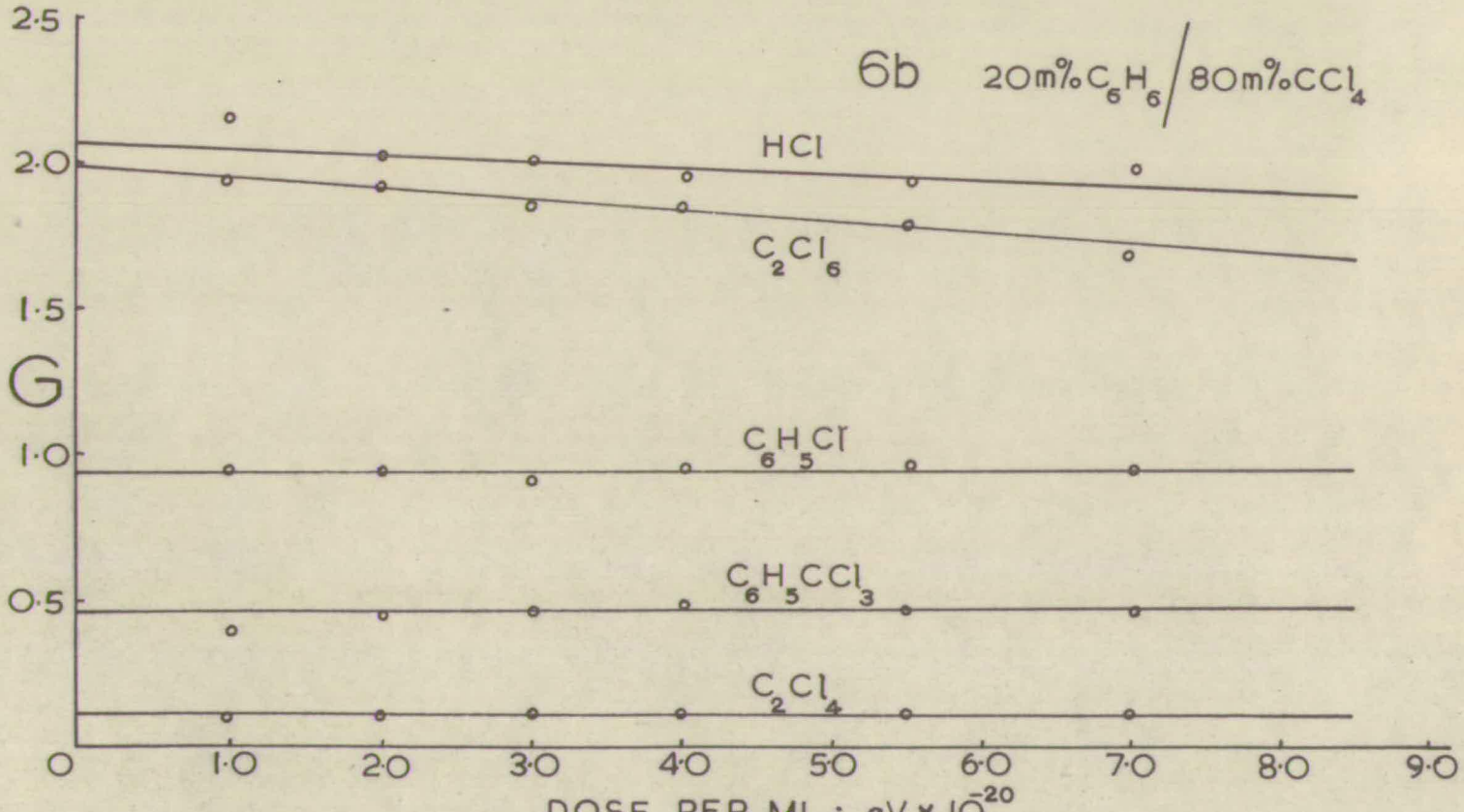

50m%C6H6/50m%CCl4
MOLES OF PRODUCT PER ML x 10^6
28·0
24·0
20·0
16·0
12·0
8·0
4·0
0
1·0
2·0
3·0
4·0
5·0
6·0
7·0
8·0
9·0
HCl
C2Cl6
C6H5Cl
C6H5CCl3
TOTAL DOSE PER ML
eV x 10^-20

GRAPH 5


20m% C_6H_6 / 80m% CCl_4
MOLES OF PRODUCT PER ML x 10^6
28·0
24·0
20·0
16·0
12·0
8·0
4·0
0
1·0
2·0
3·0
4·0
5·0
6·0
7·0
8·0
HCl
C_2Cl_6
C_6H_5Cl
$C_6H_5CCl_3$
C_2Cl_4
TOTAL DOSE PER ML.
eV x 10^{20}

GRAPH 6


6a 50m%C6H6/50m%CCl4
HCl
C2Cl6
C6H5Cl
C6H5CCl3
G
2·5
2·0
1·5
1·0
0·5
0
1·0
2·0
3·0
4·0
5·0
6·0
7·0
8·0
9·0
eV x 10-20


6b 20m%C6H6/80m%CCl4
HCl
C2Cl6
C6H5Cl
C6H5CCl3
C2Cl4
G
2·5
2·0
1·5
1·0
0·5
0
1·0
2·0
3·0
4·0
5·0
6·0
7·0
8·0
9·0
DOSE PER ML : eV x 10-20

Measurement of Compounds less volatile than Diphenyl.

The presence of higher boiling material, which was eluted from the column a considerable time after diphenyl, was observed in all the residues. Since the material was so involatile and its composition unknown, gas chromatographic procedures were of no further assistance.

In order to ascertain the weight of higher boiling material formed in each tube and the percentage of the total product which it represented, a 2.0 ml sample of each 5.0 ml residue was pipetted into the cup of a cup-still molecular distillation unit and heated in an oil bath at 40-45°C at 0.01 mm Hg. pressure for 30 minutes. Preliminary experiments had shown that a solution of benzene containing chlorobenzene, hexachloroethane, benzotrichloride and diphenyl, heated at 40°C/0.01 mm Hg. pressure for 15 minutes was sufficient to reduce the cup to its initial weight, provided care was taken to remove all oil and grease from the exterior. It was found desirable, firstly, to remove the low boiling solvent (benzene) by water pump and gradually raise the temperature until all dissolved air and low boiling compounds had been removed. The unit was then connected to a rotary oil pump for 30 minutes. G.L.C. analysis of the discarded residues showed that heating for this time was necessary to remove the benzotrichloride and diphenyl from the viscous liquid. It was not easy to judge when all the compounds measured by G.L.C. had been removed, but approximately constant weight was obtained under these conditions. By

standardising the time and temperature of distillation, the relative yields are considered to be comparable but the absolute weights may be correct to ± 10%.

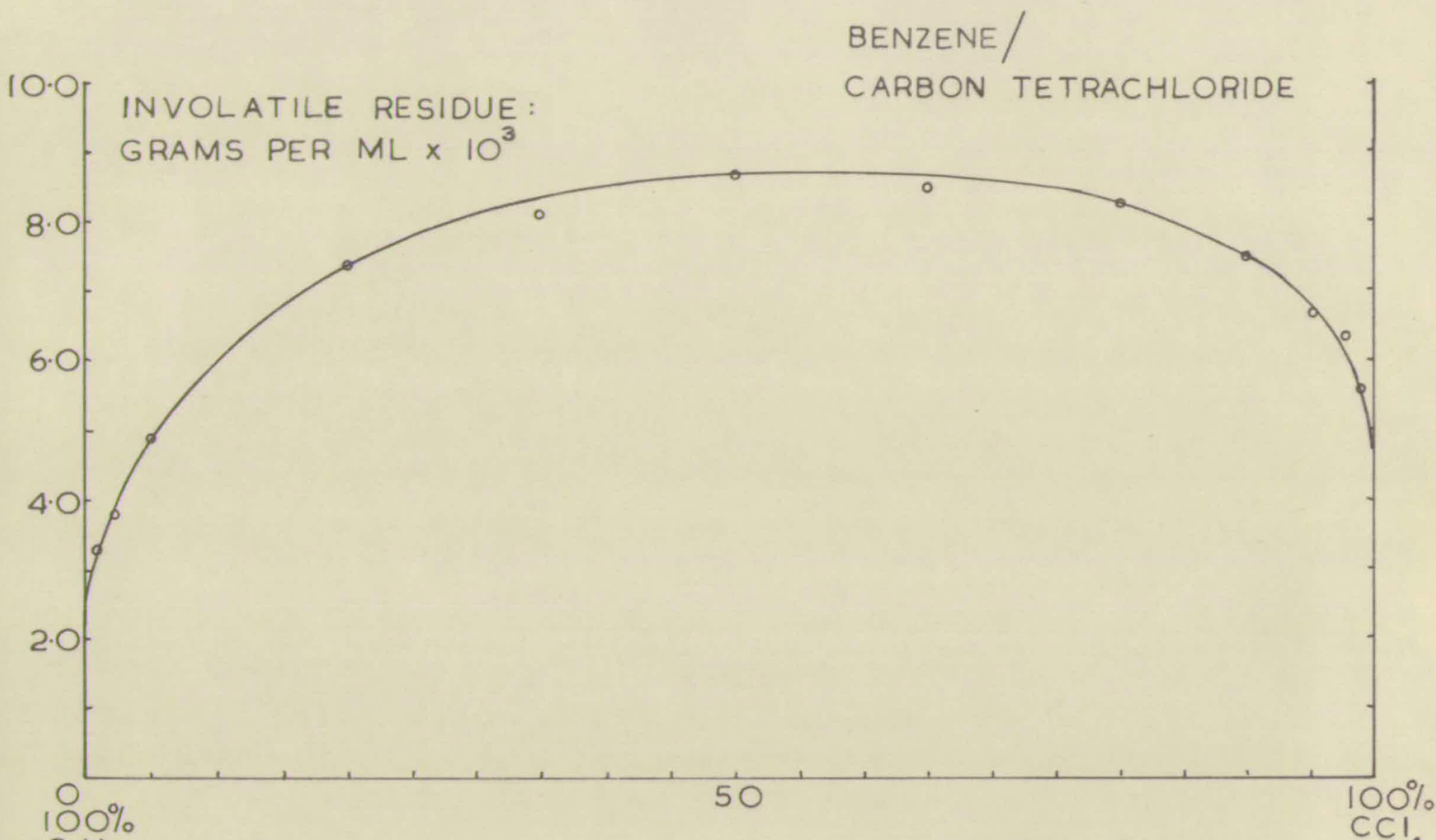
See Table 9 (below) and Graph 7.

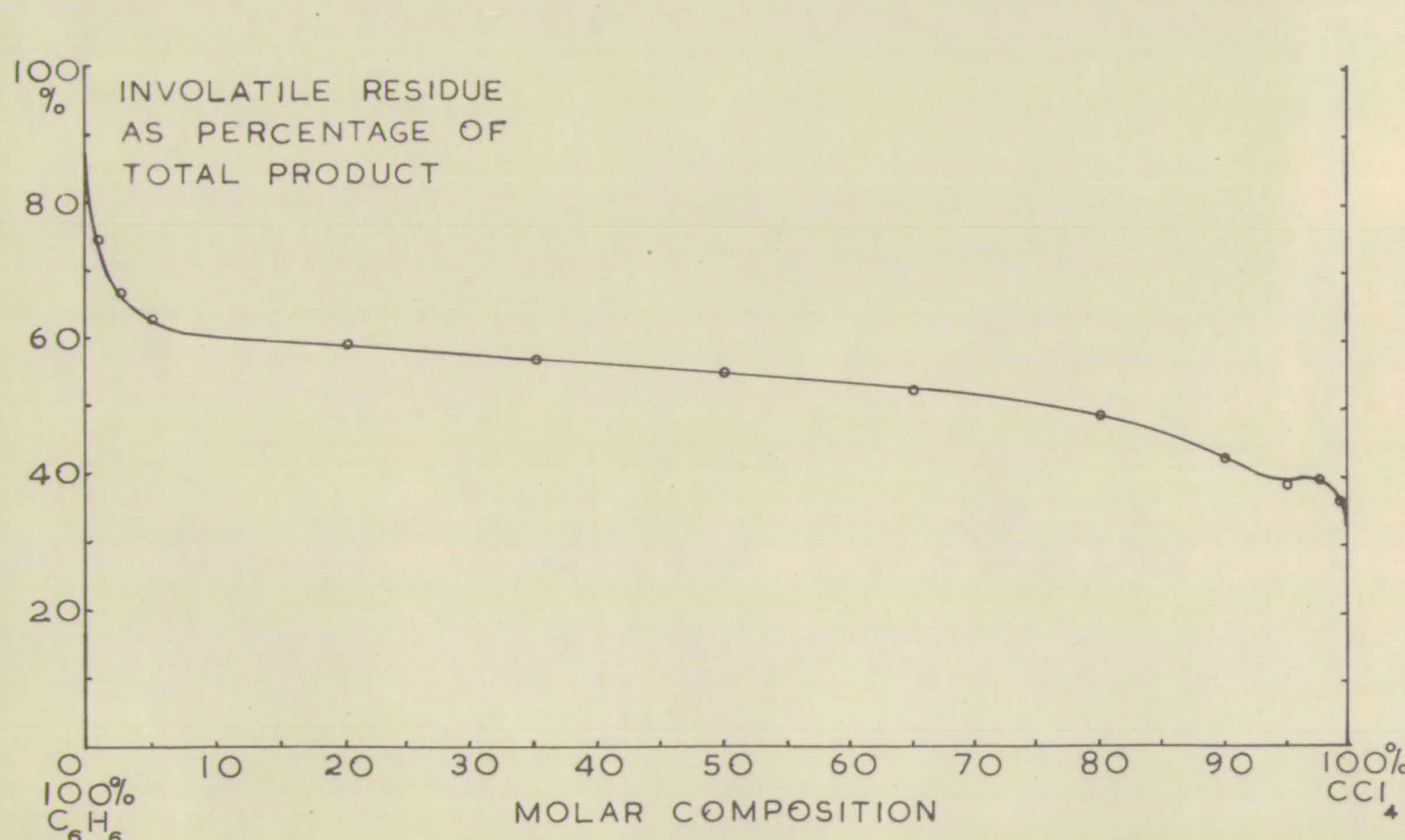
Mole % CCl_4	Vol. Irr. mls	Residue in 2 mls; gms	Residue in Vol. Irr.; gms	Residue per ml; gms x 10^3	Volatile Products per ml; gms x 10^3	Residue as % of Total Product
1.0	82	0.108	0.270	3.3	1.13	74.5
2.5	84	0.128	0.320	3.8	1.90	66.7
5.0	83	0.164	0.410	4.9	2.91	62.7
20	82.5	0.246	0.615	7.4	5.12	59.1
35	82	0.267	0.667	8.1	6.19	56.7
50	80	0.279	0.697	8.7	6.97	55.5
65	81	0.276	0.690	8.5	7.78	52.2
80	83	0.274	0.685	8.3	8.61	49.1
90	81	0.242	0.605	7.5	9.93	43.0
95	84	0.228	0.570	6.7	10.41	39.2
97	80.5	0.206	0.515	6.4	9.70	39.8
99.0	81.5	0.184	0.460	5.6	9.65	36.7

The curve for the yield of involatile material, as a function of molar composition, passes through a smooth maximum in the region of 50 m% benzene, but the yield, expressed as a percentage of the total irradiation yield, decreases rapidly with addition of up to 5 m% carbon tetrachloride, but thereafter, only very slowly with further large increases in the percentage of carbon tetrachloride showing that, as in the case of the pure hydrocarbon,

high boiling material is a major product of the radiolysis but, in this system, represents a smaller percentage of the total product.

GRAPH 7


BENZENE/
CARBON TETRACHLORIDE
INVOLATILE RESIDUE:
GRAMS PER ML x 10^3
10·0
8·0
6·0
4·0
2·0
0
100%
C_6H_6
50
100%
CCl_4


100
%
INVOLATILE RESIDUE
AS PERCENTAGE OF
TOTAL PRODUCT
80
60
40
20
0
100%
C_6H_6
10
20
30
40
50
60
70
80
90
100%
CCl_4
MOLAR COMPOSITION

The irradiation of 2 litres 5 m% Benzene - 95 m% Carbon Tetrachloride Solution.

It is apparent from the quantitative results that, in the region of low benzene concentration, a large number of chlorine atoms are not accounted for and it was hoped to find support for the suggestion that compounds such as tetrachlorocyclohexene and hexachlorocyclohexane are products of the irradiation.

The benzene and carbon tetrachloride were purified and dried as previously described and irradiated for 1512 hours at a dose rate of 1.51×10^{16} eV/ml/min.

After irradiation, unchanged benzene and carbon tetrachloride were distilled off, accompanied by much hydrogen chloride. The solution gradually became yellow in colour as the volume was reduced to ~ 80 mls. The distillation was continued under reduced pressure, firstly by water pump and then by rotary oil pump, using a Vigreux fractionating column and oil bath temperatures up to 60°C. 2-3 ml fractions of distillate were collected and, together with the material in the liquid nitrogen cold traps, were monitored by G.L.C.

The first fractions consisted mainly of residual benzene and carbon tetrachloride with small amounts of chlorobenzene but at O.B.T. 30-35°C/0.5 mm Hg., the last product and the compound preceding it on G.L.C., (assumed to the present to be tetrachloroethylene), were the main components. White crystals of hexachloroethane condensed in the Vigreux column and water condenser above an O.B.T. of 35°C and were repeatedly washed from the column

and condenser by ether, a total of 22 gms crude hexachloroethane being isolated. The fractions collected between 50-60°C were composed largely of hexachloroethane and benzotrichloride. The residue (36.8 gms) was deep yellow in colour and very viscous.

Isolation and Identification of Tetrachloroethylene.

The identity of the small peak preceding that for chlorobenzene in all benzene-carbon tetrachloride irradiation residues was tentatively identified as tetrachloroethylene by a comparison of its G.L.C. behaviour with authentic tetrachloroethylene. It had, however, never been isolated in a pure state in order to compare its physical constants with those of an authentic sample.

The fractions of distillate which were shown to be rich in this compound, containing chlorobenzene as the major component, were combined and subjected to slow fractional distillation at atmospheric pressure using a 6", 15 mm diameter column packed with glass helices. This type of column was very efficient and 8-10 mls of mixture were obtained, sufficiently rich in the compound, to allow its isolation by means of the large scale G.L.C. unit, using the 3' column packed with 30% S.E. on celite (60-80 mesh) at 47°C and a flow rate of 260 mls N_2/min.

Refractive index after purification:-

Irradiation Compound:	Pure Tetrachloroethylene:
$n_D^{23.5} = 1.5038.$	$n_D^{23.5} = 1.5038.$

The infrared spectrum (No. 7) was recorded and shown to be identical with that for pure tetrachloroethylene.

The mechanism of formation of tetrachloroethylene may be as suggested in the Appendix to Section II, i.e., as a secondary product from hexachloroethane. Graph 2 shows that this is partly borne out by the increase in the yield of tetrachloroethylene which parallels the increasing yield of hexachloroethane but which, on the other hand, decreases before the maximum yield of the latter is attained. This premature decrease can be accounted for by the rapid increase in the number of free radicals in this composition region causing the pentachloroethyl radicals to undergo combination reactions in preference to chlorine atom elimination.

Examination of the High Boiling Residue.

The 36.8 gms of yellow, viscous residue were subjected to further fractional distillation using a 7" vacuum-jacketed Vigreux column. Five fractions were collected as the temperature of the oil bath was gradually increased from 60°-180°C/0.01 mm Hg pressure, and then the remaining residue was transferred to a molecular cup-still unit and a further seven fractions collected as the temperature was increased to 210°C.

Details of the fractions collected are shown in Table 10.

5.4 gms of black, tarry non-distillable material remained in the bottom of the cup-still; it was soluble in both benzene and chloroform.

TABLE 10.

Fraction	O.B.T.	Dist. Temp.	Observations	n_D^{20}	I.R.	Analysis
1	60-80°C/10^{-2}	25°C	C_2Cl_6 $C_6H_5CCl_3$			
2	80-120°	30°	$C_6H_5CCl_3$			
3	160°	72°	Mobile colourless liquid	1.5600	8a	A
4	160°	72°	"	1.5595		
5	180°	75°	Pale yellow, mod. viscous	1.5590		
6	140°/5 x 10^{-3}		Pale yellow, viscous	1.5712		B
7	140°		"	1.5710		
8	145°		Pale yellow, very viscous	1.5760	8b	C
9	150°		Pale yellow, extremely viscous	1.5805		
10	170°		"	1.5850		D
11	180-190°		Yellow and immobile	1.5900		
12	200-210°		Deep yellow, immobile	1.5950	8c	E

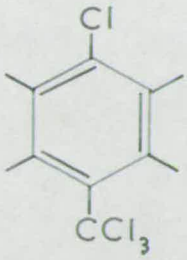
Analysis of the more volatile fractions by G.L.C. at 170°C, showed Fraction 3 to contain about 10% of two lower boiling compounds, one of which appeared to be diphenyl. Fraction 6, was composed of two compounds in approximately equal quantities, the first being the main component of the previous fractions and the second of much greater retention time, hence the increase in viscosity of the sample.

The retention times of the α, β and γ isomers of hexachlorocyclohexane were of the same order as those of the compounds of the residue but no peak corresponded with any of the isomers and it can be said that hexachlorocyclohexane is not formed as a major product of irradiation, as it is in the photochlorination of benzene.

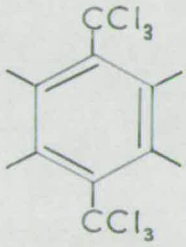
Results of Analyses.

Analysis	Fraction	% C	% H	% Cl	Total
A	3	18.22	1.67	79.50	99.39
B	6	24.72	2.71	72.70	100.13
C	8	22.25	2.33	75.40	99.98
D	10	22.88	1.55	75.20	99.63
E	12	26.56	1.31	72.35	100.22

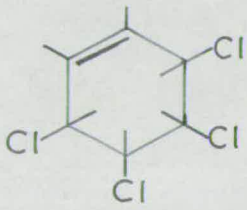
Since the samples, whose analyses figures are shown above, are composed of two or three components, the calculation of empirical formulae for each fraction is of little value. However, the theoretical analyses for some possible components of the residue are given on the following page:-



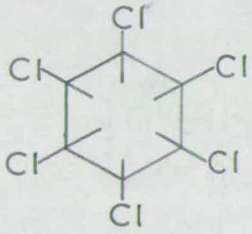
$C_7H_4Cl_4$ %C = 36.56 %H = 1.76 %Cl = 61.65



$C_8H_4Cl_6$ %C = 30.71 %H = 1.29 %Cl = 68.00



$C_6H_6Cl_4$ %C = 32.75 %H = 2.76 %Cl = 64.45



$C_6H_6Cl_6$ %C = 24.77 %H = 2.08 %Cl = 73.14

Although the percentages for the last of these compounds, hexachlorocyclohexane, correspond fairly closely to those of the analyses, this cannot be taken as proof of its presence; what is indicated is that each fraction, taken as a whole and known to contain two or three components, has approximately equal numbers of carbon, hydrogen and chlorine atoms.

The infrared spectra, some of which are shown in photographs 8a, 8b and 8c are poorly resolved but show both aromatic and aliphatic C-H, unsaturation and the presence of halogen. Comparison with the spectra published by Daasch[120] show that certain absorptions present could be caused by some of the hexachlorocyclohexane isomers but that they are definitely not the main components of the residue.

Information as to the nature of the viscous residues was obtained by treatment with alcoholic potassium hydroxide. A liquid with an ester-like smell and a solid were obtained. The solid gave a positive fluorescein test, indicating it to contain phthalic acid. The liquid was examined by G.L.C. (S.E. and T.C.P. columns) and the compounds positively identified, by comparison with standards, were:

(a) diphenyl (b) ethyl chlorobenzoates

(c) diethyl phthalate (d) diethyl terephthalate

(e) possibly 2-chlorodiphenyl in very small yield.

There were several other unidentified peaks which were <u>not</u> produced by ethyl 4-chlorophthalate, ethyl 2,4-dichlorobenzoate, ethyl 3,4-dichlorobenzoate or 4,4 -dichlorodiphenyl.

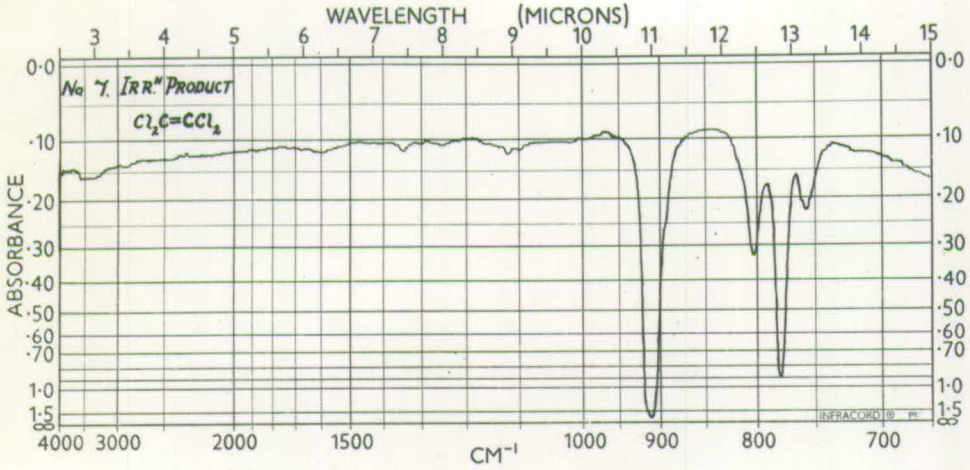
Hydrolysis of the liquid with aqueous-ethanolic potassium hydroxide yielded an acidic solid which was examined by paper chromatography.[121] By comparison of R_F values of authentic samples of substituted benzoic acids, the presence of o,-m- or p-chlorobenzoic acid(s), phthalic and terephthalic acids was confirmed. Other acids, used as standards, which were shown <u>not</u>

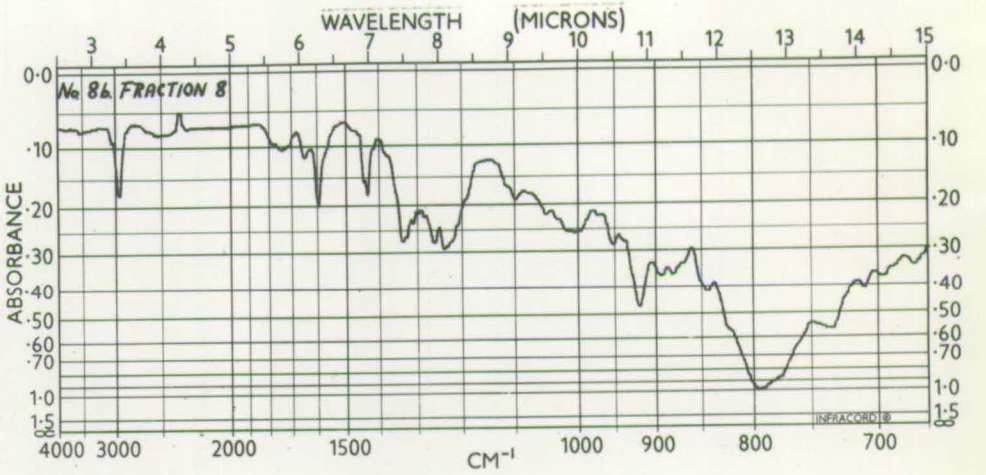
to be present, were 2,4-dichlorobenzoic, 3,4-dichlorobenzoic, o-phenylbenzoic, 4-chlorophthalic and 2,2-dicarboxydiphenyl.

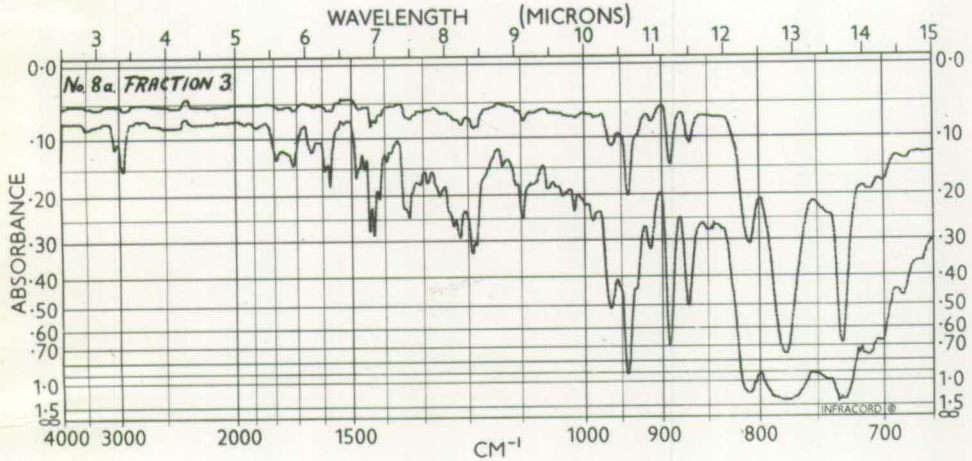
The esters (and acids) formed as a result of the potassium hydroxide treatment, are derived from the corresponding substituted benzene by the hydrolysis of the trichloromethyl groups present in the molecule. Therefore, the parent compounds, components of the viscous residue, are o-, m- or p-chlorobenzotrichloride and o- and p-bistrichloromethylbenzene.

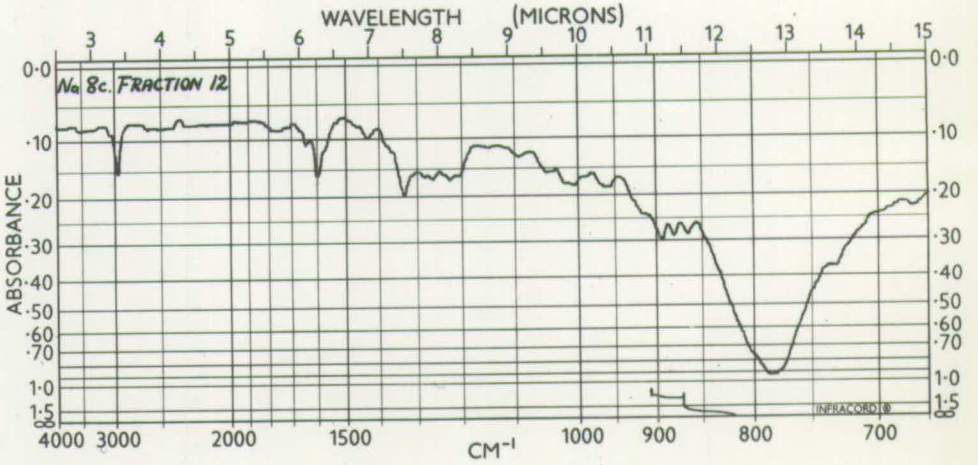
To summarise, the products positively identified as being formed during the radiolysis of benzene-carbon tetrachloride solution are:-

(1) hydrogen chloride
(2) chloroform
(3) tetrachloroethylene
(4) chlorobenzene
(5) hexachloroethane
(6) benzotrichloride
(7) diphenyl
(8) o-, m- or p-chlorobenzotrichloride
(9) o- and p-bistrichloromethylbenzene
(10) 2-chlorodiphenyl (not positive)


WAVELENGTH (MICRONS)
No 7. IRR.N PRODUCT
$Cl_2C=CCl_2$
ABSORBANCE
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No 8b. FRACTION 8
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WAVELENGTH (MICRONS)
No 8a. FRACTION 3
ABSORBANCE
CM^{-1}
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WAVELENGTH (MICRONS)
No 8c. FRACTION 12
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Discussion.

The graphs of yield versus dose for the solutions of the two molar compositions studied (6a and 6b) show that the relationship is linear for all products formed in low yield, ($G \leqslant 1.0$), over the dose range studied but a tendency to depart from linearity for the products formed in larger yield, i.e., hydrogen chloride and hexachloroethane. The primary formation of these products is probably linear but subsequent decomposition occurs during the irradiation period. This emphasises the desirability of working with as low doses as possible.

The results obtained for the solutions of differing molar composition show an interesting variation in product yields depending on composition. Although the results have not been repeated "in toto", the agreement between the product yields in the separate dose v. yield experiments carried out on the solutions of 50 m% and 20 m% C_6H_6 and those obtained in this series of solutions is good, except in the case of the hydrogen chloride values found in the solutions of 20 m% C_6H_6/80 m% CCl_4 composition which are high by comparison. It is questionable whether, in Graph 3, the $G_{(HCl)} = 1.72$ is correct or should have the value 1.98 found in the other experiment, which would mean that $G_{(HCl)} = 1.95$ for the 35 m% C_6H_6 solution was not high as indicated and that the line of the graph should form a less decided curve. This would, however, displace neighbouring points from the graph and for the results obtained, the curve shown is the most satisfactory.

Considering the yields of chloroform, a high value was also obtained in the 35 m% C_6H_6 solution (cf. HCl) by comparison with the yields for adjacent compositions and again a higher value in the 20 m% C_6H_6 solution would allow plotting of the graph for chloroform in a more horizontal attitude, avoiding the necessity of introducing the rise in the graph between 15 m% and 5 m% C_6H_6 composition; but measurement of the chloroform yield in the solution irradiated for the corresponding period in the set of 20 m% C_6H_6/80 m% CCl_4 solutions, confirmed the lower yield at this point, verifying the overall shape of the graph. This matter will be discussed again later.

The products detected and measured were:-

(1) Hydrogen chloride
(2) Chloroform
(3) Tetrachloroethylene
(4) Chlorobenzene
(5) Hexachloroethane
(6) Benzotrichloride
(7) Diphenyl

The formation of hexachloroethane occurs by the normal dimerisation of trichloromethyl radicals and the formation of tetrachloroethylene has already been discussed.

The stability of aromatic compounds in general to radiolytic decomposition will result in the primary decomposition of benzene, into phenyl radicals and hydrogen atoms, occurring only to a very small extent in comparison with that of carbon tetrachloride.

The latter is very much more sensitive to radiation and Chapiro et al.,[112] report a G-value of 20 for free radical formation in pure carbon tetrachloride, determined by the use of D.P.P.H. It is the attack of these chlorine atoms and trichloromethyl radicals on benzene molecules that is considered responsible for the formation of the major part of the yields of products (1), (2), (4) and (6).

Direct abstraction of a hydrogen atom from a benzene molecule by these radicals may occur:

$$C_6H_6 + \cdot Cl \longrightarrow HCl + \cdot C_6H_5 \qquad (1)$$

$$C_6H_6 + \cdot CCl_3 \longrightarrow CHCl_3 + \cdot C_6H_5 \qquad (2)$$

Reaction (1) has been suggested as the chain propagation step in the high temperature vapour phase halogenation of benzene.[122] Kooyman,[123] investigating the ability of trichloromethyl radicals to abstract hydrogen rather than add to an olefinic double bond, studied the retarding effect of benzene on the carbon tetrachloride-cetene-benzoyl peroxide reaction and he observed that benzene was apparently unreactive towards the trichloromethyl radical. He later studied the reactivities of polycyclic aromatic hydrocarbons towards trichloromethyl radicals by measuring their retarding effect on the benzoyl peroxide initiated addition of carbon tetrachloride to hexadecene-1.[124] The inhibiting effects were attributed to the addition of the chain carrying trichloromethyl radicals to the aromatics. The scale of reactivities thus obtained extended

from the least reactive, benzene, to 3,4-benzopyrene, the latter being over 10^5 times more reactive than the former. The reaction between phenyl radicals, produced from benzoyl peroxide, and carbon tetrachloride was first studied in 1924 by Boeseken and Gelissen,[125] who isolated as the main products chlorobenzene, hexachloroethane and w,w,w-trichloro-p-toluic acid. Recently Hey and Peters,[126] reinvestigating this and similar reactions, found that the addition of benzoic acid to the carbon tetrachloride-benzoyl peroxide system did not increase the yield of the w,w,w-trichlorotoluic acid (~ 95% p-isomer), indicating that the aromatic nucleus in benzoic acid is resistant to attack by trichloromethyl radicals. The evidence would, therefore, suggest that neither reaction (2), nor the addition reaction of the radical to benzene (6), is likely to occur to any extent in this system.

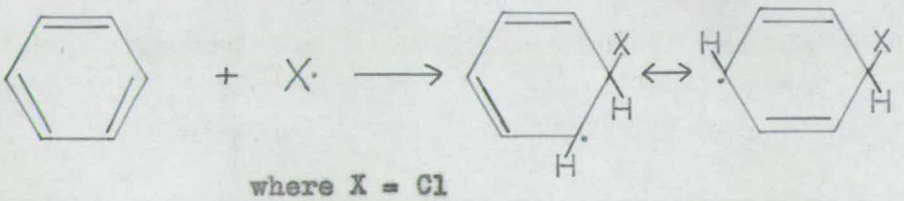
In addition to combination reactions between phenyl radicals, formed, for example, as in (1), and the other radical species present, e.g.,

$$\cdot C_6H_5 + \cdot CCl_3 \longrightarrow C_6H_5CCl_3 \qquad (3)$$

$$\cdot C_6H_5 + \cdot Cl \longrightarrow C_6H_5Cl \qquad (4)$$

$$\cdot C_6H_5 + \cdot C_6H_5 \longrightarrow C_6H_5C_6H_5 \qquad (5)$$

the formation of the products can also be explained if it is assumed that chlorine atoms add to benzene molecules forming chlorocyclohexadienyl radicals:



(6)

where X = Cl

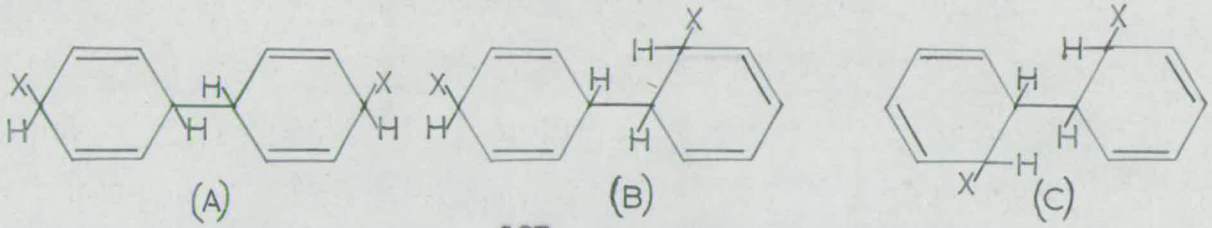
which can then undergo the following alternative reactions:-

(a) loss of a hydrogen atom, leaving a substituted benzene molecule

(b) combination with another radical

(c) initiation of a polymerisation reaction involving benzene

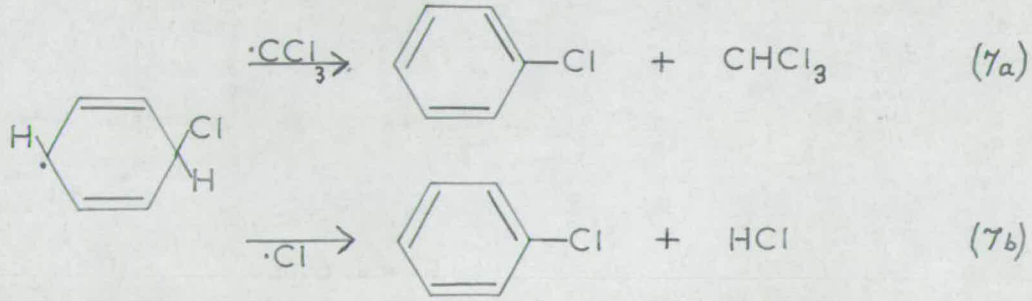
(d) dimerisation to give any of the following products



Szwarc and co-workers[127] have shown that methyl radicals readily add to many aromatic compounds in solution, and DeTar and Long[128] showed that phenyl radicals add to benzene and were able to isolate the phenyl-substituted analogue (X = C_6H_5) of compound (A). However, the evidence cited against the corresponding reaction between trichloromethyl radicals and benzene is strong and so reaction (6), where X = CCl_3, can be omitted.

Reaction (a)

Chlorobenzene, can be formed by the removal of a hydrogen atom from the intermediate chlorocyclohexadienyl radical, accompanied by formation of chloroform or hydrogen chloride depending on the species involved in the abstraction reaction,



This type of mechanism, abstraction after addition, has been suggested by Charles and Whittle[129] to account for the reactions of photolytically generated trifluoromethyl radicals with aromatic hydrocarbons in the gas phase, and also by Levy et al.[130] to explain the acetyl peroxide-induced reaction of methyl radicals with benzene in the liquid phase.

The preferential occurrence of abstraction after addition, rather than direct abstraction, may be justified on thermochemical grounds. For direct abstraction, a C_6H_5-H bond must be broken, requiring 102 k cal/mole. In the scheme proposed above, however, the C-H bond involved should be much weaker because, when it is broken, the aromatic character of the ring is restored. The dissociation energy of this bond can be estimated as that of a normal C-H bond, $\sim$ 100 k cal., less the resonance energy of the benzene ring, $\sim$ 36 k cal., so that in this case D(C-H) is $\sim$ 64 k cal.. This estimate may be low because the cyclohexadienyl radical should also possess some resonance energy (maybe 5-10 k cals.). Hence abstraction from the intermediate radical should occur much more easily than from benzene itself.

Of the three products under discussion, two are probably formed by both mechanisms, whereas benzotrichloride would appear to be formed only by radical combination. It is not possible to detail a precise reaction scheme to explain the observed yields of the measured products since competing reactions of unknown importance lead to the formation of these products as well as the

formation of a considerable amount of unidentified "polymer". However, the general features of the product yields will be discussed shortly.

Reactions (b), (c) and (d).

These possible reactions for the intermediate cyclohexadienyl radicals are responsible for the large yield of high molecular weight products formed in the radiolysis of benzene solutions.

An examination of the numbers of chlorine atoms and trichloromethyl radicals accounted for in the measured products shows an increasing loss of chlorine atoms in all solutions containing more than 10 m% CCl_4. The formation of a cyclohexadienyl radical in which the group "X" can be phenyl or chlorine (6), followed by addition of another radical, addition to a benzene molecule initiating a polymerisation reaction or simple dimerisation, are all processes leading to the formation of high molecular weight compounds. As a number of radicals may be involved and the resulting cyclohexadienes will all be very much more reactive to addition, it is not surprising that so much high boiling material of an irresolvable character is obtained.

The positive identification of diphenyl, o-, m- or p-chlorobenzotrichloride, ortho- and para-bistrichloromethylbenzene can be explained by this mechanism. The extremely viscous nature of the material isolated, containing a high percentage of chlorine, supports the postulation of a polymerisation reaction involving

reactive chlorinated species and simultaneously accounts for the apparent deficiency of chlorine atoms. In the solutions of high benzene concentration, the composition of the "polymer" will presumably differ, containing a higher proportion of cyclohexene and cyclohexadiene structures. Dannley et al.[131] have noted that in all free radical substitution reactions involving phenyl radicals, large quantities of tars are formed.

Graphs 2 and 3 show certain features of interest. The graph of $G_{(HCl)}$, as a function of composition, shows a pronounced rapid increase reaching a maximum value at 35 m% CCl_4 composition, decreasing in value to a minimum of 1.72 at 80 m% CCl_4 before increasing again rapidly to a maximum of 2.65 at 0.10 m% C_6H_6. The similarity in the yields of hydrogen chloride in the two solutions of lowest benzene concentration studied, 0.5 and 0.1 m% respectively, indicates that a second maximum occurs close to this point, as, of course, must be expected by virtue of the decreasing concentration of benzene. This behaviour is reflected to a lesser extent in the yields of chloroform and benzotrichloride. The yields of chlorobenzene and hexachloroethane differ in some respects; a similar rapid increase is observed in solutions of low carbon tetrachloride composition, which in the former case becomes much more gradual before a smooth decrease occurs to zero yield between 15 and 0 m% C_6H_6, while in the case of hexachloroethane, the yield becomes progressively greater with decreasing benzene concentration, reaching a maximum value between 5 and

1.0 m% C_6H_6, followed by an extremely rapid decrease to the value found in pure carbon tetrachloride (G = 0.8). The G-value for diphenyl shows a similar increase up to 5 m% CCl_4 before decreasing to undetectable quantities. It is interesting to note that $G_{(C_6H_5:C_6H_5)}$ is greater in those solutions containing a small quantity of carbon tetrachloride than in pure benzene (0.09).

A more detailed study of the yields of chloroform, benzotrichloride and hexachloroethane, formed in solutions of composition 20 to 0.10 m% C_6H_6 is shown in Graph 2a. The experimental results obtained indicate that each of the peaks in the curves for hexachloroethane and chloroform yields may consist of two maxima, one of which, in each case, would coincide with that of the benzotrichloride curve, i.e., between 1 and 2 m% C_6H_6. Before any conclusions or comments are made regarding this peculiar effect, it will be necessary to irradiate a series of solutions of carbon tetrachloride containing between zero and 20 m% C_6H_6, the increments in the benzene concentration being very small in the first 5-7%, to verify the existence of this phenomenon.

The overall shape of the curve for hydrogen chloride production bears a strong resemblance to that obtained by Chapiro and co-workers[112] for the radical yield of the system. A straight line drawn from the origin at 100% C_6H_6 to the point of maximum yield of hydrogen chloride, shows that considerably more hydrogen chloride is formed in solutions containing more than 32 m% C_6H_6

and less in solutions containing a lower molar percentage of benzene, than expected, if the benzene and carbon tetrachloride reacted independently of each other, to an extent directly proportional to their electron fractions in the solutions. Chapiro explains this type of behaviour as being due to sensitisation in the former case and protection in the latter. The yields of the other products (except tetrachloroethylene) all exhibit this sensitisation effect, to a lesser degree, and also the protection effect, in the solutions of low benzene concentration, to a small extent.

The protective effect of small quantities of benzene on other organic compounds (e.g. cyclohexane) is well known and although the precise mechanism of protection is not yet established, it is generally attributed to a transfer of excitation energy from the other species to the aromatic ring which is able to dissipate it by internal conversion without undergoing decomposition. Very recently, however, Swallow[132] has suggested that the protective action of benzene (on cyclohexane) is due to the preferential absorption of the energy of the fast electrons by the π-electrons of the aromatic ring, rather than to an initially random absorption of energy followed by some form of energy transfer to the benzene.

As the concentration of benzene decreases from about 20 m% to zero in the irradiated solutions, this protective action of the benzene gradually decreases since fewer molecules of benzene will be present in the solvent "cages" and therefore there will be less

opportunity for energy transfer, resulting in a consequently greater dissociation of carbon tetrachloride molecules into free radicals. The chlorine atoms appear to preferentially abstract hydrogen atoms rather than form chlorobenzene although addition to the ring must still be an important process. The trichloromethyl radicals can either dimerise to yield hexachloroethane (major reaction), abstract hydrogen from some species to give an increased yield of chloroform or form benzotrichloride, also in increased yield. The subsequent, final decrease in the yields of benzotrichloride and chloroform is caused by the concentration of benzene becoming too low to compete effectively with the dimerisation reaction. In the solutions containing 0.5 and 0.1 m% C_6H_6, the decrease in the hexachloroethane yield, as a consequence of the decreasing formation of hydrogen chloride, indicates the growing importance of the back reactions between the radiolysis products of carbon tetrachloride.

The sensitisation effect is suggested by Chapiro to involve the transfer of energy from a primarily excited benzene molecule to a carbon tetrachloride molecule raising it to an excited state which is inaccessible, or difficultly so, by direct excitation, e.g., a triplet state. This excited species can then decompose to form radicals and hence products. In carbon tetrachloride, only a singlet state lying above the lowest singlet and triplet states of benzene is known but the authors have found evidence, in a study of the absorption spectrum of carbon tetrachloride, of the presence of a lower state lying below those of

benzene. However, they do not, as yet, consider their findings to be established since the possibility exists that the absorptions might also have been caused by traces of impurities.

As a consequence of the transfer of energy from primarily excited carbon tetrachloride molecules to benzene molecules (protection), Chapiro et al. postulate a second transfer reaction, involving the energy of these secondarily excited benzene molecules (assumed to be the same as the primarily excited species) and other carbon tetrachloride molecules, resulting in the formation of this proposed triplet state. This explains why there is not a greater decrease in the radical yield as a result of the protection effect in solutions containing more than a few per cent of benzene.

Hamill, who has studied electron capture by solutes in hydrocarbons,[133] has suggested that the rapid rise in the yields of products at low, but increasing, halogen compound concentration, is the result of dissociative electron capture by carbon tetrachloride:

$$CCl_4 + e \rightarrow \cdot CCl_3 + Cl^-$$

giving rise to a greater yield of trichloromethyl radicals than would normally be expected. The fate of the chloride ion is not clear but it is probably destroyed in reactions such as

$$C_6H_6^+ + Cl^- \longrightarrow C_6H_6 + \cdot Cl$$

$$\text{or} \quad C_6H_6^+ + Cl^- \longrightarrow \cdot C_6H_5 + \cdot H + \cdot Cl$$

The possibility that carbon tetrachloride might absorb energy preferentially in solutions of this composition range and decompose as a result, leading to an increased yield of radicals, is similar to the recent suggestion by Swallow, proposed as an alternative explanation for the mechanism of the protective effect of benzene, but differs in this respect that, whereas benzene does not decompose as a consequence, carbon tetrachloride does so. However, in conclusion, it has to be pointed out that preferential absorption of energy by carbon tetrachloride in solutions of high benzene concentration cannot occur in the same system in which the protective influence of benzene on solutions of high halogen concentration is explained by preferential absorption of energy by the benzene.

The foregoing discussion has dealt with feasible explanations for the observed experimental results but it is not possible at present to decide between them.

APPENDIX

TO

SECTION III.

The results obtained from the irradiation of the benzene-carbon tetrachloride solutions, prepared with the benzene containing the unidentified impurity, believed to be a saturated hydrocarbon, are detailed in Tables 11 and 12 and Graphs 8 and 9.

TABLE II

RESULTS FROM THE IRRADIATION OF EQUIMOLAR BENZENE - CARBON TETRACHLORIDE SOLUTIONS

DOSE RATE (Fe^{++}) = 2.930×10^{16} eV/ml/min.; Conversion Factor = 1.104; DOSE RATE (Org.) = 3.232×10^{16} eV/ml/min.

VOL. IRR.	TIME HOURS	DOSE ABS. eV/ml.	HCl		C_6H_5Cl		C_2Cl_6		$C_6H_5CCl_3$	
			moles/ml. $\times 10^5$	G	moles/ml. $\times 10^6$	G	moles/ml. $\times 10^6$	G	moles/ml. $\times 10^6$	G
80	48	0.931×10^{20}	0.70	4.37	1.57	0.99	2.94	1.84	-	-
79.5	96	1.862×10^{20}	1.32	4.14	3.24	1.02	4.94	1.55	3.53	1.11
79	144	2.793×10^{20}	2.02	4.23	5.01	1.05	8.09	1.69	5.42	1.13
79.5	240	4.655×10^{20}	3.19	4.01	8.65	1.10	12.61	1.58	8.03	1.01
82.5	336	6.517×10^{20}	4.35	3.90	11.78	1.06	17.08	1.53	11.62	1.04
$G_{(initial)}$				4.45		0.96		1.87		1.14

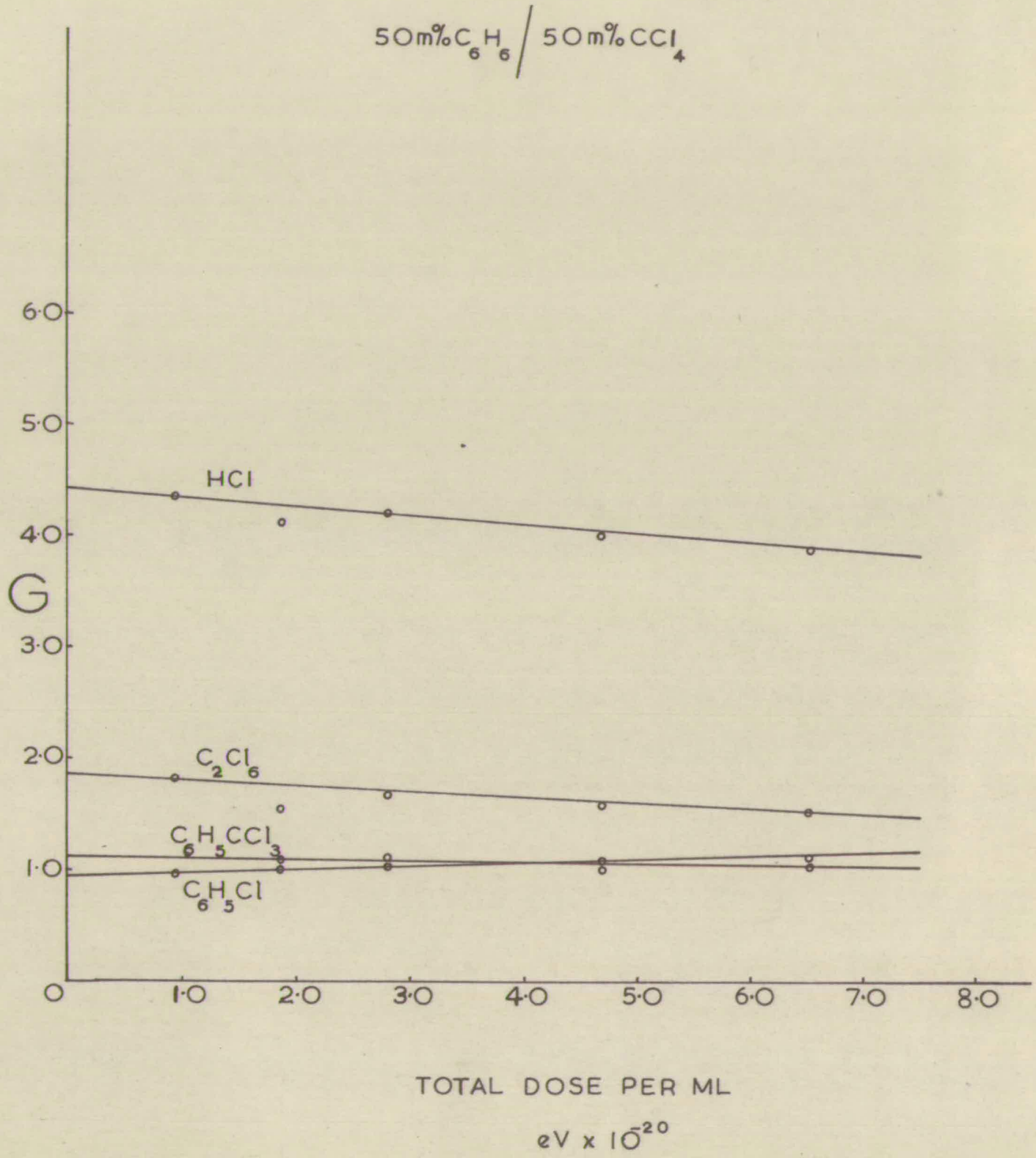
TABLE 12

RESULTS FROM THE IRRADIATION OF BENZENE - CARBON TETRACHLORIDE SOLUTIONS

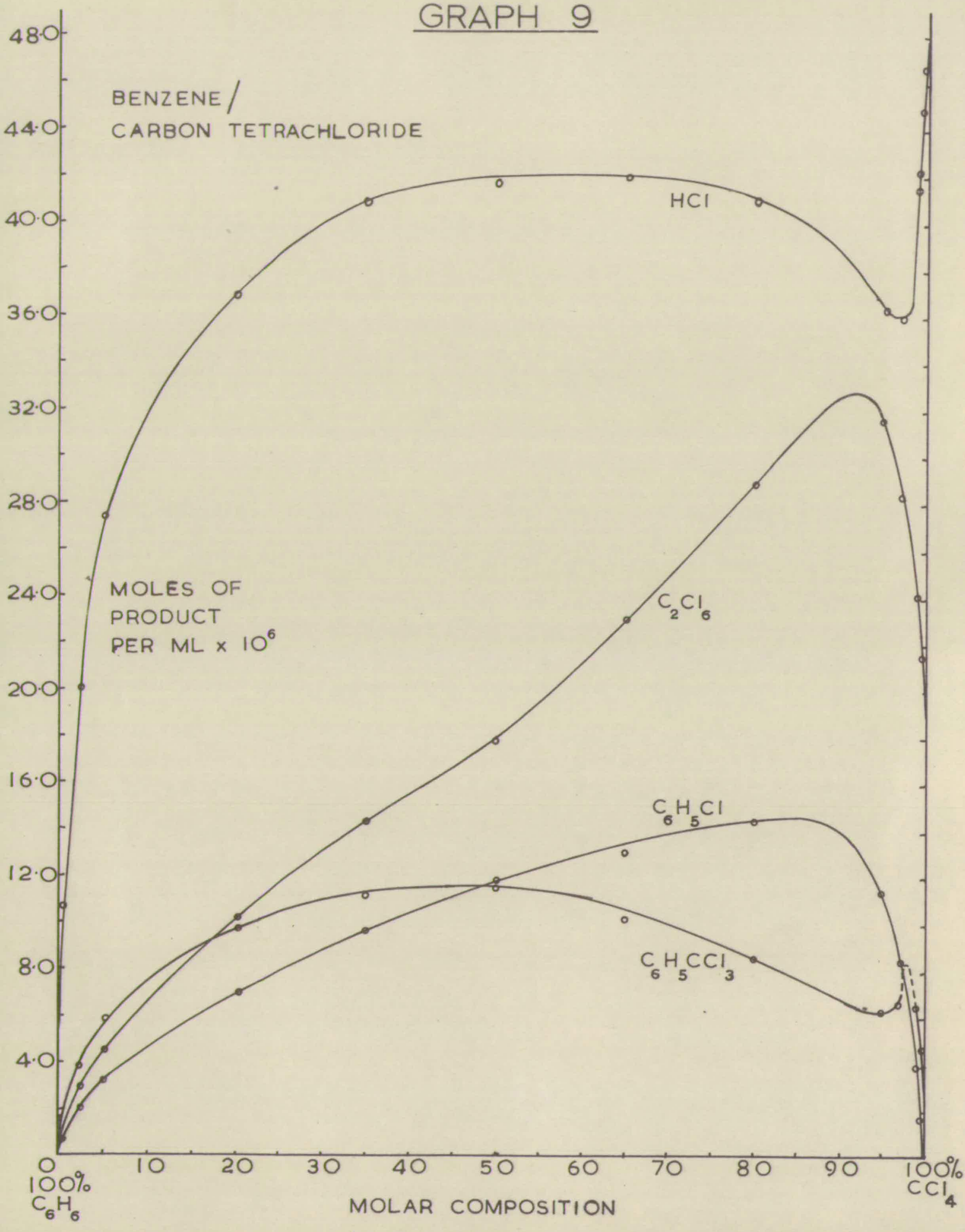
DOSE RATE (Fe^{++}) = 2.960×10^{16} eV/ml/min.; IRRADIATION TIME = 336 HOURS

Mole % CCl_4	Vol. IRR.	HCl		C_6H_5Cl		C_2Cl_6		$C_6H_5CCl_3$	
		moles/ml. $\times 10^5$	G	Moles/ml. $\times 10^6$	G	Moles/ml. $\times 10^6$	G	Moles/ml. $\times 10^6$	G
0.50	80.5	1.08	1.27	0.68	0.08	0.79	0.09	1.57	0.18
2.50	81	2.17	2.52	2.06	0.24	2.99	0.35	3.77	0.44
5.0	81.5	2.74	3.10	3.32	0.38	4.45	0.51	6.03	0.68
20	77	3.69	3.81	7.02	0.73	10.19	1.06	9.66	1.00
35	79	4.09	3.90	9.64	0.92	14.42	1.38	11.02	1.05
50	79	4.17	3.86	11.80	1.05	17.97	1.58	11.73	1.04
65	80	4.20	3.47	13.02	1.07	23.11	1.91	10.20	0.84
80	81.5	4.01	3.19	14.43	1.11	28.88	2.25	8.61	0.67
95	78	3.64	2.67	11.39	0.83	31.61	2.32	6.30	0.47
97	83	3.60	2.65	8.40	0.62	28.36	2.08	6.59	0.49
99.0	77.5	4.16	3.03						
99.25	80	4.23	3.08	3.91	0.29	24.05	1.75	6.49	0.48
99.50	77	4.49	3.27						
99.75	78.5	4.67	3.39	1.69	0.13	21.51	1.56	4.69	0.34

GRAPH 8


50m% C_6H_6 / 50m% CCl_4
6·0
5·0
4·0
3·0
2·0
1·0
0
G
HCl
C_2Cl_6
$C_6H_5CCl_3$
C_6H_5Cl
1·0
2·0
3·0
4·0
5·0
6·0
7·0
8·0
TOTAL DOSE PER ML
eV x 10^{-20}

GRAPH 9


BENZENE /
CARBON TETRACHLORIDE
MOLES OF
PRODUCT
PER ML x 10^6
HCl
C_2Cl_6
C_6H_5Cl
$C_6H_5CCl_3$
48·0
44·0
40·0
36·0
32·0
28·0
24·0
20·0
16·0
12·0
8·0
4·0
0
10
20
30
40
50
60
70
80
90
100%
C_6H_6
100%
CCl_4
MOLAR COMPOSITION

The Irradiation of Benzene-Chloroform and Benzene-Dichloromethane Solutions.

A brief description of the qualitative results, along with an approximate, comparative estimate of the yields of products formed in the radiolysis of equimolar solutions of benzene-dichloromethane, benzene-chloroform and benzene-carbon tetrachloride is now included.

The three degassed solutions ($\sim$ 80 mls) received the same total dose. Upon opening the tubes, hydrogen chloride was evolved from each solution; the carbon tetrachloride solution was colourless, the chloroform solution was pale yellow and the dichloromethane solution, golden yellow. Each was subject to the same working up procedure, the residues being concentrated to volumes of 2 mls and were respectively pale yellow, deep yellow and dark brown in colour.

The G.L.C. analyses of the distillates and residues were carried out under identical conditions for each solution and the peaks have been designated large (l), medium (m), medium-small (m-s), small (s) and trace (t) depending on their relative sizes. Results in Table 13.

TABLE 13.

The Irradiation of Equimolar Solutions of:

(A) C_6H_6/CCl_4	(B) $C_6H_6/CHCl_3$	(C) C_6H_6/CH_2Cl_2
HCl	HCl	HCl
		CH_3Cl (s)
	CH_2Cl_2 (s)	
$CHCl_3$ (s)		
		CH_2Cl-CH_2Cl (m-s)
$CCl_2=CCl_2$ (t)	$CCl_2=CCl_2$? (t)	
C_6H_5Cl (m)	C_6H_5Cl (m)	C_6H_5Cl (m)
	$CHCl_2-CHCl_2$ (m)	
	$CHCl_2-CCl_3$ (m-s)	
CCl_3-CCl_3 (1)	CCl_3-CCl_3 (s)	
		$C_6H_5CH_2Cl$ (1)
	$C_6H_5CHCl_2$ (1)	$C_6H_5CHCl_2$ (m-s)
$C_6H_5CCl_3$ (m)	$C_6H_5CCl_3$ (m-s)	

Discussion.

The mechanisms of formation of the products in system (A) has already been discussed and applies largely to the two other systems.

In the benzene-chloroform system, the yield of hexachloroethane is very much less than in system (A) and also in pure irradiated chloroform. As in the pure chloroform system, trichloromethyl radicals are formed by hydrogen abstraction from chloroform molecules, but in this system the operative radicals (mainly $\cdot Cl$ and $\cdot CHCl_2$) can react by alternative routes, thereby decreasing the concentration of trichloromethyl radicals and hence the yields of products incorporating them. For example, addition to the benzene ring, subsequently resulting in the formation of benzal chloride, a major product of the radiolysis, must be an important reaction. Also, chlorine atoms can abstract hydrogen from benzene molecules, or react to form chlorobenzene, instead of abstracting from chloroform, again resulting in a decrease in the yield of trichloromethyl radicals. However, the presence of trichloromethyl radicals in the system accounts for the formation of benzotrichloride.

In system (C), the formation of methyl chloride is analogous to the formation of dichloromethane and chloroform in the other two systems, i.e., by a hydrogen abstraction reaction of the primary radical, in this case $\cdot CH_2Cl$. Dimerisation of this

radical yields 1,2-dichloroethane. The other compounds, chlorobenzene and benzyl chloride, are the expected substitution products; the formation of benzal chloride is analogous to that of benzotrichloride in system (B), probably occurring thus:

$$CH_2Cl_2 \rightsquigarrow \cdot CH_2Cl + \cdot Cl$$

$$\cdot CH_2Cl + CH_2Cl_2 \longrightarrow CH_3Cl + \cdot CHCl_2$$

$$\cdot CHCl_2 + \cdot C_6H_5 \longrightarrow C_6H_5CHCl_2$$

No evidence could be found for the formation of sym-tetrachloroethane, the counterpart of hexachloroethane in system (B), but from a consideration of the high yield of benzyl chloride and the not insignificant yield of benzal chloride, along with the relatively high yield of non-volatile "polymer" formed, it would appear that benzene reacts readily with these radicals.

The free radical reactions occurring in the three systems are similar, indicating that the three halogenated methanes studied undergo radiolytic decomposition in a comparable manner, and a detailed quantitative study would provide information as to the relative importance of the reactions in each system.

S E C T I O N I V.

THE IRRADIATION OF CYCLOHEXANE-CARBON TETRACHLORIDE SOLUTIONS.

Purification.

Samples of both Spectroscopic and Ordinary grades of cyclohexane manufactured by Hopkin and Williams, Eastman Kodak, May and Baker and B.D.H. all contained small amounts of two lower boiling impurities, variously reported as being n-hexane, methyl cyclopentane and 2,4-dimethylpentane. B.D.H. "Special for Spectroscopy" cyclohexane, manufactured several years ago, was found to be free of these impurities but contained two higher boiling impurities in small quantity. Distillation of this cyclohexane, using a 2' silvered vacuum-jacketed fractionating column packed with $\frac{1}{4}$" glass helices to hold back the impurities, produced sufficient pure cyclohexane for the irradiations described in this Section. After drying with anhydrous calcium chloride, it was distilled in an atmosphere of oxygen-free nitrogen.

Refractive index, $n_D^{20.5} = 1.4263$; lit. value, $n_D^{20} = 1.4262$.

Purification of cyclohexane containing the lower boiling impurities by distillation through the 4' Stedman ring column was not successful; the initial distillate contained only twice the concentration of impurity, resulting in a very slow reduction in concentration in the reservoir. This was surprising, considering how effectively chloroform can be removed from carbon tetrachloride under the same conditions, as the boiling points of the impurities and solvents in both systems are similar. Freezing and decanting, the method used successfully for the purification of benzene, was very much less efficient in this case, and gave little enrichment

of the impurities in the decanted liquid, irrespective of the rate of freezing. Formation of the thiourea complex of cyclohexane from a 50% aqueous-acetone solution saturated with thiourea, using volumes of cyclohexane one-sixth to one-twentieth of the complexing solution, gave partial purification but the recovery of cyclohexane was generally less than 50%.

Carbon tetrachloride was purified by the same procedure as described in Section III.

The Irradiation of 20 m% Cyclohexane - 80 m% Carbon Tetrachloride Solution.

2 litres of solution were irradiated for 1176 hours at a dose rate of 1.39×10^{16} eV/ml/min.

The irradiated solution was clear and colourless, evolving hydrogen chloride and phosgene gases. Distillation was commenced using the 2' silvered, vacuum-jacketed fractionating column packed with glass helices and eight 2 ml fractions of the distillate were collected for examination of the products more volatile than the starting materials. The bulk of the unchanged carbon tetrachloride and cyclohexane were distilled off using a 12" Widmer fractionating column until the volume was reduced to about 300 mls. Distillation was continued at 15 mm pressure until peaks representing higher boiling compounds were detected by G.L.C. A 27 µl injection of the residue on 3'6" S.E./celite at 81°C produced several peaks after those for residual cyclohexane and carbon tetrachloride:-

(1) minor component at 11 mins., corresponding to tetrachloroethylene

(2) major component at 17 mins., corresponding to chlorocyclohexane

(3) minor component at 31 mins., unidentified

(4) minor component at 38 mins., unidentified

(5) trace component at 57 mins., unidentified

(6) major component at 61 mins., corresponding to hexachloroethane

(7) major component at 168 mins., believed to be trichloromethyl-cyclohexane.

The light brown residue (120 mls) was transferred to a 250 ml flask fitted with a 9" Vigreux column and fractions of distillate were collected under reduced pressure. The first few fractions were found to be rich in tetrachloroethylene and were combined for further treatment. Subsequent fractions were nearly pure and composed of chlorocyclohexane, the product formed in greatest yield in the radiolysis, of which 62 mls were isolated in a virtually pure state. (Spectrum No. 9)

Refractive index, $n_D^{22.5} = 1.4613$;

authentic sample, $n_D^{22.5} = 1.4613$.

It is of interest to note that this represents approximately 11% conversion of cyclohexane to chlorocyclohexane.

The remaining residue, now composed mainly of the two unidentified compounds, hexachloroethane, trichloromethylcyclo-hexane and higher boiling material, was transferred to a smaller flask fitted with a 7" vacuum-jacketed Vigreux column and water condenser, terminating in a three way collection unit. The

pressure was reduced to 0.01 mm Hg. and seven fractions were collected as the temperature of the oil bath was increased to 40°C. The fractions contained some residual chlorocyclohexane and became progressively richer in the unidentified compounds and hexachloroethane. These seven fractions were combined and their subsequent treatment is described later. Hexachloroethane, which repeatedly formed a white crystalline mass at the top of the Vigreux column and in the condenser, weighed 32 gms, including the material which crystallised from the residues on cooling. Four further 1-2 ml fractions, obtained by increasing the oil bath temperature to 55-60°C, were composed mainly of a liquid, believed to be trichloromethylcyclohexane, and some dissolved hexachloroethane. The flask contained 13.4 gms of brown residue which was considerably less viscous than that remaining at the corresponding stage in the working up of the irradiated benzene-carbon tetrachloride mixture, previously described. (p.111)

Examination of the Distillate.

Injection of the first two fractions showed them to be rich in three components more volatile than carbon tetrachloride. The least volatile of these had the same retention time as chloroform and was present in high concentration; the second compound, present in much smaller quantity, was dichloromethane while the

first and most volatile (minor) component of the distillate, with a retention time half that of dichloromethane, was unidentified but is believed to have been methyl chloride. Examination of the other fractions of the distillate showed that the two most volatile components decreased in concentration rapidly, while the chloroform, a major product of the radiolysis, continued to distil over with the starting materials for a considerable period.

These results, obtained by use of a silicone elastomer/celite column packing at 35°C, were confirmed by a series of similar injections on a 25% T.C.P. column at 52°C.

The products of the irradiation, more volatile than carbon tetrachloride, were therefore:

(1) Hydrogen chloride

(2) Carbonyl chloride

(3) Methyl chloride (?)

(4) Dichloromethane

(5) Chloroform.

Dichloromethane is formed as a secondary product from chloroform and it would appear probable that, provided the small amount of very volatile product was methyl chloride, it was formed as a secondary product from dichloromethane.

Isolation and Identification of Tetrachloroethylene.

The combined fractions, containing most of the tetrachloroethylene, were distilled further at atmospheric pressure using a 6" helix-packed fractionating column to concentrate it as

much as possible before attempting isolation by means of the large scale G.L.C. unit under the same conditions as described on p.110, Section III.

After passing through the column a second time to remove traces of chlorocyclohexane, etc., the infrared spectrum was recorded and found to be identical with that of an authentic sample and that shown in spectrum No. 7.

Refractive index, $n_D^{21.5} = 1.5046$;

authentic sample, $n_D^{21.5} = 1.5050$.

Examination of the Unidentified Minor Products.

The seven combined fractions were subjected to further distillation under reduced pressure (water pump), using the 6" helix-packed column to remove as much of the chlorocyclohexane as possible. The remaining liquid (15 mls) was rich in the unidentified products; the higher boiling compound (B) was present in three times the amount of the other compound (A), and was now causing full scale deflections on the G.L.C. recorder. Crystals of hexachloroethane appeared in the liquid on cooling.

The isolation of these two compounds was achieved by use of the 3' large scale G.L.C. column (30% w/w S.E./celite (60-80 mesh)) at a temperature of 76°C. 24 injections (0.5) were made, the required components of the mixture being collected in separate traps in the usual way. It was not possible to isolate any of the trace component which was eluted with the hexachloroethane, making the latter appear slightly moist. It was believed

this compound may have been dichloromethylcyclohexane. The compounds were rechromatographed as they were both found to contain small amounts of chlorocyclohexane as well as being mutually contaminated.

Compound (A)

The infrared spectrum was recorded (No. 10) and found to be identical to that of pure pentachloroethane.

Refractive index:

Found, $n_D^{20} = 1.5032$ authentic sample, $n_D^{20} = 1.5030$

lit. value, $n_D^{20} = 1.5035$

In this way, the first unidentified minor component was shown to be pentachloroethane, presumably formed as a secondary product by radiolytic decomposition of the primary product, chloroform,

$$CHCl_3 \rightsquigarrow \cdot CHCl_2 + \cdot Cl$$

followed by the combination reaction

$$\cdot CHCl_2 + \cdot CCl_3 \longrightarrow CHCl_2\text{-}CCl_3$$

Compound (B)

The infrared spectrum (No. 11) shows the compound to be a chlorinated cyclohexane derivative. The results of a carbon, hydrogen and chlorine analysis are shown on the following page, along with the theoretical percentages calculated for dichloro-cyclohexane and dichloromethylcyclohexane:-

	$C_6H_{10}Cl_2$	Analysis Found.	$C_7H_{12}Cl_2$
% C	47.07	47.42	50.31
% H	6.58	7.27	7.24
% Cl	46.31	45.40	42.43

Although the figures do not agree exactly, the results of the analysis correspond more closely with those for dichlorocyclohexane. It has been noticed previously that samples trapped from a large scale G.L.C. column frequently show high percentages for carbon and hydrogen and consequently low chlorine analysis (cf. analysis of heptachloropropane, p. 48) and that when there is sufficient material to allow distillation before analysis, results are generally improved.

The boiling point of the liquid was determined by Siwoloboff's micro-method and found to be 167 $\pm$ 1.5°C. The accuracy of the method was checked by a determination of the boiling point of chlorocyclohexane, b.p. 143°C. The figures obtained, on increasing and decreasing the temperature, were 143°-141°, 142°-140° and 142°-141°C; the average figure, 141.5°C, is approximately 1% low.

Refractive index, $n_D^{20} = 1.4803$.

There are seven isomers of dichlorocyclohexane, cis and trans 1,2-, cis and trans 1,3-, cis and trans 1,4- and 1,1-dichlorocyclohexane. Of these, the last name appears to correspond to the irradiation product.

Isomer	n_D^T	M.P.	B.P.
1,1-dichloro	$n_D^{20} = 1.4803$	-	59°/14 mm
cis 1,2- "	$n_D^{20} = 1.4986$	-	81°/14 mm
transl,2- "	$n_D^{20} = 1.4904$	-6°C	70°/14 mm
cis 1,4- "	$n_D^{25} = 1.4924$	18°C	82°/14 mm
trans 1,4- "	-	101°C	-
cis 1,3- "	-	-	-
trans 1,3- "	-	-	-

As can be seen from the Table, the refractive index of the irradiation product is identical with that of 1,1-dichlorocyclohexane.[134,135] The recorded refractive indices for the 1,2-isomers[136,137] are higher and the 1,4-isomers are solids.[137,139] There appears to be no information about the 1,3-isomers. The infrared spectra of the four 1,2-[138] and 1,4-isomers[139] differ from that shown in No. 11, and spectra for the 1,1- and cis and trans 1,3-isomers do not appear to have been published. The evidence suggests that the irradiation compound is either 1,1- or cis and/or trans 1,3-dichlorocyclohexane, most probably the former in view of the identical refractive indices. It might be anticipated that the C-H bond in chlorocyclohexane would be weakened by the presence of the chlorine atom and hence that secondary

chlorination might occur at the same carbon atom; (the most easily chlorinated site in 2-chlorobutane is the 2- position.)[140]

Time did not permit the preparation and isolation of a pure sample of this isomer.

The Isolation and Identification of Trichloromethylcyclohexane.

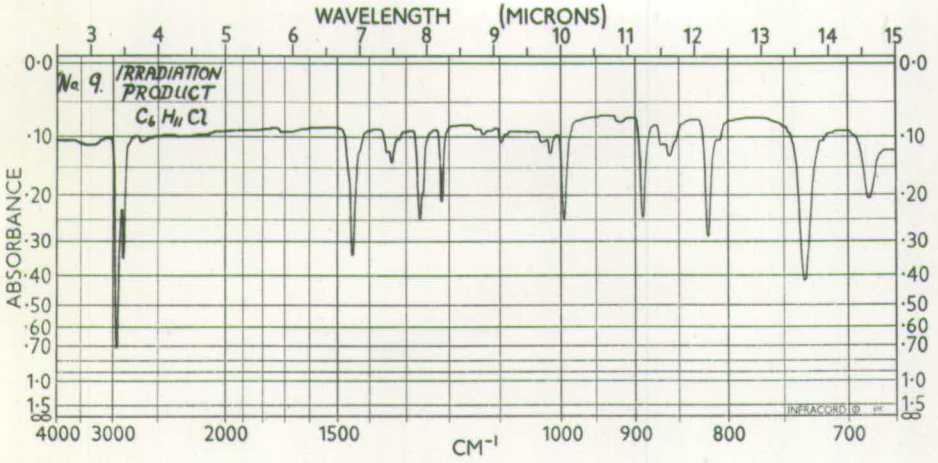
The last four fractions of distillate collected from the residue were composed of a colourless liquid containing some dissolved hexachloroethane. Several injections of this mixture on the 18", 15 mm i.d. column (30% S.E./60-80 celite) at 97°C produced 2-3 mls of the pure compound. Each injection took 1 hour 30 minutes to complete and it is worth noting that a liquid, whose boiling point is over 200°C, can be purified from high boiling impurities in this way, (in a reasonably short period), at a temperature below 100°C, thereby minimising the risk of thermal decomposition.

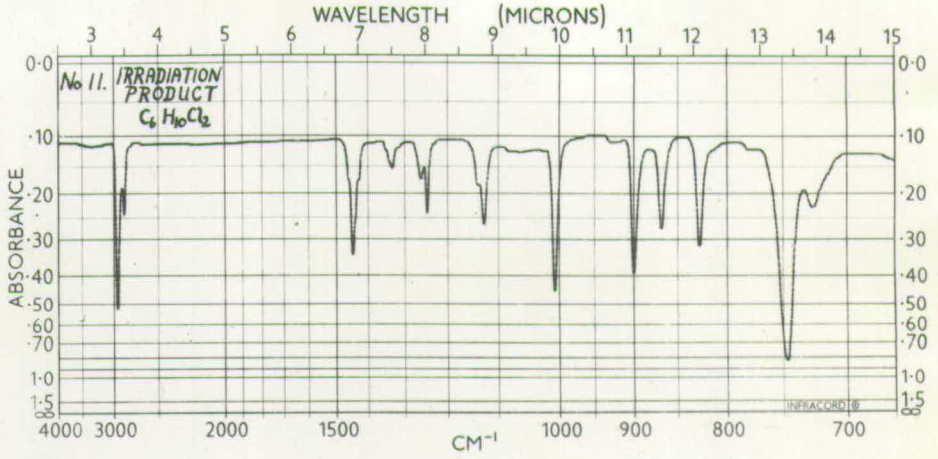
Chemical analysis of a sample agrees well with that calculated for the compound $C_6H_{11}CCl_3$:

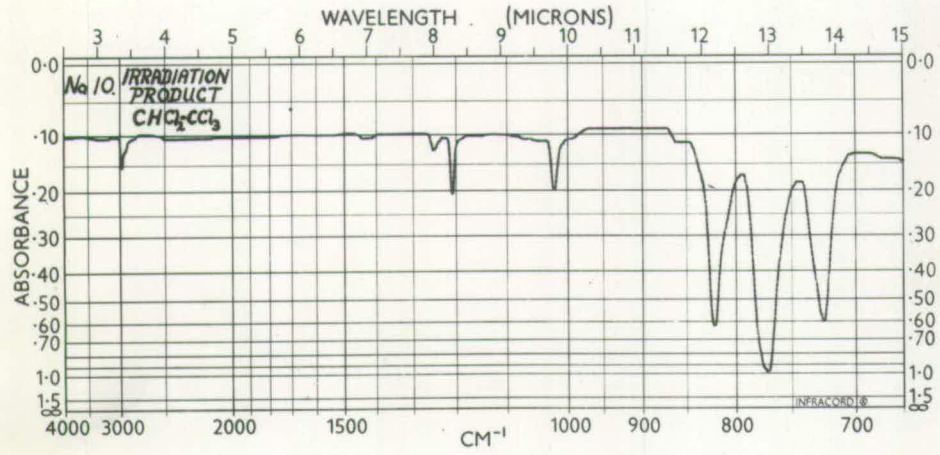
	Analysis found		Analysis calculated for $C_6H_{11}CCl_3$
% C	42.20	% C	41.71
% H	5.29	% H	5.51
% Cl	52.80	% Cl	52.77
	100.29		

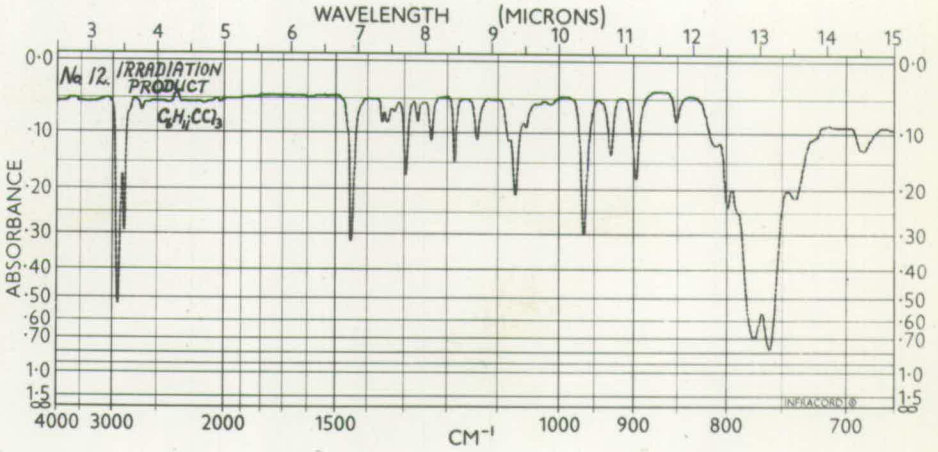
The infrared spectrum was recorded (No. 12) and values for the refractive index, density and boiling point were determined:

Refractive index	Density	Boiling Point
$n_D^{20} = 1.5022$	$D_4^{21.2} = 1.261$	$217 \pm 2.5^{\circ}C$


WAVELENGTH (MICRONS)
No 9. IRRADIATION PRODUCT
$C_6H_{11}Cl$
ABSORBANCE
CM^{-1}
INFRACORD


WAVELENGTH (MICRONS)
No 11. IRRADIATION PRODUCT
$C_6H_{10}Cl_2$
ABSORBANCE
CM^{-1}
INFRACORD


WAVELENGTH (MICRONS)
No 10. IRRADIATION PRODUCT
$CHCl_2CCl_3$
ABSORBANCE
CM^{-1}
INFRACORD


WAVELENGTH (MICRONS)
No 12. IRRADIATION PRODUCT
$C_2H_3CCl_3$
ABSORBANCE
CM^{-1}
INFRACORD

Examination of the High Boiling Residue.

The 13.4 gms of brown, moderately viscous residue were fractionated in the same manner as described on p. 111 for the benzene-carbon tetrachloride residue. Eight fractions were collected but again high temperature G.L.C. analysis of the more mobile fractions showed them to be composed of three or four compounds, one of which appeared to be dicyclohexyl. Three further fractions were obtained with the aid of a molecular cup-still, evacuated to 10^{-3} mm pressure by an oil diffusion pump.

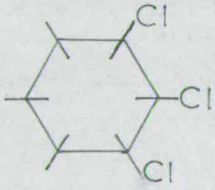
Fraction	O.B.T.	Dist.^{n} Temp.	Observations	n_D^{20}	I.R.	Analysis
1	100°C/10^{-2} mm	42°C	colourless, mobile liquid	1.5159		
2	100-103°C	43°C	" "	1.5184		
3	"	"	" "	1.5186	13a	F
4	110°C	45°C	" "	1.5209		
5	"	"	" "	1.5207		
6	115°C	"	" "	1.5205	13b	G
7	134°C	54°C	" "	1.5190		
8	138°C	58°C	colourless, slightly viscous	1.5199		
9	145°C/10^{-3} mm		mod. viscous, pale yellow	1.5425		H
10	155°C		viscous yellow	1.5470		I
11	170°C		very viscous, deep yellow	1.5630	13c	J

1.56 gms of black, non-distillable residue were left, difficultly soluble in chloroform.

Results of Analyses.

Fraction	Analysis	% C	% H	% Cl	Total
3	F	38.85	4.66	56.20	99.71
6	G	38.48	4.72	57.00	100.20
9	H	32.55	3.93	63.40	99.88
10	I	31.59	3.52	65.00	100.11
11	J	28.01	3.88	67.80	99.69

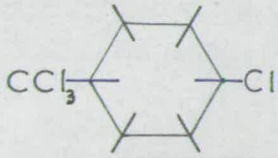
The percentage of chlorine contained in this residue is less than that in the residue of the benzene-carbon tetrachloride irradiation, but there is a similarity in the infrared spectra, especially below 1000 cm^{-1}. There is also a resemblance between the absorption pattern of trichloromethylcyclohexane and that of the residues between 800 and 700 cm^{-1}, suggesting the presence of trichloromethyl substituents in the latter. As in the previous case, the calculation of empirical formulae is of little value and possible structures, whose theoretical analyses approximate to those found, include:-



$C_6H_9Cl_3$ %C = 38.43 %H = 4.85 %Cl = 56.75 (F & G)

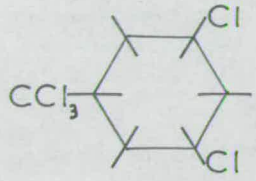
but the conditions under which the compound distilled suggest its molecular weight to be twice that indicated i.e.

$C_{12}H_{16}Cl_6$ %C = 38.64 %H = 4.33 %Cl = 57.05



$C_7H_{10}Cl_4$ %C = 35.59 %H = 4.27 %Cl = 60.17%

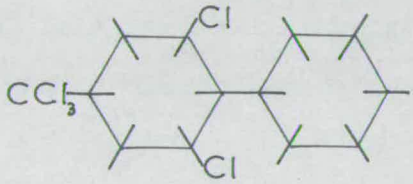
or the dimer $C_{14}H_{18}Cl_8$ %C = 35.77 %H = 3.87 %Cl = 60.37%



$C_7H_9Cl_5$ %C = 31.09 %H = 3.36 %Cl = 65.54

or the dimer $C_{14}H_{16}Cl_{10}$ %C = 31.20 %H = 3.00 %Cl = 65.80

Structures containing one unsubstituted cyclohexane ring are probably not present as they contain a higher percentage of carbon than found, for example,



$C_{13}H_{19}Cl_5$ %C = 44.28 %H = 5.44 %Cl = 50.29

Multiple substitution of the cyclohexane ring and combination of substituted rings appear to be the most probable reactions leading to the formation of the high molecular weight products formed during irradiation.

To summarise, the products formed by the irradiation of a 2 litre solution of 20 m% cyclohexane - 80 m% carbon tetrachloride were,

(1) Hydrogen chloride (2) Methyl chloride (not positive)

(3) Dichloromethane (4) Chloroform

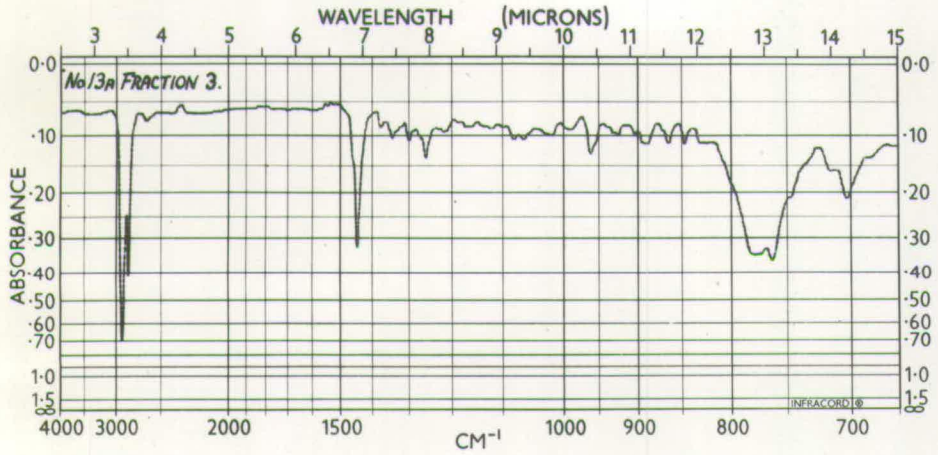
(5) Tetrachloroethylene (6) Chlorocyclohexane

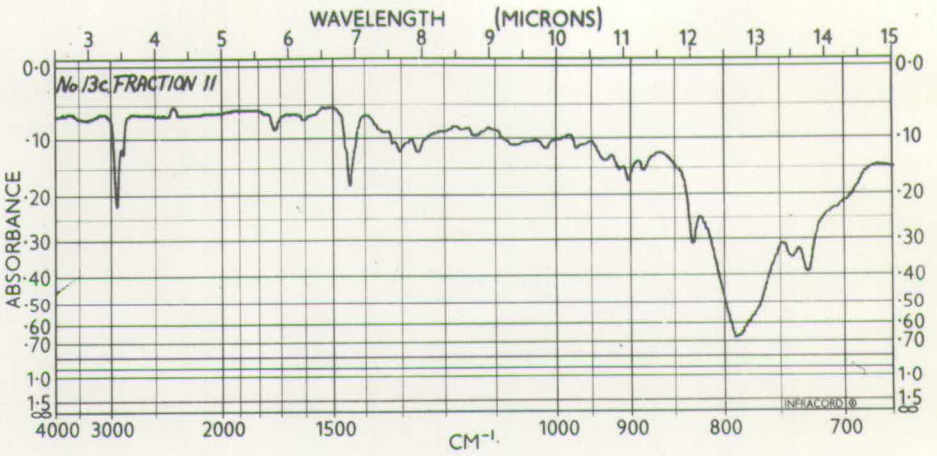
(7) Pentachloroethane (8) Dichlorocyclohexane

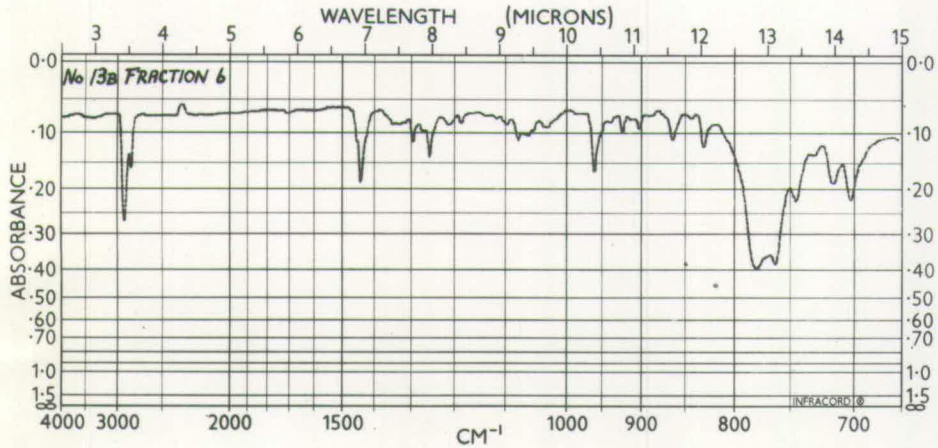
(9) Dichloromethylcyclohexane (?) (10) Hexachloroethane

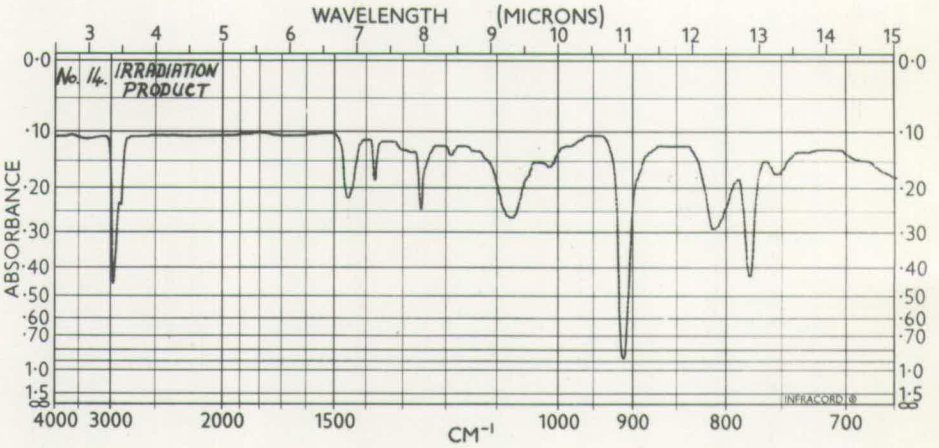
(11) Trichloromethylcyclohexane (12) Dicyclohexyl

and higher molecular weight products.


WAVELENGTH (MICRONS)
No 13A FRACTION 3.
ABSORBANCE
CM⁻¹
INFRACORD®


WAVELENGTH (MICRONS)
No 13C FRACTION 11
ABSORBANCE
CM⁻¹
INFRACORD®


WAVELENGTH (MICRONS)
No 13B FRACTION 6
ABSORBANCE
CM⁻¹
INFRACORD®


WAVELENGTH (MICRONS)
No. 14. IRRADIATION PRODUCT
ABSORBANCE
CM⁻¹
INFRACORD®

The Irradiation of Degassed Solutions of Cyclohexane and Carbon Tetrachloride.

Purification.

The procedures adopted for the purification of cyclohexane and carbon tetrachloride were described at the beginning of this Section.

The quantitative results presented in Table 14 and Graphs 10, 11 and 12 were obtained from the irradiation of a set of tubes of differing molar composition. Time did not permit the irradiation of solutions of fixed composition for increasing time intervals, which would have allowed calculation of the initial G-values for the yields of the products in these mixtures. That such irradiations will require to be carried out, is apparent from the fact that the secondary products identified in the residue of the 2 litre irradiation, pentachloroethane and dichlorocyclohexane, were detectable in some of the residues, especially in those solutions which contained large yields of chloroform and chlorocyclohexane.

The irradiation time was 240 hours, two-thirds that of the benzene-carbon tetrachloride solutions, at a dose rate of 2.363×10^{16} eV/ml/min.

Measurement of the Products.

The yields of hydrogen chloride and chloroform were measured by the procedures described on p. 104, but in this case it was necessary to reduce the sensitivity of the detector to accommodate the large volume of chloroform present in the solutions.

During the measurement of the chloroform, it was apparent that the concentration of chlorocyclohexane present in the irradiated solutions ($\sim$ 80 mls) was sufficiently large to allow direct determination of this product without preliminary concentration. Accordingly, after removal of the hydrogen chloride, the solutions were dried with anhydrous calcium chloride and transferred to 100 ml graduated flasks, the calcium chloride mass being broken up and extracted with chloroform which was then added to the organic solution to make up the required volume.

Before measurement of the remaining products, hexachloroethane, trichloromethylcyclohexane and dicyclohexyl, the volumes of the irradiated solutions were reduced to 25 mls by distilling off unchanged starting materials and some chlorocyclohexane. (Hence the reason tetrachloroethylene could not be determined.) Samples of chlorocyclohexane and trichloromethylcyclohexane, isolated from the 2 litre irradiation were used for preparing standard solutions of these compounds for measurement of the corresponding peaks in these irradiations; the other compounds were available commercially.

G-values were calculated in the same way as for the benzene-carbon tetrachloride solutions, using

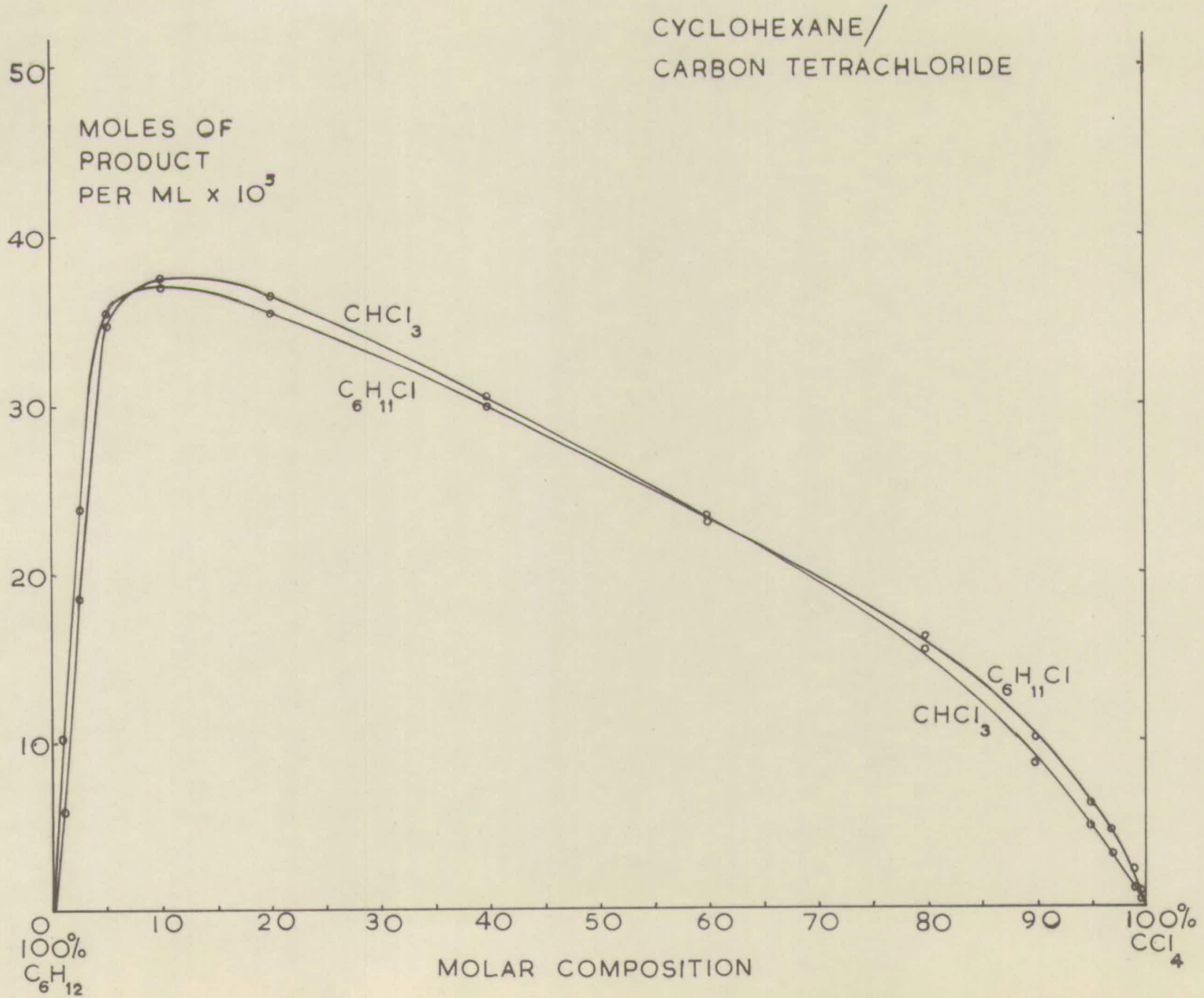
$$N_e(C_6H_{12}) = \frac{0.7787}{84.16} \times 48 \times N = 0.4441 \times N.$$

TABLE 14

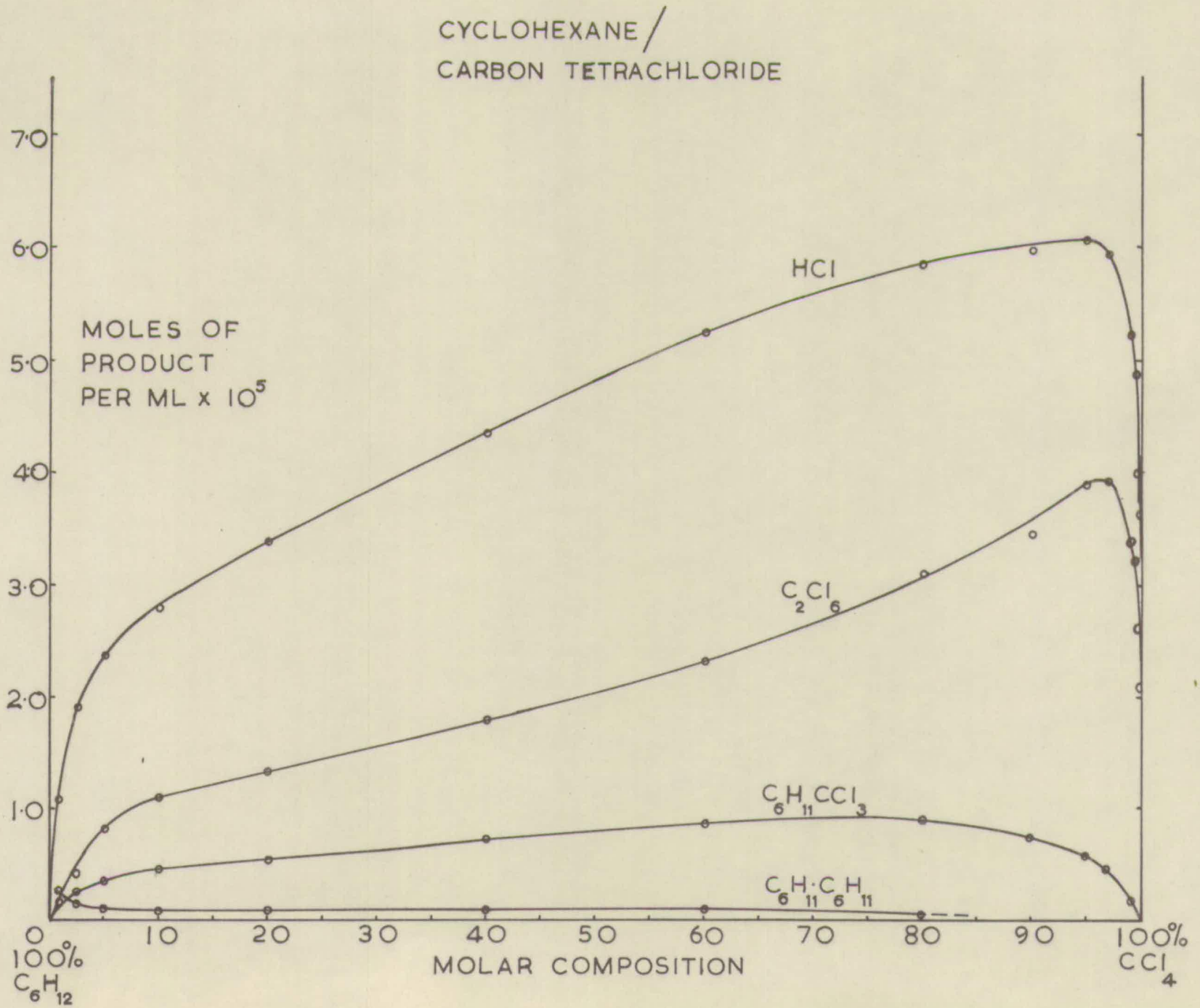
RESULTS FROM THE IRRADIATION OF CYCLOHEXANE – CARBON TETRACHLORIDE SOLUTIONS

DOSE RATE (Fe^{++}) = 2.363×10^{16} eV/ml/min.; IRRADIATION TIME = 240 HOURS

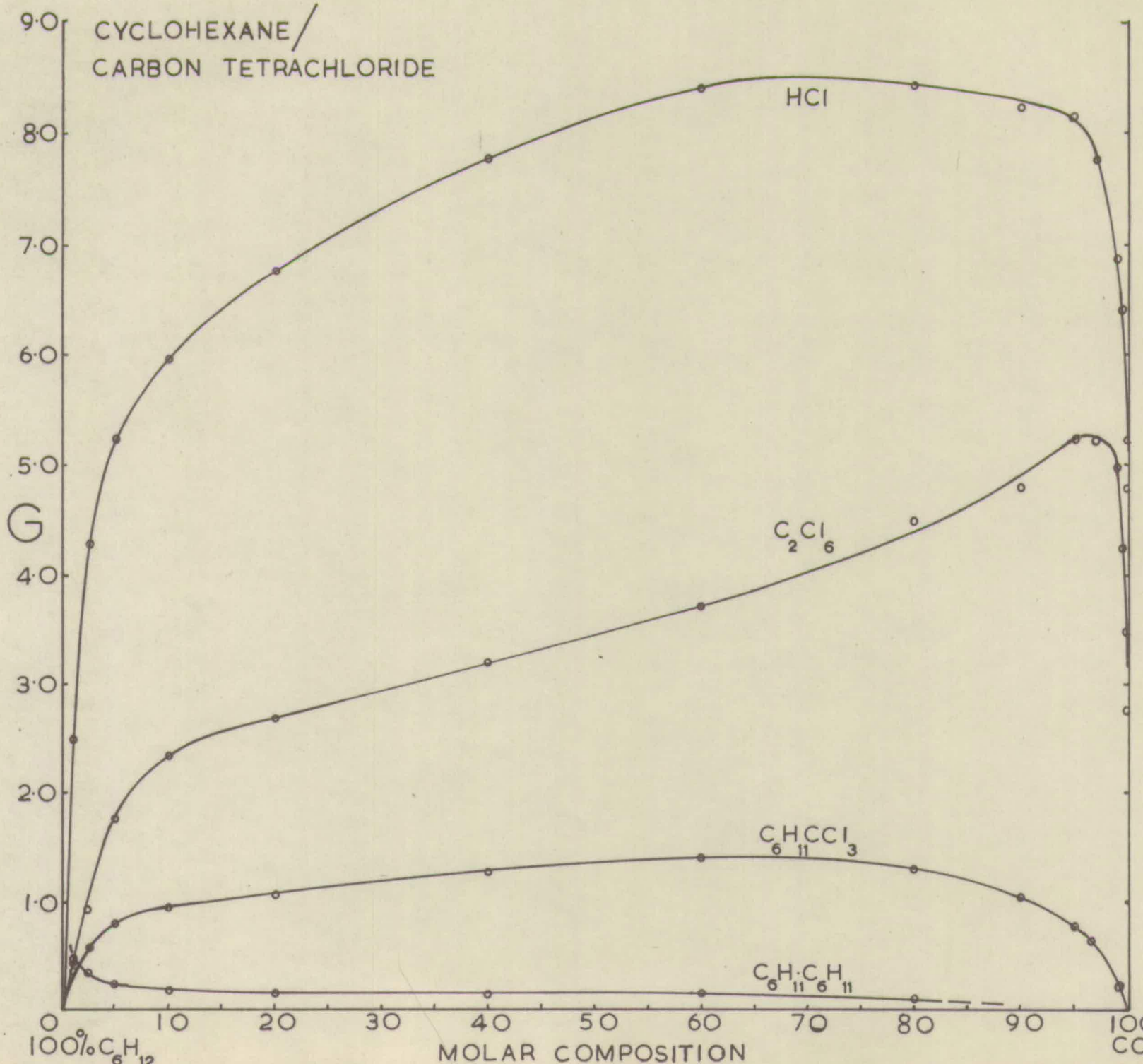
Mole % CCl_4	Vol. IRR.	HCl		$CHCl_3$		$C_6H_{11}Cl$		C_2Cl_6		$C_6H_{11}-CCl_3$		$C_6H_{11}C_6H_{11}$	
		Moles/ml. $\times 10^5$	G	Moles/ml. $\times 10^5$	G	Moles/ml. $\times 10^5$	G	Moles/ml. $\times 10^5$	G	Moles/ml. $\times 10^5$	G	Moles/ml. $\times 10^5$	G
1.0	81.5	1.11	2.49	5.99	13.46	10.34	23.24			0.17	0.38	0.22	0.49
2.5	81	1.94	4.31	18.72	41.69	23.93	53.29	0.42	0.93	0.25	0.55	0.15	0.34
5.0	76.5	2.39	5.24	34.68	75.98	35.48	77.74	0.83	1.81	0.37	0.81	0.10	0.22
10	80	2.80	5.95	37.43	79.50	37.09	78.78	1.11	2.36	0.45	0.95	0.08	0.18
20	82	3.39	6.77	36.43	72.79	35.26	70.45	1.34	2.68	0.54	1.08	0.08	0.16
40	82	4.37	7.77	30.57	54.45	30.12	53.64	1.80	3.21	0.73	1.31	0.08	0.15
60	76	5.26	8.41	22.71	36.31	23.08	36.91	2.33	3.73	0.87	1.40	0.09	0.15
80	81	5.84	8.42	15.60	22.51	16.44	23.72	3.13	4.51	0.90	1.30	0.07	0.09
90	84	5.99	8.23	8.48	11.66	10.03	13.78	3.47	4.77	0.75	1.02		
95	83	6.08	8.15	4.99	6.70	6.30	8.45	3.92	5.26	0.58	0.78		
97	81.5	5.84	7.76	3.29	4.38	4.65	6.19	3.94	5.23	0.46	0.61		
99.0	78	5.23	6.89	1.20	1.58	2.38	3.13	3.41	4.49	0.16	0.21		
99.50	79.5	4.90	6.43	0.60	0.79	1.38	1.81	3.24	4.25				
99.90	80	4.00	5.24	0.13	0.16			2.64	3.46				
99.95	82	3.65	4.78	0.09	0.11			2.11	2.77				


CYCLOHEXANE/
CARBON TETRACHLORIDE
MOLES OF
PRODUCT
PER ML x 10^3
50
40
30
20
10
$CHCl_3$
$C_6H_{11}Cl$
$C_6H_{11}Cl$
$CHCl_3$
0
100%
C_6H_{12}
10
20
30
40
50
60
70
80
90
100%
CCl_4
MOLAR COMPOSITION

GRAPH 10


CYCLOHEXANE /
CARBON TETRACHLORIDE
MOLES OF
PRODUCT
PER ML x 10^5
7·0
6·0
5·0
4·0
3·0
2·0
1·0
HCl
C_2Cl_6
$C_6H_{11}CCl_3$
$C_6H \cdot C_6H_{11}$
0
100%
C_6H_{12}
10
20
30
40
50
60
70
80
90
100%
CCl_4
MOLAR COMPOSITION

GRAPH 11


CYCLOHEXANE/
CARBON TETRACHLORIDE
HCl
C_2Cl_6
$C_6H_{11}CCl_3$
$C_6H_{11}.C_6H_{11}$
G
9·0
8·0
7·0
6·0
5·0
4·0
3·0
2·0
1·0
0
10
20
30
40
50
60
70
80
90
100%
100%C_6H_{12}
MOLAR COMPOSITION
CCl_4

GRAPH 12

Discussion.

The most striking features of the radiolysis of the cyclohexane-carbon tetrachloride system are the very large yields of chloroform and chlorocyclohexane, with G-values reaching a maximum of approximately 80. G-values of this order, and frequently very much greater, are characteristic of unsaturated systems in which chain reactions are easily initiated, but they are about 100 times greater than the G-values for the corresponding products in the benzene-carbon tetrachloride system.

The radiolysis of carbon tetrachloride results in the formation of chlorine atoms and trichloromethyl radicals and when irradiated in solution with cyclohexane, these radicals are probably the main species present, although radiolytic decomposition of cyclohexane will occur yielding cyclohexyl radicals and hydrogen atoms. These reactive species may then attack other molecules or undergo dimerisation or combination reactions resulting in the formation of the observed products. The following reaction scheme illustrates these mechanisms:

$$CCl_4 \rightsquigarrow \cdot CCl_3 + \cdot Cl \qquad (1)$$

$$C_6H_{12} \rightsquigarrow \cdot C_6H_{11} + \cdot H \qquad (2)$$

$$\cdot CCl_3 + C_6H_{12} \longrightarrow CHCl_3 + \cdot C_6H_{11} \qquad (3)$$

$$\cdot C_6H_{11} + CCl_4 \longrightarrow C_6H_{11}Cl + \cdot CCl_3 \qquad (4)$$

$$\cdot Cl + C_6H_{12} \longrightarrow HCl + \cdot C_6H_{11} \qquad (5)$$

$$\cdot C_6H_{11} + CCl_4 \longrightarrow C_6H_{11}CCl_3 + \cdot Cl \qquad (6)$$

$$\cdot C_6H_{11} + \cdot Cl \longrightarrow C_6H_{11}Cl \qquad (7)$$

$$\cdot C_6H_{11} + \cdot CCl_3 \longrightarrow C_6H_{11}CCl_3 \qquad (8)$$

$$\cdot H + \cdot Cl \longrightarrow HCl \qquad (9)$$

$$\cdot H + \cdot CCl_3 \longrightarrow CHCl_3 \qquad (10)$$

$$\cdot H + CCl_4 \longrightarrow HCl + \cdot CCl_3 \qquad (11)$$

$$\cdot H + CCl_4 \longrightarrow CHCl_3 + \cdot Cl \qquad (12)$$

$$2 \cdot CCl_3 \longrightarrow CCl_3\text{-}CCl_3 \qquad (13)$$

$$2 \cdot C_6H_{11} \longrightarrow C_6H_{11}\text{-}C_6H_{11} \qquad (14)$$

The large, equivalent yields of chloroform and chlorocyclohexane can be satisfactorily accounted for by a short length chain reaction involving reactions (3) and (4). The ability of cyclohexane and carbon tetrachloride to undergo a hydrogen-halogen exchange chain reaction in the presence of peroxide initiators has already been mentioned in the introduction to this Section and the mechanism of the reaction appears to be equally applicable to both systems, even although the initiating radicals are produced by different methods. The results obtained by DeTar and Wells[116] show that the approximately equivalent yields of chloroform and chlorocyclohexane vary in the same manner as in this system, increasing as the concentration of cyclohexane increases until the ratio of the concentration of cyclohexane to carbon tetrachloride is approximately 4:1.

The irradiations give a general picture of the variation in the yields of the different products with changing composition but little information as to the importance of the alternative reactions by which the products can be formed. The reactions suggested have not all been proved to occur and until information is obtained as to the relative importance of the radical species present in solution (e.g., by the use of a scavenger, such as iodine), rigid conclusions cannot be made with regard to the relative importance of these reactions.

The quantitative results can be considered in three sections:

(a) 1.0 to 10 m% carbon tetrachloride

(b) 10 to 80 m% carbon tetrachloride

(c) 80 to 99.95 m% carbon tetrachloride.

In section (b) reaction (1) is considered to be the major result of the action of radiation although (2) will occur also. The chlorine atoms are believed to react with cyclohexane molecules by reaction (5) to form hydrogen chloride and cyclohexyl radicals. The trichloromethyl radicals formed in (1) can either dimerise by reaction (13) to form hexachloroethane or combine with cyclohexyl radicals to form trichloromethylcyclohexane. Both trichloromethyl and cyclohexyl radicals initiate the chain reaction shown in steps (3) and (4). Reactions (5) and (6) appear capable of forming a chain sequence, but that this is not the case, is evident from the relatively low yields of hydrogen chloride and trichloromethylcyclohexane, the former being produced in 6-8 times the

yield of the latter. Considering reactions (4) and (6), if there are two alternative paths for a reaction, the preferred mechanism is likely to be that which results in the formation of the most stable reactive species, which in this case is believed to be the trichloromethyl radical. This conclusion is supported by the presence of the chain reaction based on reaction (4) and would suggest that (6) occurs to a negligible extent. The radicals formed in (2) may react by (8) and (9) and presumably (7), (10) and (11) also occur to some extent. (12) is energetically unfavourable.

In this composition region, the majority of the chlorine atoms and trichloromethyl radicals can be accounted for to within close limits. For example, considering the solution of composition 40 m% CCl_4/60 m% C_6H_{12}, for the products formed in low yield

$$G_{(Cl)} = G_{(HCl)} = \underline{7.77}$$

$$\text{and } G_{(CCl_3)} = G_{(C_6H_{11}CCl_3)} + 2\,G_{(C_2Cl_6)}$$

$$= 1.31 + 2 \times 3.21$$

$$= \underline{7.73}$$

The values for the products of the chain reaction are $G_{(C_6H_{11}Cl)} = 53.64$ and $G_{(CHCl_3)} = 54.45$, giving

$$\underline{\text{Total } G}_{(Cl)} = \underline{61.41}$$

and $\underline{\text{Total } G}_{(CCl_3)} = \underline{62.18}$; $G_{(Cl)}$ undetected = 0.77

Considering the cyclohexyl radicals;

production, $G_{(C_6H_{11})} = G_{(HCl)} + G_{(CHCl_3)}$

$= 7.77 + 54.45$

$= \underline{62.22}$

removal, $G_{(-C_6H_{11})} = G_{(C_6H_{11}CCl_3)} + G_{(C_6H_{11}Cl)} + 2\,G_{(C_6H_{11}C_6H_{11})}$

$= 1.31 + 53.64 + 0.30$

$= \underline{55.25}$ $\quad G_{(-C_6H_{11})}$ undetected = 6.97

For the other solutions in this composition region, the material balance is slightly less satisfactory for the hydrogen chloride, hexachloroethane and trichloromethylcyclohexane, there being a deficiency of trichloromethyl radicals in the solutions of lower carbon tetrachloride composition and a deficiency of chlorine atoms in the solutions containing a higher percentage of carbon tetrachloride; however, in each case the yields of chloroform and chlorocyclohexane differ in such a way as to reduce the discrepancies:-

For example,

10 m% CCl_4/90 m% C_6H_{12}		80 m% CCl_4/20 m% C_6H_{12}	
$G_{(Cl)}$	$G_{(CCl_3)}$	$G_{(Cl)}$	$G_{(CCl_3)}$
5.95	4.72	8.42	9.02
	0.95		1.30
5.95	5.67	8.42	10.32
78.78	79.50	23.72	22.51
84.73	85.17	32.14	32.83

$G_{(Cl)}$ undetected = 0.44 $\qquad$ $G_{(Cl)}$ undetected = 0.69

10 m% CCl_4/90 m% C_6H_{12}		80 m% CCl_4/20 m% C_6H_{12}	
$G(C_6H_{11})$	$G(-C_6H_{11})$	$G(C_6H_{11})$	$G(-C_6H_{11})$
= 85.45	= 80.09	= 30.93	= 25.20
$G(-C_6H_{11})$ undetected = 5.36		$G(-C_6H_{11})$ undetected = 5.73	

Section (c); molar composition 80 to 99.95% carbon tetrachloride.

The addition of 0.05 m% cyclohexane to carbon tetrachloride results in the production of hydrogen chloride in considerable yield, G = 4.78, accompanied by an increase in $G_{(C_2Cl_6)}$ from 0.88 (pure CCl_4) to 2.77. This rapid rise in product formation, increasing progressively with the addition of up to 5 m% cyclohexane, indicates a rapid decrease in the importance of back reactions (as in pure CCl_4) and, conversely, the rapidly increasing importance of hydrogen abstraction, accompanied by the dimerisation of trichloromethyl radicals.

With the addition of 0.05-20 m% cyclohexane, the yield of trichloromethylcyclohexane increases slowly (reaction (8)), as the availability of cyclohexyl radicals increases by virtue of the growing concentration of cyclohexane. Similarly, reaction (14) becomes operative, forming a barely measurable yield of dicyclohexyl under these conditions of measurement.

At the composition in which maximum yield of the hydrogen chloride and hexachloroethane occurs (95 m% CCl_4), there is a greater deficiency of chlorine atoms (1.4) than in the solutions already discussed, but the G of undetected cyclohexyl radicals

(5.62) is approximately the same.

$$\underline{G_{(Cl)}} = G_{(HCl)} + G_{(C_6H_{11}Cl)} = 8.15 + 8.45 = \underline{16.60}$$

$$\underline{G_{(CCl_3)}} = 2\,G_{(C_2Cl_6)} + G_{(C_6H_{11}CCl_3)} + G_{(CHCl_3)} = 10.52 + 0.78 + 6.70 = \underline{18.00}$$

Reactions (3) and (4) must be of extremely short chain length, if, indeed, they can be considered as forming a chain reaction at all. The termination steps, for example, reaction (13), must be very efficient and also the small concentration of cyclohexane will reduce the rate of the reaction.

Section (a); composition 1.0-10 m% carbon tetrachloride.

As in the benzene-carbon tetrachloride system, there is a rapid increase in the yields of products upon addition of small quantities of carbon tetrachloride to the cyclohexane. In the region 1.0 to 5.0 m% CCl_4, the increase is particularly rapid for chloroform and chlorocyclohexane which, however, are not formed in equal quantities. The yield of chloroform is 60% that of chlorocyclohexane in the 1.0 m% CCl_4 solution but rises to 80% in the 2.5 m% CCl_4 solution and the yields are almost equal in the 10 m% solution, indicating a rapid decrease in the reaction(s) responsible for this discrepancy. This divergence in the yields can be considered either as resulting from an increased formation of chlorocyclohexane or from a decrease in the rate of formation of chloroform, or as the result of destruction of chloroform during radiolysis by reactions operative in these solutions.

Any explanation must accomodate the fact that none of the yields of the other measured products show a proportional increase in this region.

It is interesting to note that only in these two solutions was dichloromethane, formed as a secondary product from chloroform, detectable at all, even although greater concentrations of chloroform were formed in other solutions. The estimated yields, G = 1.7 and 1.2 respectively, exhibit the same rapid change in value, in the opposite direction, as do those of the chloroform, but are inadequate to explain the results. This observation would appear, however, to lend support to the suggestion that chloroform may be decomposed in these solutions during the irradiation period. This could be verified by the irradiation of a series of solutions containing, say 1m% CCl_4, for short but increasing periods i.e., doses, and observing whether chloroform and chlorocyclohexane are formed initially in equivalent yields at low doses, followed by a decrease in the yield of the former with increasing dose.

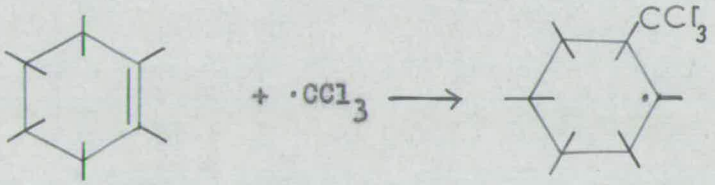
There is a poor material balance in the first two solutions of this composition range. Calculating as before:

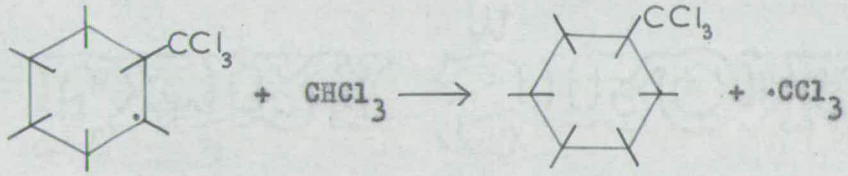
1m% CCl_4/99m% C_6H_{12}		2.5m% CCl_4/97.5m% C_6H_{12}	
$G_{(Cl)}$	= 25.73	$G_{(Cl)}$	= 57.60
$G_{(CCl_3)}$	= 14.74	$G_{(CCl_3)}$	= 44.10
$G_{(CCl_3)}$ undetected	= 10.99	$G_{(CCl_3)}$ undetected	= 13.50
$G_{(C_6H_{11})}$	= 15.95	$G_{(C_6H_{11})}$	= 46.00
$G_{(-C_6H_{11})}$	= 24.60	$G_{(-C_6H_{11})}$	= 54.52
$G_{(C_6H_{11})}$ undetected	= 8.65	$G_{(C_6H_{11})}$ undetected	= 8.52

The G-value for the undetected trichloromethyl radicals is approximately equal to the apparent loss of chloroform.

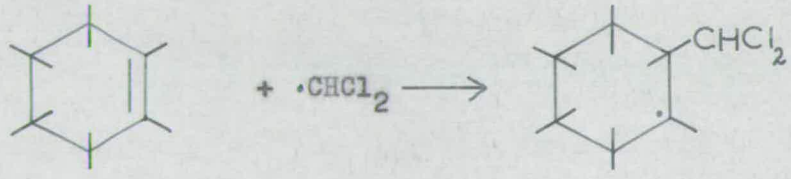
The possibility that cyclohexene is formed in solutions of high cyclohexane concentration cannot be overlooked, since it is a major product of the irradiation of pure cyclohexane.

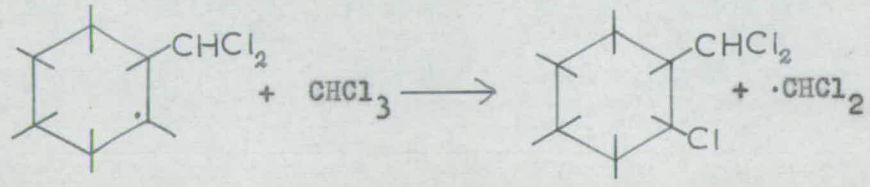
A chain reaction involving cyclohexene and chloroform does not provide an explanation for the low chloroform yield because the expected product from such a reaction would be trichloromethyl-cyclohexane:





If hydrogen abstraction did not occur from chloroform, especially in view of the very high concentration of hydrogen available in cyclohexane, but rather chlorine abstraction,





the main product would be 1-chloro-2-dichloromethylcyclohexane, which has the same molecular composition as trichloromethylcyclohexane and hence would have a similar retention time on G.L.C.

It would appear that the undetected product(s) are either substituted cyclohexane compounds containing at least two trichloromethyl radicals or similarly substituted dicyclohexyl compounds.

The yields of the products increase very much more rapidly than would be expected from the change in the concentration of carbon tetrachloride indicating, as in the benxene-carbon tetrachloride system, that a "sensitisation" effect exists. Possible mechanisms for this effect were outlined in the previous Section. Since cyclohexane can transfer energy to benzene (protection effect) and if, as Chapiro suggests, benzene is capable of transferring energy to carbon tetrachloride, then it is possible that energy transfer from cyclohexane to carbon tetrachloride may be occurring in this system, with resulting increased decomposition of carbon tetrachloride molecules. On the other hand, preferential absorption of energy by carbon tetrachloride or dissociative electron capture may be the processes responsible for the observed results.

S E C T I O N V.

The Irradiation of

a) Acetylene - Carbon Tetrachloride and
Acetylene - Chloroform Solutions.

b) Methylcyclopentane - Carbon Tetrachloride Solution.

a) The Irradiation of Solutions of Acetylene in Carbon Tetrachloride and Chloroform.

The irradiation of solutions of acetylene in carbon tetrachloride and chloroform were carried out originally to discover whether acetylene, a minor product formed in the radiolysis of pure benzene, might have been responsible for the formation of the unidentified compound formed in the first irradiations of benzene and carbon tetrachloride, by an addition reaction with the free radicals present in the system.

In irradiated carbon tetrachloride solution, chlorine atoms and trichloromethyl radicals are present and addition of these to acetylene would result in the formation of the products:

a) dichloroethylene, b) 1,3,3,3-tetrachloroprop-1-ene and c) 1,1,1,4,4,4-Hexachlorobut-2-ene by the following reactions;

(1) $CH{\equiv}CH + \cdot Cl \longrightarrow ClCH{=}\dot{C}H$
$ClCH{=}\dot{C}H + \cdot Cl \longrightarrow ClCH{=}CHCl$

(2) $CH{\equiv}CH + \cdot Cl \longrightarrow ClCH{=}\dot{C}H$
$ClCH{=}\dot{C}H + \cdot CCl_3 \longrightarrow ClCH{=}CH{-}CCl_3$

(3) $CH{\equiv}CH + \cdot CCl_3 \longrightarrow Cl_3C{-}CH{=}\dot{C}H$
$Cl_3C{-}CH{=}\dot{C}H + \cdot CCl_3 \longrightarrow Cl_3C{-}CH{=}CH{-}CCl_3$

(4) $2 \cdot CCl_3 \longrightarrow CCl_3{-}CCl_3$

Hydrogen abstraction reactions would not be expected to occur to any extent since the only source of hydrogen is acetylene with a high C-H bond dissociation energy of 121 k.cal./mole.

The suggested products contain α,β-disubstituted double bonds and may, therefore, occur in cis and trans isomers; prolonged irradiation, of course, may result in further addition to these

compounds, resulting in the formation of secondary, saturated products.

Experimental.

A saturated solution of acetylene in carbon tetrachloride was prepared by bubbling the gas for 2 hours 30 minutes through the carbon tetrachloride (435 mls) contained in the irradiation vessel. The acetylene, from a cylinder, was first purified by passing it through an aqueous solution of 2,4-dinitrophenylhydrazine in 2$\bar{N}$ hydrochloric acid to remove acetone vapour and subsequently through a set of anhydrous calcium chloride tubes.

The vessel was irradiated for 108 hours at a dose rate of 1220r/ml/min.

After irradiation, the solution was colourless, with no pungent smell of hydrogen chloride. It was then distilled, the first fractions of the distillate and the concentrated residue being analysed by gas chromatography.

Examination of the distillate at 52°C on a silicone oil/celite column, revealed the presence of two small peaks, the first of which corresponded to trans-dichloroethylene (b.p. 48°C), while the second agreed by retention time with both cis-dichloroethylene (b.p. 60°C) and chloroform (b.p. 61°C). The use of a 30% T.C.P. column confirmed the presence of the trans isomer, as well as the cis isomer, which was eluted immediately before the carbon tetrachloride peak, whereas chloroform is eluted after carbon tetrachloride on this type of column packing.

The absence of hydrogen chloride and chloroform are in accordance with the improbability of hydrogen abstraction reactions.

The residue contained the following components (S.O./celite,98°C);

(1) tetrachloroethylene (minor product)

(2) two incompletely separated compounds, the smaller preceding (major products)

(3) Hexachloroethane (major product)

No higher boiling compounds were detected after hexachloroethane.

Analysis on a T.C.P. column at 140°C gave the following pattern of peaks:

(1) tetrachloroethylene

(2) two incompletely separated compounds, the larger preceding.

(3a)unidentified compound (minor component)

(4) hexachloroethane.

The absence of this last unidentified compound (3a) in the first analysis must be due to it having a retention time similar to one of the major components.

No attempt was made to isolate the major unidentified products, most probably cis and trans isomers of the tetrachloropropene, after it was found that their behaviour on G.L.C. was different from the unidentified component of the benzene-carbon tetrachloride residue.

However, the experimental results appear to agree with the reaction scheme detailed earlier, with the exception of hexachlorobutene, whose boiling point is greater than that of hexachloroethane, but which does not appear to be formed, and the presence in small yield of an unidentified product (3a).

Acetylene - Chloroform Solution.

The examination of the distillate of an irradiated solution of acetylene in chloroform, smelling strongly of hydrogen chloride, showed that neither cis- nor trans-dichloroethylene was formed, but only dichloromethane, a normal product of irradiated chloroform.

The residue was found to be composed of the following compounds, in order of elution, on T.C.P. at 135°C:

(1) tetrachloroethylene (minor product)
(2) unidentified compound (major product)
(3) sym-tetrachloroethane (major product)
(4) penta- and/or hexachloroethane (major product)
(5) three components at greater retention times.

An injection on a silicone oil/celite column at 104°C showed the presence of:

(1) carbon tetrachloride (not definite; minor product)
(2) tetrachloroethylene (minor product)
(3) sym-tetrachloroethane (major product)
(4) unidentified compound (major product)
(5) pentachloroethane (major product)
(6) unidentified compound (minor product)
(7) hexachloroethane (major product)
(8) two higher boiling compounds.

The products identified in the above list are the compounds normally formed during the radiolysis of chloroform. As in the acetylene-carbon tetrachloride system, no attempt was made to

identify the other major product, but in this system, since hydrogen abstraction reactions can compete with radical addition reactions, the probable nature of the compound is less certain. For example,

$$CHCl_3 \rightsquigarrow \cdot CHCl_2 + \cdot Cl \qquad (1)$$

$$HC{\equiv}CH + \cdot CHCl_2 \longrightarrow H\dot{C}{=}CH{-}CHCl_2 \qquad (2)$$

$$H\dot{C}{=}CH{-}CHCl_2 + CHCl_3 \longrightarrow CH_2{=}CH{-}CHCl_2 + \cdot CCl_3 \qquad (3)$$

$$HC{\equiv}CH + \cdot CCl_3 \longrightarrow H\dot{C}{=}CH{-}CCl_3 \qquad (4)$$

$$H\dot{C}{=}CH{-}CCl_3 + CHCl_3 \longrightarrow CH_2{=}CH{-}CCl_3 + \cdot CCl_3 \qquad (5)$$

Reactions (4) and (5) could form a chain process but this is apparently not the case, since the yield of the major unidentified compound is of average size for this type of system.

If reaction (3) does not occur, but instead an addition reaction

$$H\dot{C}{=}CH{-}CHCl_2 + \cdot R \longrightarrow RCH{=}CH{-}CHCl_2 \qquad (6)$$

where $R\cdot = \cdot Cl$, $\cdot CHCl_2$ or $\cdot CCl_3$, a variety of products are possible, two of which would have C_4 skeletons, thus explaining the high boiling compounds eluted after hexachloroethane. When $R\cdot = \cdot Cl$, the product would be 1,3,3-trichloroprop-1-ene, an isomer of compound formed by reaction (5), and should occur in cis and trans forms. The symmetrical form of the peak for the major unidentified component of the residue suggests that it is a single compound, for example, that produced by reaction (5), 1,1,1-trichloropropene, but there remains the possibility that the geometrical isomers of the other trichloropropene are not resolved by G.L.C. under these conditions.

The isolation of this product, and that formed in the other system, by large scale G.L.C., would be a simple matter and the structures could probably be determined by infrared analysis.

b) The Irradiation of Methylcyclopentane-Carbon Tetrachloride Solution.

Preparation.

B.D.H. methylcyclopentane was distilled using a 12" fractionating column of ¼" glass helices which removed a lower boiling impurity almost completely. 20 mls were mixed with chloroform-free carbon tetrachloride to form a 10% v/v solution of the hydrocarbon.

The solution was irradiated for 308 hours at an unmeasured dose rate.

The irradiated solution was very pale yellow and evolved hydrogen chloride. The working up procedure was similar to that described for the 2 litre cyclohexane-carbon tetrachloride irradiation, but adapted to suit the smaller volume, and need not be repeated. No attempt was made to examine the small volume of residue of boiling point higher than that of the trichloromethyl-substituted methylcyclopentane.

Distillate.

Examination of the first fractions of the distillate showed that the following compounds were present; in addition to the starting materials,

(1) dichloromethane (trace)

(2) chloroform (major product)

Residue.

A complex pattern of peaks was obtained from an injection of the residue on a 3'6" S.E./celite column at 100°C. After residual

carbon tetrachloride, the following peaks were eluted:

(1) minor peak: tetrachloroethylene

(2) major peak, which could be resolved into four components on reducing the size of the injection. The first, a major component, the others decreasing progressively by approximately 25% were, presumably, all isomeric monochloro-substituted methylcyclopentanes.

(3) peak of medium size

(4) minor peak

(5) major peak: hexachloroethane

(6) medium-sized peak: trichloromethyl-substituted compound(s)

Sufficient residue was obtained to allow concentration by distillation of the lower boiling products, peaks (1) and (2) above, leaving the residue correspondingly richer in the other products.

This distillate was treated batchwise, 0.5 - 1.0 ml samples being injected on to the 3' large scale G.L.C. column (30% $^{W}/_{W}$ S.E./celite at 50°C), and the tetrachloroethylene and monochloro-compounds were collected in separate traps, A and B. 8.5 gms of residue remained, from which 3.5 gms of crude hexachloroethane were isolated. The residual 5.0 gms of brown liquid were passed through the column (temperature 97°C) and peaks (3) and (6) condensed in traps C and D.

Examination of Fractions A, B, C and D.

Fraction A. The infrared spectrum (No. 14) contained the four major absorption bands of tetrachloroethylene along with several other absorptions denoting the presence of C-H and $-CH_3$ bonds. An injection on G.L.C. showed the main peak for tetrachloroethylene to be accompanied by a small amount of the monochloro-compound(s)

and while all but one of the additional absorptions can be attributed to the latter compound(s), the remaining broad absorption band at 1075cm^{-1} is unexplained. However, the intensity of the C-H absorptions at 3000cm^{-1} and in the 1500-1200cm^{-1} region, in comparison with those of the tetrachloroethylene, suggest that there may be another compound present whose retention time is identical with that of tetrachloroethylene. Unfortunately, there was insufficient sample for analysis on a T.C.P. column packing. However, the presence of tetrachloroethylene is indisputable.

Fraction B. A chemical analysis of this fraction, known to contain four compounds, gave:

%C =	60.00	Analysis required	%C = 60.76
%H =	9.41	for $C_6H_{11}Cl$	%H = 9.34
%Cl =	30.70		%Cl = 29.89
	100.11		

confirming that the composition of the fraction corresponded to the expected structure, $C_6H_{11}Cl$.

By separating the components of this mixture on an 8', 20mm i.d. G.L.C. column, containing 25%^{w}/w S.E./celite (60-80 mesh) at 62°C, 250mls N_2/min. and trapping out the main component, its refractive index, boiling point and infrared spectrum were obtained. This compound appeared pure by analytical scale G.L.C.

Refractive index, n_D^{20} = 1.4462; Boiling point = 128° ± 1°C. The infrared spectrum (No. 15) is extremely simple and does not show the normal intense absorption band(s) characteristic of carbon-chlorine bonds. The spectrum was redetermined using a Hilger H.800

double-beam infrared spectrometer which, although equipped with a sodium chloride prism and plates, recorded it down to 550 cm^{-1}. Despite the increasing opacity of sodium chloride to wavelengths above 15 μ, it was obvious that no strong absorptions occurred in this region. Bellamy[119] reports two absorption bands at 977 and 890 cm^{-1} as characteristic of the cyclopentane ring, but they could only be detected in thick films of the hydrocarbon. Little improvement was achieved on increasing the thickness of the film of the chloro-compound and it may be that the poorly defined bands at 905 and 855 cm^{-1} correspond to those mentioned above, displaced to higher wavelengths by the chlorine substituent. The presence of chlorine in this compound was further demonstrated by obtaining a positive result for chlorine in the Lassaigne sodium fusion test and the green flame characteristic of halogen in Beilstein's copper wire test.

A hydrogen atom attached to a tertiary carbon atom is normally more reactive than secondary hydrogen and secondary than primary hydrogen atoms to radical attack and, therefore, the monochloro-compound derived from methylcyclopentane would be expected to be 1-chloro-1-methylcyclopentane. This compound was synthesised from cyclopentanone by a Grignard reaction and the infrared spectrum (No. 16) is shown for two thicknesses of film.

Refractive index, $n_D^{20} = 1.4470$.

It will be observed that again no carbon-halogen absorption is visible, although chlorine was undoubtedly present, and that the spectrum differs from that of the irradiation product, by having

strong absorptions at 1190, 1030 and 1020 cm^{-1} and several other weak absorptions. If impurities were responsible for the additional absorptions, the concentration required to cause such absorptions would be expected to alter the value of the refractive index by considerably more than 0.0008.

The absorption maxima at 1450, 1370 and 1345 cm^{-1} occur in both methylcyclopentane and the irradiation product and are attributed, in the pure hydrocarbon, to the asymmetrical and symmetrical deformation frequencies of the hydrogen atoms of the methyl group and the tertiary hydrogen atom respectively. It would appear, therefore, that the chlorine atom is substituted on C_2 or C_3, thereby leaving unchanged the absorptions of the methyl group and tertiary hydrogen atom.

The presence of four peaks of similar retention time indicates that substitution of a chlorine atom occurs at different positions in the molecule and not specifically at a particular carbon atom. In conclusion it can be said that the isomer formed in largest yield during irradiation does not appear to be the expected 1-chloro-1-methylcyclopentane. The irradiation of a large volume (2 litres) of methylcyclopentane-carbon tetrachloride solution would allow isolation of all the isomers and facilitate their identification.

Fraction C.

This fraction was passed through the 3' column again at 94°C and the middle portion was collected. Immediately after

condensing, the liquid was colourless but after standing in daylight for about an hour it turned pale blue and then gradually green.

Refractive index, n_D^{20} = 1.4793; Boiling point = 161° ± 1°C

The infrared spectrum (No. 17) contains the three main carbon-chlorine absorptions characteristic of pentachloroethane (compare No. 10 and n_D^{20} = 1.5030), as well as other strong absorptions, indicative of the presence of methylcyclopentane derivatives, most probably dichloro-compound(s). The boiling point of 161°C is exactly that of pentachloroethane but that of a dichloro-methylcyclopentane must also be similar, probably in the range 165 ± 5°C (c.f. dichlorocyclohexane). The value of the refractive index, which is much lower than that for pure pentachloroethane, indicates that there is present a considerable quantity of some other compound. As in the cyclohexane-carbon tetrachloride irradiation, pentachloroethane will be formed as a secondary product from chloroform.

Fraction D.

The crude material was brown and, after being passed through the column again at 100°C, it condensed to a pale yellow liquid. Only one compound could be detected by G.L.C.
Refractive index, n_D^{20} = 1.4998; Boiling point = 206° ± 2°C (decomp.)

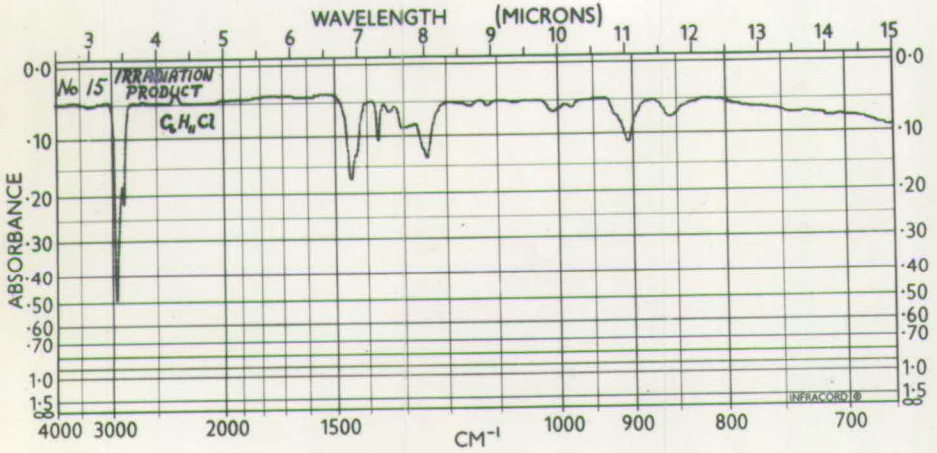
A chemical analysis gave the following result:

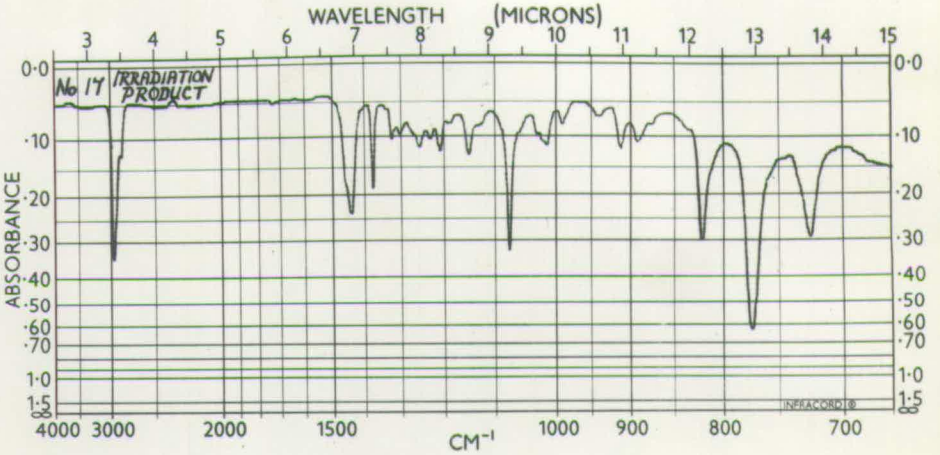
% C = 42.93	Analysis required for $C_7H_{11}Cl_3$	% C = 41.71
% H = 5.17		% H = 5.51
% Cl = 51.70		% Cl = 52.77
99.80		

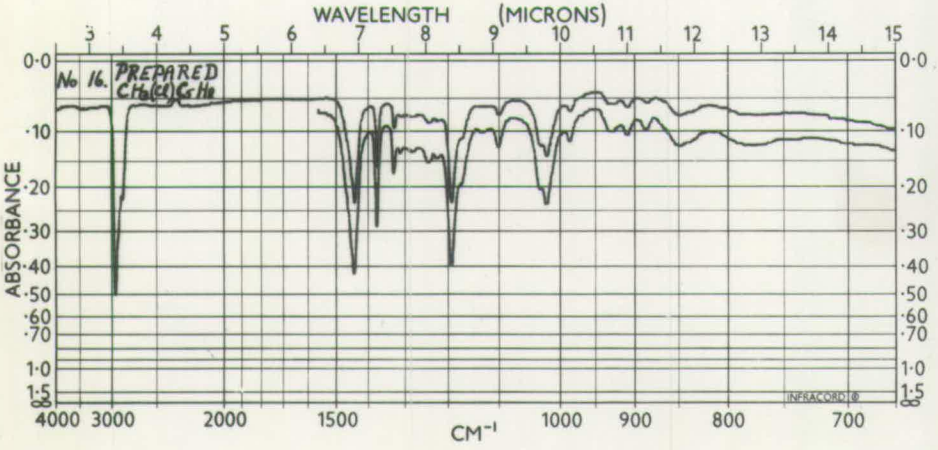
Agreement is moderately satisfactory, confirming that the compound is a trichloromethyl-methylcyclopentane. The infrared spectrum (No. 18) shows a strong, broad absorption band at 770 cm^{-1} and a less intense band at 705 cm^{-1} in the carbon-halogen region. Examination of the spectrum between 700 and 550 cm^{-1} failed to reveal further absorptions.

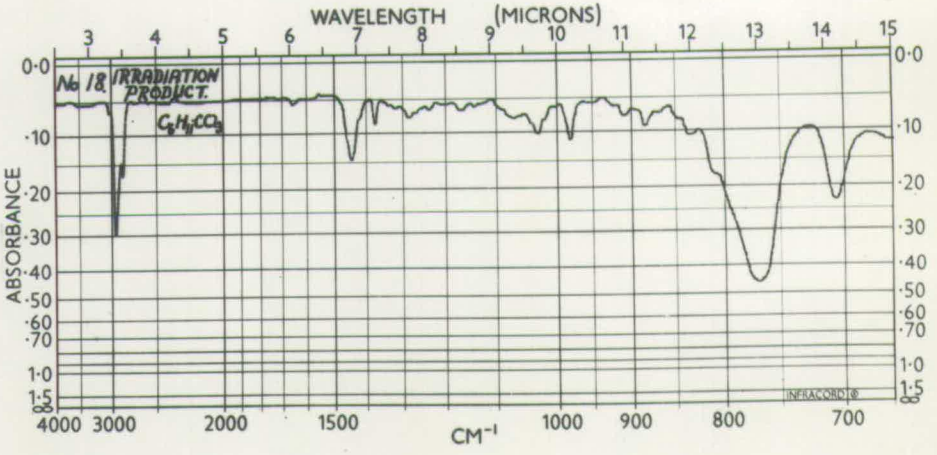
Conclusion.

The radiolysis of methylcyclopentane in carbon tetrachloride solution appears to be similar to that of the cyclohexane-carbon tetrachloride system. The large yields of chloroform and the monochloro-compound indicate the existence of a hydrogen-halogen exchange chain reaction although the formation of four monochloro-isomers shows that hydrogen abstraction is not restricted to the tertiary hydrogen atom.


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GENERAL SUMMARY.

Cobalt-60 has been used as a source of high energy (gamma) radiation and the induced chemical effects have been studied in chloroform, solutions of benzene in carbon tetrachloride and solutions of cyclohexane in carbon tetrachloride.

A description is given of the large-scale gas-liquid chromatographic techniques which were developed for the isolation of pure samples of the irradiation products and of the method of quantitative analysis, involving the use of micropipettes. Comparison of the infrared spectra and other physical properties of the purified products, was made whenever possible with those of authentic samples. A Perkin-Elmer Infracord spectrophotometer was used to record the infrared spectra and photographic reproductions are included.

The yields of the products formed during radiolysis have been expressed as G-values which represent the number of molecules of product formed per 100 eV of energy absorbed. From the identity and the yields of the products formed in the irradiations, the nature of the primary interactions and the ensuing reactions of the reactive species have been inferred.

The previously reported products from the irradiation of chloroform have been confirmed but there are discrepancies in the G-values. The results are consistent with homolysis of a carbon-chlorine bond as the primary act, followed by hydrogen atom abstraction and combination reactions by the free radicals in the system. The principal components of the high molecular weight residue have been isolated and identified as 1,1,2,3,3-pentachloropropane, 1,1,2,2,3,3- and 1,1,1,2,3,3-hexachloro-

propanes and 1,1,1,2,2,3,3-heptachloropropane. Solutions of chloroform containing added trichloroethylene and tetrachloroethylene were irradiated to evaluate their contribution to the formation of the C_3 products. Only trichloroethylene appears to be involved and a reaction scheme is proposed but a completely satisfactory explanation is lacking; alternative mechanisms are discussed.

Chlorine atom elimination from the pentachloroethyl radical is proposed as a mechanism of formation of tetrachloroethylene in this and other systems containing a large quantity of hexachloroethane.

G-values have been obtained (0.02-2.65) for the products of irradiated benzene-carbon tetrachloride solution i.e., hydrogen chloride, chloroform, tetrachloroethylene, chlorobenzene, hexachloroethane, benzotrichloride and diphenyl, in solutions of molar composition ranging from 1.0 to 99.95% carbon tetrachloride. High boiling residue was found to be a major product, representing about 50% of the total product yield. Large volumes of benzene-carbon tetrachloride solution have been irradiated and 2-chlorodiphenyl, ortho- and para-chlorobenzotrichloride and ortho- and para-bistrichloromethylbenzene identified as components of the high boiling residue. Hexachlorocyclohexane, the major product of the photochlorination of benzene, was not found to be present.

The variation of G-values with composition has been discussed in terms of "sensitisation" and "protection" effects. The formation of the products is accommodated by a reaction scheme

involving an initial carbon-chlorine bond fission, followed by chlorine atoms undergoing hydrogen abstraction reactions or addition to the aromatic ring to form reactive chlorocyclohexadienyl radicals. Subsequent reactions involving these intermediate species are discussed and are considered to be responsible for the formation of the high molecular weight products. Combination and abstraction reactions by the trichloromethyl radicals are important processes. The proposed reactions are discussed in relation to thermochemical data and the results reported by previous workers studying free radical attack on aromatic compounds.

The benzene-chloroform and benzene-dichloromethane systems have also been irradiated and the qualitative results are described briefly.

Irradiated cyclohexane-carbon tetrachloride solution has been examined and the primary products found to be analogous to those of the previous system; the yields, however, differ greatly. G-values for chloroform and chlorocyclohexane reach a maximum of 80 at 90 mole % cyclohexane, and are explained by a short length chain reaction. The yields of hydrogen chloride, hexachloroethane, trichloromethylcyclohexane and dicyclohexyl are small by comparison but 2-3 times those of the corresponding products in the benzene-carbon tetrachloride system. The mechanism proposed is based on abstraction and combination reactions. There is some evidence for the existence of a "sensitisation" effect in solutions of low halogen content.

Methylcyclopentane in carbon tetrachloride solution has been examined briefly and appears to undergo radiolytic decomposition in a similar manner to cyclohexane.

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