

IRRADIATION OF ORGANIC
SYSTEMS WITH
GAMMA RAYS

by

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TO MY MOTHER.

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INTRODUCTION.

Although Röntgen and Becquerel in 1895 were the first to observe radiation effects, "radiation chemistry" or the chemistry of the interaction of ionising radiation with organic and inorganic materials, has not been studied as intensively as the cognate photochemistry. Most of the early work^{1,2} utilised the radiations produced by naturally occurring radioactive isotopes such as radium: sporadic work using X-rays and the corpuscular radiations produced by accelerators like the Van de Graaff generator, does, however, appear in the literature.

The intense interest in nuclear weapons in the 1939-1945 war, and the subsequent transfer of this interest to the peaceful applications of "atomic energy", has led to the production of large quantities of waste radioactive materials, in addition to facilitating the large-scale production of such materials as are required for specific purposes. These radioactive materials all emit ionising radiation, namely, protons, neutrons, alpha particles, fast electrons (beta rays), or electromagnetic radiation (gamma rays). As a few ounces of one of these isotopes may produce vast quantities of energy in the form of radiation, this energy source is, for the first time, readily available. Thus, only in the last decade, has radiation research been possible on a large scale.

Ionising radiations have a high potential value in

chemical reactions, although many new problems are introduced. The mode of interaction of these radiations with molecules does not follow the old, well-understood and well established photochemical laws: no substances appear to be completely inert, and hence the solvents of more conventional chemistry become reactants: by no means the least problem is the health hazard offered to the worker in this field.

Electromagnetic Radiation.

The source of the radiation used in the present work is the cobalt isotope of atomic number 60 (Co^{60}). This material emits beta rays with energy of 0.31 Mev, and gamma rays of 1.12 and 1.33 Mev³. As the beta rays are very weak, and possess little power of penetration, the chemistry to be discussed is effectively that of gamma ray interaction with matter. For this reason, only electromagnetic radiation will be further discussed here.

Electromagnetic radiation loses energy by three processes⁴⁻⁶, namely, the photoelectric effect, the Compton recoil and the pair production effect. At low energies, the most important effect is the photoelectric. The electromagnetic quantum of energy ejects a bound electron from a molecule with an energy equal to the difference of the quantum energy and the binding energy of the electron. The quantum ^{is} ~~of~~ completely destroyed and the ionisation

produced by the photoelectron causes the major chemical effect.

Above photon energies of about 0.2 Mev the photoelectric effect becomes insignificant and Compton scattering occurs. In this case the quantum is only degraded in energy, and is deflected from its original path by a bound or free electron, the process being predicted by the conservation of energy and momentum laws.

The third process, pair production, cannot come into effect until the energy of the photon is greater than 1.02 Mev, and is not the predominant process until much higher energies are reached.

These projected electrons have, of course, a very limited range in liquids and solids compared with the photons, and usually dissipate all their energy in the medium in which they arise. This energy, which is the kinetic energy of the secondary electron, is the energy absorption of the medium.

While photochemical absorption depends, in general, on the molecular structure of the medium and is uniformly absorbed, the absorption of energy from X- and gamma-rays is independent of molecular structure, or mode of electron bonding. The ions formed have a spacial distribution along the tracks of the secondary electrons. From a chemical viewpoint, ionisation, electron capture, radical reactions and intermolecular or intramolecular transfers of energy may occur. In these respects radiation chemistry differs greatly from photochemistry.

Radiation Doses and Definitions.

The accurate measurement of dose rates and doses received by irradiated materials has been a protracted problem⁴⁰. The most satisfactory method at present, utilises the following reaction:



The rate of oxidation of the ferrous ion in dilute sulphuric acid solution is linear up to quite high dose rates, and the concentration of ferric ions is easily measured by examining the absorption of the solution at 304 m μ . The number of ferrous ions oxidised when 100 ev of energy is absorbed has been investigated by many workers⁴⁰, and for present purposes, that number will be taken as 16. This is the G value for the oxidation of ferrous ions.

If this determination of energy absorbed is made using a vessel in a fixed position with regard to a certain source, then the energy absorption of other liquids UNDER IDENTICAL CONDITIONS with regard to the geometry of the system can be calculated.

Dose rates were determined periodically and an explanation of the procedure used is included in the experimental work.

The term Roentgen is frequently used throughout the text as a measure of radiation received. For convenience, this will be defined as the radiation unit from which one ml. of water absorbs 93 ergs of energy, though it must be em-

phasised that this is not the original definition.

A more general definition of the expression G value, is that it represents the number of molecules of reactant used up, or of product formed, per 100 ev absorbed, the precise significance being indicated by a subscript. e.g. $G(\text{Rad})$ and $G(-\text{CCl}_4)$ imply that the number of free radicals produced and the number of carbon tetrachloride molecules removed as product respectively, are being considered.

Chemical Effects of Radiolysis.

Although a wide variety of reactions have been investigated, the mechanisms have not been elucidated. From a qualitative and quantitative determination of products, however, tentative mechanisms can be suggested. Attempts have been made to trap free radicals initially produced thus providing a more direct measure of radiation effects. Magat and co-workers have⁷ used the diphenyl picrylhydrazyl (DPPH) radical as a radical scavenger. They found, for example, that $G(\text{Rad}) = 1.8$ and 59.5 for benzene and chloroform respectively. The use of DPPH has, however, been criticised on the grounds of its own instability to high energy radiation. The same workers observe that if the nature and number of initially formed fragments can be determined, then the subsequent reactions should be predictable on a normal chemical kinetics basis. Hence two approaches have

been made to the problem, the former being reliable and, at present, the more informative method.

The inherent biological dangers of radiation have, of course, stimulated researches in aqueous solution chemistry as the obvious introduction to studies of body cells, and most of the chemical work in the literature involves this medium. This is unfortunate, because water is in many ways an unusual substance and there has been ^{until lately} no general agreement over the complex action of radiation on water. Until this problem has been resolved, an exact theory of aqueous systems is unobtainable. Nevertheless, a considerable variety of interesting facts has been obtained, and is presented in a number of reviews⁸⁻¹³.

Aqueous Solutions.

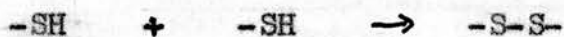
Water produces H-, HO-, HO₂- and other radicals³⁵ and if dilute solutions of benzene¹⁴, nitrobenzene¹⁵, phenols¹⁶, benzoic acid¹⁷, and chlorobenzene¹⁸ are irradiated, hydroxyl groups are introduced into the nucleus of the monosubstituted benzene, in a manner independent of the nature of the group already present. This suggests free radical attack rather than the usual ionic substitution of the aromatic nucleus. Stacey¹² has pointed out that these substitution reactions may assume importance in the preparation of less common isomers of benzene derivatives.

Aqueous solutions of carboxylic acids^{19,20} have provided

both synthetic and degraded products. Hydroxy acids yield keto acids^{21,22}, the oxidation yield in most of these reactions being greater when oxygen is present^{22,23}. This type of reaction suggests possible applications in carbohydrate chemistry. Phillips²⁴ reported that the secondary alcohol groups are unaffected, although primary alcohol groups are oxidised to aldehyde. At present, however, he seems dissatisfied with these results²⁵ and further publications on the topic are pending. If large doses are employed, the carbohydrate degrades.

Aqueous solutions of amino acids eliminate ammonia¹⁶, yielding the lower aldehyde and carbon dioxide. X-ray bombardment causes remarkably specific changes in dilute aqueous solutions of the sterols^{26,27}, oxidised, reduced or acetylated products being obtained, sometimes in yields of 48%.

Enzyme solutions are deactivated in aqueous solution, probably by free hydroxyl radicals²⁸. Indeed, the "protective effect" of certain materials is based on their ability to react preferentially with the hydroxyl radicals produced, before the latter attack other molecules. Proteins containing essential -SH groups are very radio-sensitive. The formation of disulphides has been observed²⁹ from many thiols:



This reaction could result in protein dimers being formed, and indeed, increased in molecular weight occur. Dale and Davies

have recently³⁰ cast doubt on disulphide formation from thiourea which is a "protecting agent", but they have not questioned the reaction for other thiols.

The irradiation of vitamins is of interest in connection with the radiation sterilisation of food³¹. However, they have been little investigated along with polysaccharides, nucleoproteins and viruses. Parallel with this work is the investigation by the radiobiologists of animal survival and radiation damage to specific organs.

Non-aqueous Organic Systems.

The classical work of Kailan² has, in the main, been confirmed by later workers.

When organic molecules are irradiated, rupture usually occurs at a weak bond, and the two fragments then dimerise, polymerise or, in general, attain a stable state. For example, heavy irradiation of hydrocarbons leads to hydrogen^{32,33} and products of higher and lower molecular weight. Cross linking occurs if irradiation is prolonged. Trans-forms of the nine isomers of the octadecenes after pile irradiation showed higher yields of cross linking than the cis isomers³⁴.

Radiation action on monomer molecules such as vinyl chloride causes polymerisation, the product being very similar to that obtained by other initiation methods. Polymerisation can also be induced in the solid state. When acrylamide

solid cooled to -18°C is subjected to gamma radiation no appreciable polymerisation occurs. As the temperature of the irradiated solid is raised to about 22°C the whole mass warms up and polymerisation occurs³⁶. This also happens with tetraethylene glycole dimethacrylate³⁷.

Halides are highly radiosensitive. Chloroform and carbon tetrachloride yield HCl and Cl_2 respectively in addition to hexachloroethane. If oxygen is present, there is also a tendency for peroxide formation. Collinson and Swallow mention an interesting case arising from the radiolysis of methyl iodide³⁸. Iodine and ethane with a little methane and methylene iodide are produced. The photolysis of methyl iodide, on the other hand, yields methane and methylene iodide along with a little iodine and ethane. Also the energy requirement in the form of ultra violet light is about ten times the energy of ionising radiation required. This points to a fundamental difference in the two processes and suggests that ionic reactions may play a considerable part in the radiolysis along with the free radical reactions occurring in the photolysis.

When high polymers, such as polyvinyl halides, are irradiated³⁹, three effects may be observed: cross-linking, main chain and side chain degradation. An increasing degree of unsaturation appears to lower the energy required to form a cross-link.

Stacey¹² observes that synthesis by radiolysis is much more likely to be of use in the pharmaceutical and fine chemical fields than in heavy chemical industry. This does seem very likely, except in the synthetic polymer field, where high energy radiation is the only initiator for some polymerisations. Perfluoropropylene and some other perfluoromonomers have been polymerised by no other method. Also the cross-linking of high polymers like polyethylene changes their properties and solubility so markedly, that industrial use of the technique seems probable.

THE PRESENT APPROACH.

When the present work was commenced, there was no experience of radiation chemistry in the department. A survey of the literature revealed a preponderance of kinetic and mechanistic approach based on rather fragile qualitative determinations. It was decided, therefore, to adopt an essentially organic attitude to the problem, and investigate groups of related substances, placing equal importance on quantitative and qualitative aspects. In this way the effects of ionising radiation should yield much more easily to correlation and subsequent explanation.

The initial requirement was a simple organic compound of high electron density, in expectation of a consequently high G-value. The chemical chosen must be easily obtainable in a pure state, and the possible products relatively easy to determine. Magat and co-workers⁷ investigated several compounds using DPPH, as has already been mentioned. They found that the most radiation sensitive material in quite a wide range of types was carbon tetrachloride. This substance satisfied the other requirements of symmetry, density etcetera and was therefore the first material to be investigated. Subsequently it was used as a chlorinating agent and a number of aliphatic hydrocarbons were irradiated in carbon tetrachloride solution. Parallel to these investigations, Miller and Stafford⁴¹ have irradiated solutions of benzene, toluene and p-xylene in carbon tetrachloride.

In order to extend the scope of the approach unsaturated systems were also investigated. Due to their ready availability and simplicity, the chloroethylenes were chosen. These chemicals have markedly different properties: some are polymerised commercially, others have never been polymerised. In this thesis, the radiolysis of cis- and trans-1; 2-dichloroethylene and trichloroethylene are described in detail. Miller and Stafford⁴¹ have studied 1; 1-dichloroethylene (vinylidene chloride) and tetrachloroethylene and their results will be mentioned here for comparison purposes. A few copolymerisations have been attempted.

Techniques

Radiation Unit.

A radiation unit rather similar in design and operation to that described by Gibson and Pierce⁴² was set up, in conjunction with A.E.R.E., Harwell. Initially in 1954, a 102 Curie source of Co^{60} was installed. In July 1957, this source was found to be 64.2 Curies (the half-life of Co^{60} is 5.3 years,) and an additional source of 139.5 Curies was installed in the same radiation chamber. The greater part of the work described on the following pages was carried out using the first source between October 1955 and March 1957.

Apart from a few irradiations for which conditions are

specified in the text, all solutions were irradiated in annular Pyrex glass vessels fitted with Quickfit stoppers. Unless otherwise stated, no/rigorous precautions were taken to exclude air except for distillation of materials immediately prior to irradiation. The results obtained should therefore be viewed accordingly.

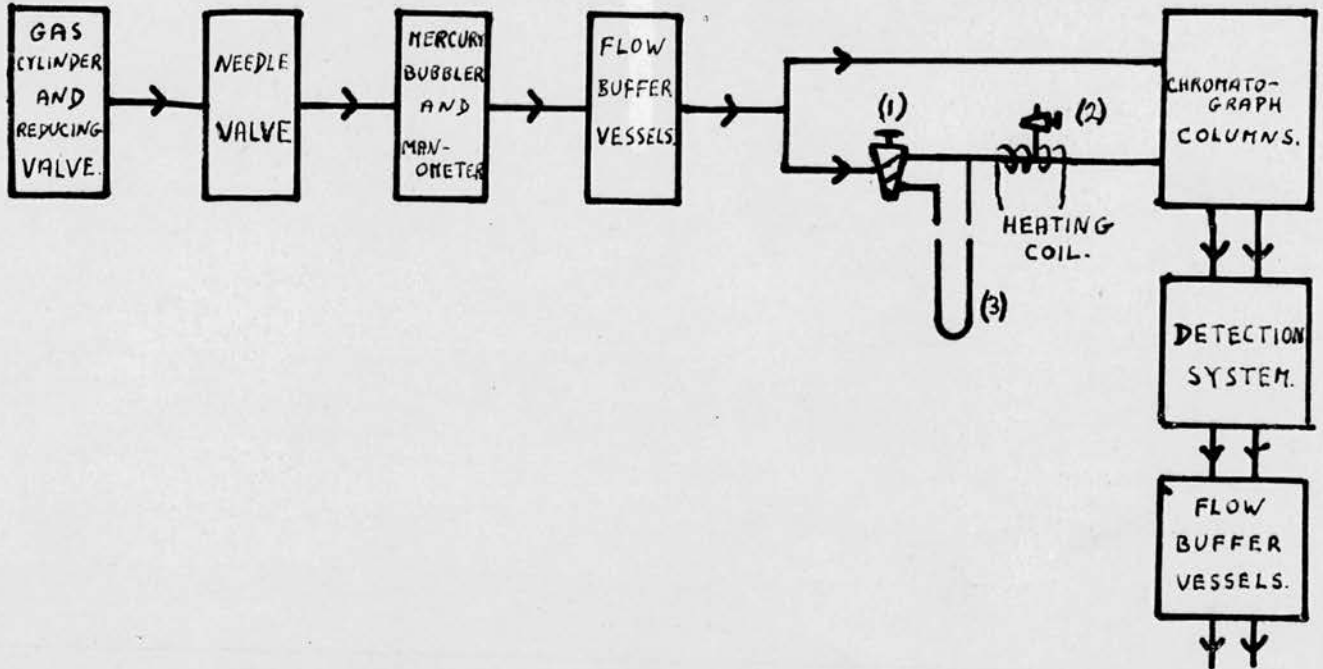
Gas Chromatography.

The low G values of most reactions necessitated the use of some highly sensitive analytical techniques. Gas chromatography was found admirable, so several units were constructed and used throughout the course of the work. The apparatus and mode of use was conventional, and since the technique has now become commonplace and the literature vast, only a cursory description will be appended. There are several reviews of the subject.⁴³

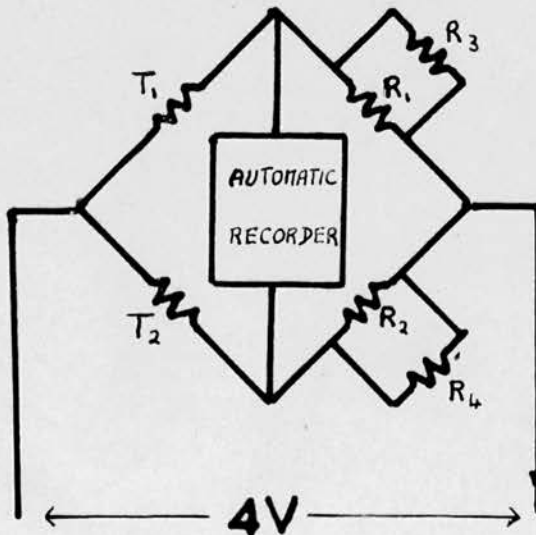
The principal parts of the system are shown in diagrams I and II. Oxygen-free nitrogen was used from a cylinder, the flow being controlled by a reducing valve and a needle valve. Although a bubbler was incorporated in the apparatus, it was later considered unnecessary and was retained only as a safety valve. The injection system consisted simply of a stopcock (1) to cut off the nitrogen flow and a stopcock (2) through which the sample was injected using an AGLA micrometer syringe. An alternative method for injection of fractions obtained in liquid air traps consisted of

DIAGRAM I

CHROMATOGRAPH ASSEMBLY



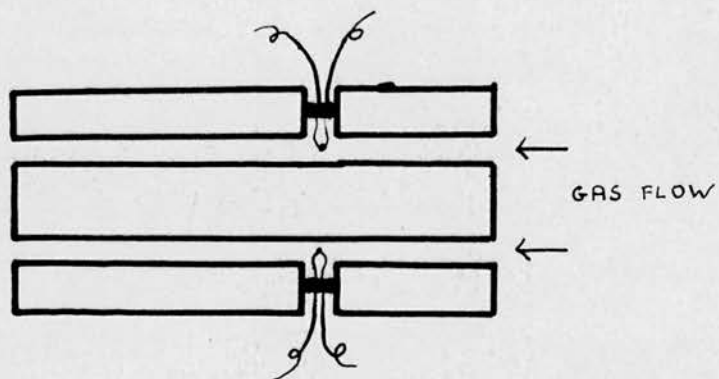
ELECTRICAL CIRCUIT



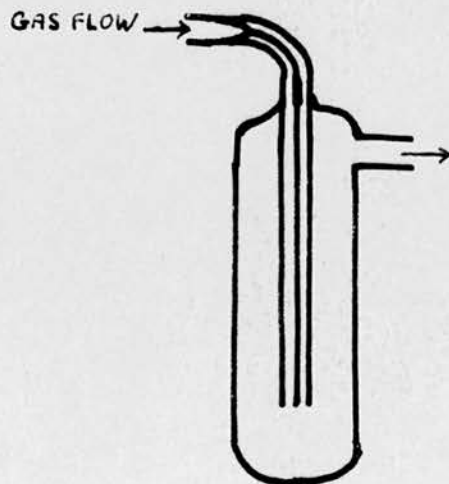
T. = THERMISTORS
R = VARIABLE RESISTANCES.

DIAGRAM II

THERMISTOR BLOCK



BUFFER VESSELS



a small U-tube (3) through which the nitrogen flow could be diverted. The capillary tubing around the injection point was wound with resistance wire in series with the winding of the column jacket. Using a Claude-Lyons Variac transformer, the temperature of the two coils could be easily controlled, the temperature of the coil at the point of injection being rather higher than that of the column, in order to vaporise the sample rapidly.

The chromatograph columns were U-tubes of about 175 cm. total length and 8 mm. internal diameter. Packings were varied considerably. The most useful was silicone oil MS 550 absorbed on Johns-Mansville graded celite 545 in the ratio 1/2 by weight. Tricresyl phosphate, and squalane were occasionally employed as the stationary oil phase. Using these packings, cis and trans isomers of dichloroethylene were easily separated, as were chloroform and carbon tetrachloride. For the separation of low boiling gases such as propane and cyclopropane, BDH silica gel of 30-120 mesh was used.

The detection device consisted of a pair of thermistors acting as catharometers, (thermistors type A2321/100 from Standard Telephones and Cables Ltd.) The glass sheaths were carefully removed and the thermistors set in a cylindrical Dural alloy block as shown. Glass metal joints were made with ARALDITE (Aero Research). The thermistors

formed two arms of a Wheatstone bridge arrangement, a Sunvic Automatic Recorder being placed across the bridge.

Under operating conditions, the chloroform contained in a 0.01 Ml injection of a carbon tetrachloride solution containing 0.1% chloroform was just on the threshold of detection. The method of injection was found to be the principal source of error, reproducibility of peak height being about 8% which was sufficiently accurate for the work carried out. Although a quantitative estimation of the components of a mixture may be made by measuring peak heights, or, more accurately, peak areas, standards which duplicated the peaks were usually run. This catered for periodic fluctuations caused by temperature and pressure changed and any other disturbing factors.

↑

CHLOROETHYLENES

THE POLYMERISATION OF SUBSTITUTED ETHYLENES.

Mono-substituted ethylenes, such as vinyl chloride and acetate, acrylic acid esters, styrene and 1-butene and also 1:1-disubstituted ethylenes, such as vinylidene and isopropenyl derivatives, esters of chloracrylic and methacrylic acids, chlorostyrene and isobutene have all been easily polymerised using well-known initiators such as peroxides. No references will be given to this work, as it is well-known and the literature on the subject is extensive.

However, the 1:2-disubstituted ethylenes such as 1:2-dichloroethylene, propenyl derivatives, crotonitrile, maleonitrile and β -substituted styrenes have proved very difficult to polymerise. Work on the di- and trichloroethylenes will now be discussed.

CIS AND TRANS DICHLOROETHYLENES.

There have been many attempts to polymerise cis- and trans-1:2-dichloroethylene over the last twenty years. However, the success of these attempts has been very limited and no high polymers comparable with polyvinyl and polyvinylidene chlorides have been prepared in quantity, although varying yields of oils of up to six monomeric units have been obtained.

The first observation of an insoluble polymer appears to have been made by Ebert and Bull⁴⁴, who initiated the reaction

of the trans isomer photochemically. They did not succeed in obtaining a similar product from the ^{trans}cisomer⁴⁵. Mahncke and Noyes⁴⁶ using ultra violet light obtained a little solid from the vapour of both isomers. This polymer, however, appears to differ from the solid reported by all the other workers in the field; for example, the material from the cis-form melted sharply at 103.5-104.0°C. (Found: Cl, 72.5%. Calc. for C₂H₂Cl₂, Cl.73.1%). Muller and Ehrmann⁴⁷ obtained some resins by irradiation with ultra violet light in the presence of oxygen and nitrogen.

When subjected to pressures up to 10,000 atmospheres, the trans-isomer does not polymerise⁴⁸, but at 150°C and 10,000 atmospheres pressure an explosive reaction occurs with carbonisation⁴⁹. The addition of benzoyl peroxide causes the polymerisation to proceed smoothly⁵⁰⁻⁵¹ and various patent specifications cover the liquid phase polymerisation of both isomers with peroxide initiators and ultra violet light^{50,50A}. Weale has reviewed the field⁴⁸. The products are almost entirely liquid polymers with total yields of up to 35% and a weight ratio of dimer to higher polymers varying from 0.5 to 3.5 at higher temperatures. For example, Bauer,^{50A} by prolonged boiling (200 hours) of the trans-isomer with 1% of benzoyl peroxide, obtained 16.6% dimer, 13.5% of higher liquid polymers and also 1.5% of white powder. Weale obtained 22% dimer, 50% higher liquid and 10% of solid polymer by reacting the trans-isomer for 140 hours at

75°C and 3,000 atmospheres pressure. (Weight ratio of dimer to higher polymers about 0.37). After 70 hours at 75°C and 8000 atmospheres, he obtained 70% of dimer and higher liquids and 20% solid polymer. An 8% yield of solid was obtained from the cis-isomer at 75° and 3,000 atmospheres. Weale also found that the dimer, identified by Bauer as 1:3:4:4-tetrachlorobut-1-ene did not react in the presence of benzoyl peroxide at the highest pressure he used (8,000 atmospheres). His solid polymer is a white amorphous powder (Found: Cl, 74.6%. Calc. Cl, 73.1%). It swells in contact with organic solvents but does not dissolve. It is unchanged at 160-70°C, softens slightly at higher temperatures and fumes at 215°C.

Summing up, he observes that total yields increase markedly with temperature and to a small extent with pressure, but that high temperatures tend to increase and high pressures to decrease the ratio of dimer to higher polymers.

TRICHLOROETHYLENE.

The polymerisation of trichloroethylene is covered by a large number of patents⁵³, in which the production of polymers - principally oil polymers - is described.

By heating trichloroethylene under pressure to above 150°C, but below 200°C which is the decomposition temperature, a compound $C_4H_2Cl_6$ is prepared. By a secondary

reaction this hexachlorobutene decomposes to pentachlorobutadiene with liberation of HCl but this reaction can be prevented by adding a trace of a nitrogenous base. As an example, if 12 kilos of monomer and 0.03 gm of pyridine are heated in an autoclave for 30 minutes to 230°C, over 50% of dimer is obtained. If organic peroxides are used under similar conditions, a little trimer and traces of waxes are produced. (The lower the temperature, the higher the degree of polymerisation.)

EXPERIMENTAL

DICHLOROETHYLENE.

May and Baker "Commercial Dichloroethylene" was the source of both isomers, which were separated by fractionation, dried over calcium chloride and quickly distilled before irradiation. In both of the following large scale experiments, each isomer, as used, contained less than 10% of the other isomer as impurity. The respective proportions were determined by gas phase chromatographic methods. The materials were irradiated in large annular Pyrex glass vessels, a small quantity of air being present although Quickfit stoppers prevented free entrance of air.

After irradiation, samples of material were analysed for the cis/trans ratio as above, solid polymer was collected by filtration or centrifugation, and then all monomer

was removed by distillation. At this stage, more solid polymer usually appeared on cooling (representing only a few per cent of the initial solid). Ether was added to precipitate it completely and it was then collected. Residual oil polymers were fractionated.

Cis-isomer.

Cis-dichloroethylene (1200 ml. - 1560 gm.) was irradiated for 356 hours. The dose was not accurately determined but was estimated to be at least 4×10^6 R (200 R/min.) The trans/cis ratio was found to increase only slightly and scarcely significantly and only a trace of gelatinous precipitate (0.46 gm) was obtained. A further quantity (0.65 gm) was obtained on adding ether. The oil residue was fractionated into the following portions:

<u>DESCRIPTION.</u>	<u>Crude Wt.</u> <u>(gms)</u>	<u>n_D²⁰</u>	<u>D₄²⁰</u>	<u>B.P.</u>
"Dimer"	4.5% 70	1.5155	1.474	83-4°C/15 mm Hg
"Trimer"	2.6% 40	1.5388	1.558	105-20°C/2 mm Hg
"Tetramer"	5	1.5486	-	} Molecular distillation at 10 ⁻⁴ mm Hg
Very viscous oil	3.5% 9	1.5528	-	
Wax	1	-	-	
Charred residue	39	-	-	
(Solid polymer precipitate 0.1% 1)	<u>10.7% 165</u> gms			

The charred residues arise from high waxes which resist distillation and thermally decompose, liberating HCL.

Trans-isomer (Irradiation at room temperature)

Trans dichloroethylene (1240 ml -- 1600 gm) was irradiated for 95 hours at room temperature. The total dose was at least 1.1×10^6 R. After irradiation, the cis/trans ratio was again found to be only slightly changed and considerable HCl was present. The solid material (112 gm) was removed and ether precipitation provided a further 26 gm. From experience subsequently acquired in handling such polymers, it is now realised that this material was still swollen with some oil polymers and monomer. The quoted weight must therefore be somewhat high. Residual oils were fractionated as follows:-

<u>DESCRIPTION.</u>	<u>Crude Wt.</u> <u>(gms)</u>	<u>n_D²⁰</u>	<u>D₄²⁰</u>	<u>B.P.</u>
"Dimer"	0.4% 7	1.5146	1.473	82-4°C/15 mm Hg
"Trimer"	0.7% 10.5	1.5392	1.559	-
"Tetramer"	6	1.5493	-	} Molecular distillation at 10 ⁻⁴ mm Hg
Viscous oil	} 2.3% 6	1.5515	-	
Wax		-	-	
Charred residue (waxes)	24	-	-	
(Solid polymer precipitate	<u>138</u>) 8.6%			
	<u>191</u>) 12.0			

In this and the previous experiment, the oils designated dimer, trimer and tetramer were refractionated twice before the physical constants were measured. This process for the polymerisation of trans dichloroethylene has now been patented⁵⁶.

Trans-isomer (Irradiation at -48°C).

Trans dichloroethylene (1200 ml - 1560 gm) was irradiated, the entire unit being contained in a refrigerator at -48°C, for 92 hours. A considerable quantity of HCl was evolved, but only 3.5 gm of polymeric material was obtained - oil containing a trace of insoluble solid polymer.

Trans-isomer (Irradiated at the boiling point).

Trans dichloroethylene (1200 ml) was irradiated for 96 hours at its boiling point (approximately 48°C). An Isomantle heater was used and the system was open to the atmosphere via a reflux condenser. HCl was present in quantity. Solid polymer was filtered off (18.5 gm) leaving an oil residue (196 gm) which yielded the following fractions:

<u>DESCRIPTION.</u>	<u>Crude Wt.</u> (gms)	<u>n_D²⁰</u>
"Dimer"	52.7 3.4%	1.5159
"Trimer"	21.5 1.4%	1.5382
Charred residue (wax)	121.8 7.8%	-
(Solid polymer precipitate	18.5) 1.2%	-
	<u>214.5</u>) <u>13.8%</u>	

Dichloroethylene Dimer

A sample of mixed cis and trans isomers was polymerised

in a stainless steel autoclave at 100°C, using benzoyl peroxide as initiator. The pressure reached was of the order of 45 atmospheres. A sample of oil, identified as dimer, was refractionated and had the following constants:

$$n_D^{20} = 1.5162 \quad \text{B.P.} = 79^\circ/13 \text{ mm Hg}$$

This dimer (48 ml - 70.7 gm) was irradiated for 115 hours, receiving a total dose of approximately 9×10^6 R

On examination, a few flakes of solid polymer were seen and a little HCl was present. Unchanged material was removed at the water pump, leaving an oil residue (2.8 gm) which was fractionated:

<u>Fraction</u>	<u>Wt (gms)</u>	<u>n_D^{20}</u>
I	1.2	1.5186
II)	1.6	(1.5272
III)		(1.5522

Fraction I is obviously starting material as is II, both containing some higher oil which raises the refractive index. Fraction III is probably crude tetramer, indicating that the 1:3:4:4-tetrachlorobut-1-ene has dimerised.

A number of ampoules of about 40 ml capacity were now made. They were carefully flamed under vacuum to remove adsorbed air and water. Without conditioning the Pyrex glass of these ampoules by pre-irradiation, samples of cis and trans dichloroethylene were inserted after being purified as in previous experiments. The ampoules and contents were then cooled in liquid nitrogen and degassed using a mercury diffusion pump. The high vacuum line was closed and the ampoule rapidly warmed up by immersion in a beaker of tap

water. If the ampoule was allowed to warm up slowly in the air, it often shattered, presumably due to expansion of the solid inside the ampoule before melting had begun. When the ampoule was warmed up with tap water, the material adjacent to the inner walls of the ampoule melted in a few seconds, and this allowed sufficient space for safe expansion.

This procedure was repeated three times in each case. It was noticed that the major degassing occurred the first time the liquids were in the process of freezing. The ampoules were then sealed off and irradiated at A.E.R.E., Harwell, in an annular Co^{60} source.

The ampoules were opened, the cis/trans ratio determined and the HCl content measured by titration. Unchanged monomer was then removed by distillation and the residue determined when constant weight had been reached.

Trans dichloroethylene.

The trans dichloroethylene used had a cis isomer content of 0.5 - 0.1% and refractive index: $n_D^{20} = 1.4448$ (lit. $n_D^{20} = 1.4448$). Four ampoules were irradiated for various increasing times and the results are tabulated below. After the total polymer was weighed, it was taken up in chloroform and the insoluble residue was filtered off, dried and weighed. It was rather difficult to remove all the oil from the solid and some of the solid polymer was soluble in the oil/chloroform solution. The figures for "insoluble solid polymer" are, therefore, somewhat unreliable.

The dose rate was 6600 R/min. (Polymer yields are given as moles of monomer removed.)

Vol ~ 40 ml

TRANS DICHLOROETHYLENE.

<u>AMPOULE</u>	<u>DOSE (R.)</u>	<u>CONTENTS (gms.)</u>	<u>HCl (moles)</u>	<u>INSOLUBLE SOLID (moles)</u>	<u>TOTAL POLYMER (moles)</u>
I	1.5×10^6	51.2845	0.000078	0.00150	0.0154
II	3.0×10^6	50.6876	0.000127	0.00339	0.0303
III	4.5×10^6	52.8160	0.000207	0.00531	0.0380
IV	6.0×10^6	53.8076	0.000262	0.0131	0.0620
			<i>1.9×10^{-6}</i>		
I			0.191×10^{-5}	3.7×10^{-5}	37.8×10^{-5}
II			0.315×10^{-5}	8.4×10^{-5}	75.1×10^{-5}
III			0.495×10^{-5}	$13. \times 10^{-5}$	90.5×10^{-5}
IV			0.612×10^{-5}	$31. \times 10^{-5}$	$145. \times 10^{-5}$

In the lower table the quantities of product are reduced to moles per ml. of monomer irradiated, assuming MW = 96.95 and $D_4^{20} = 1.2569$ for trans dichloroethylene. From these values, $G(\text{HCl}) = 0.91$ and $G(\text{Total Polymer}) = 224$, using the method of least squares.

The irradiation of ampoule III was interrupted overnight after eight hours and followed by three hours, twenty-one minutes of irradiation the following morning. Whether this is the cause of the low TOTAL POLYMER and SOLID POLYMER yields is not certain and bears investigation. The HCl is apparently unaffected.

CIS DICHLOROETHYLENE.

BDH cis-1:2-dichloroethylene was the source of material in this experiment. The trans isomer present was on the threshold of detection only, probably about 0.1%. Three ampoules were irradiated at a rate of 6600 Roentgen per minute. Slight increases in the cis/trans ratios were noted. The largest increase, in the third ampoule, was to approximately 0.5%. The irradiation of ampoule I only was not continuous. (Five hours thirty-eight minutes followed by seven hours the next day.)

AMPOULE	DOSE (R.)	CONTENTS (gms.)	HCl (moles)	POLYMER (moles)
I	5.0×10^6	56.7107	0.000395	0.0318
II	7.5×10^6	56.6157	0.000435	0.0503
III	$10. \times 10^6$	53.2005	0.000668	0.0616
I			0.812×10^{-5}	71.8×10^{-5}
II			0.985×10^{-5}	$114. \times 10^{-5}$
III			1.61×10^{-5}	$149. \times 10^{-5}$

In the lower table the quantities are again reduced to moles per ml. of monomer irradiated, assuming MW = 96.95 and $D_4^{20} = 1.2820$. Hence $G(\text{HCl}) = 1.48$ and $G(\text{Polymer}) = 142$

In this case, the interrupted irradiation of ampoule I does not appear to have affected the yield, but the production of an insoluble polymer from the trans isomer does introduce different factors which may be affected by the interruption.

DIAGRAM III

TOTAL POLYMER PRODUCTION.

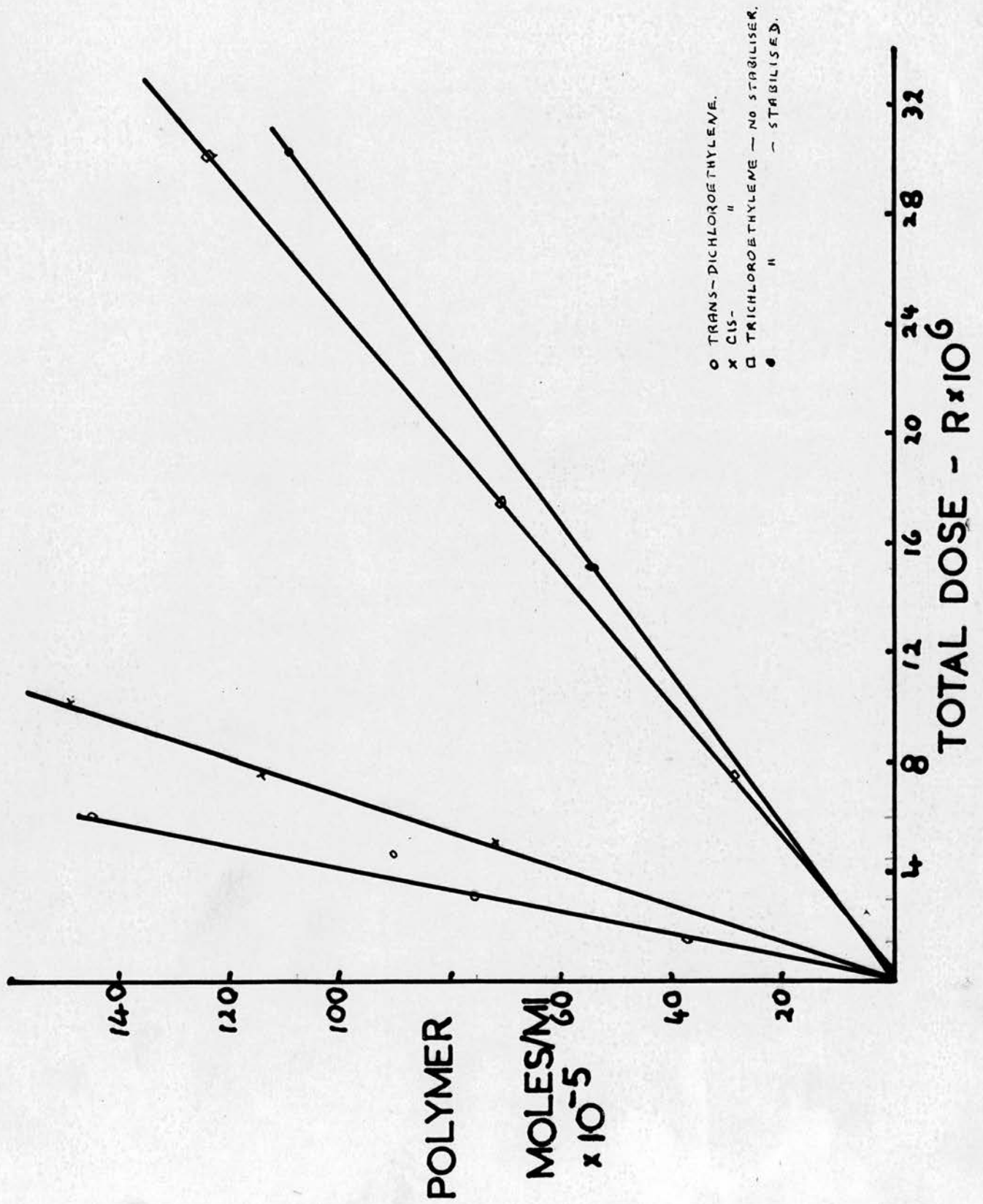
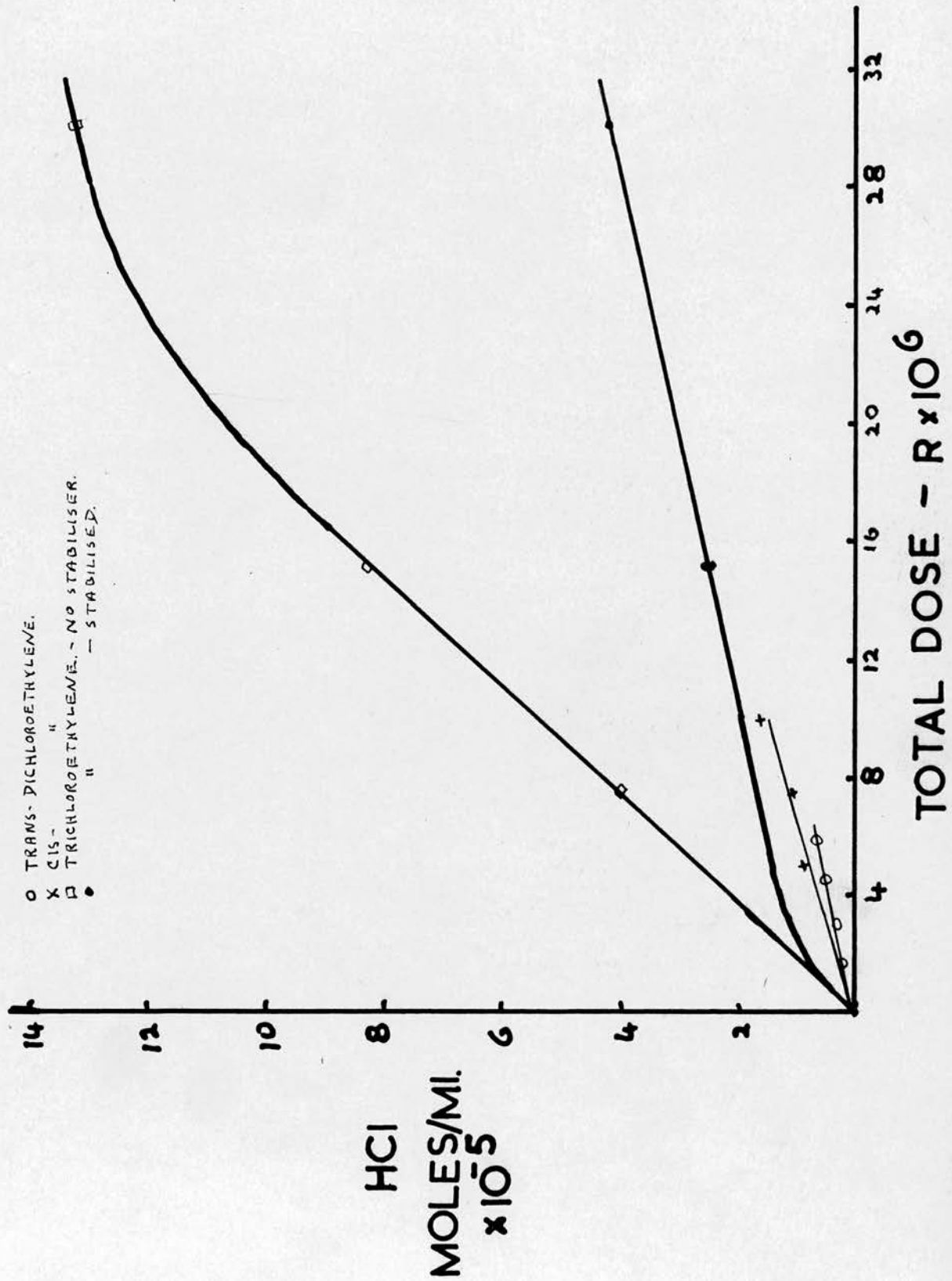


DIAGRAM IV

HCl PRODUCTION

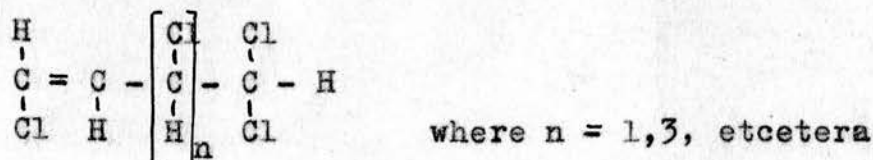


OIL POLYMERS.

These oil polymers were characterised by determining their physical constants and by the preparation of derivatives. Although the dimer and trimer could be fractionated fairly easily, higher oils and waxes could be handled only by using molecular distillation techniques. Rough separations only and not fractionations in the true sense of the word can be obtained by such methods. The constants obtained for dimer and trimer were determined on samples which had been refractionated several times, and the dimeric constants agree with those quoted by Frank and Blackham⁵¹.

	<u>B.P.</u>	<u>n_D^{20}</u>	<u>D_4^{20}</u>	
Literature constants for dimer: (1:3:4:4-Tetrachlorobut-1-ene)	88.0°C/20 mm	1.5150	1.473	
Found:				
cis:	} 83.4°C/15 mm	{	1.5155	1.474
trans:			1.5146	1.475

Following Weissberger⁵⁴, the molecular refractivities have been calculated for



$$\text{and molecular refractivity} = \left[R_D \right] = \frac{n_D^2 - 1}{n_D^2 + 2} \times \frac{M}{D}$$

where n = refractive index at temperature T
 D = density at temperature T
 M = molecular weight.

	<u>Calc.</u>	<u>Found (cis)</u>
Monomer	20.70	20.21
Dimer	39.67	39.76
Trimer	58.64	58.51

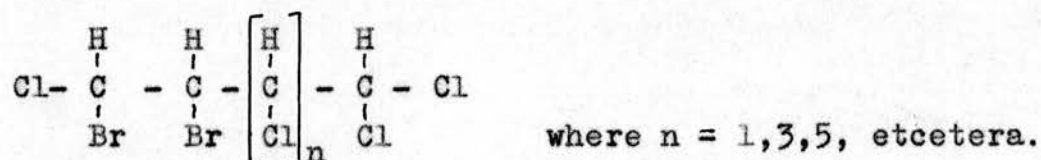
The values for the oil polymers from the trans isomer were very similar. On this basis, the oils seem authentic samples of dimer and trimer, and it seems likely that the "tetramer" constants are fairly reliable.

These oils evolve HCl on standing for a considerable time. After four months the tetramer and higher oils started to deposit waxy crystals, which may be due simply to slow crystallisation or to a slow secondary reaction, (associated with the loss of HCl.) They all soften slowly in the range 70-120°C and melt to a clear liquid, regardless of the oil fraction from which they are obtained. The translucent waxes slowly whiten and become opaque (after about one year).

Bromo Derivatives.

Bromo derivatives were easily prepared by dissolving the oil in carbon tetrachloride and adding bromine. Within twenty-four hours a white precipitate appeared and was filtered off; recrystallisation from ethanol or acetic acid

yielded colourless crystals with fairly sharp melting points. From the halogen analysis of each, confirmation of the number of monomer units in the oil was obtained, assuming the compounds to belong to the type:



The waxes also yielded bromo derivatives.

White Solid Polymer.

The white solid polymer obtained from these irradiations varied very much in melting point, depending on time of irradiation and conditions generally, and also on the treatment adopted to remove adhering oils.

For example: (1) One specimen of the polymer, after reprecipitation from dimethyl formamide, softened about 255°C and eventually melted from 265-8°C. There was very slight charring above the melting point and, on cooling, a transparent slightly yellow tinted vitreous mass resulted.

(2) Some solid polymer from the room temperature irradiation of trans dichloroethylene was extracted with 60-80° boiling fraction petrol-ether for one week using a Soxhlet extractor. From the original weight of material (11.6 gm), 1.4 gm (12%) was extracted: 0.5 gm appearing as a white crust around the flask and melting over the range 245-85°C to a clear vitreous liquid (no charring); and 0.9 gm

of oil-solid mixture remaining in ethereal solution. The residual 88%, after drying, softened to a gummy mass between 290° and 340°C with considerable charring.

Although the solid polymer is swollen in many organic solvents, it is not completely soluble in any. Dimethyl formamide, Westron (tetrachloroethane) and the oil polymers partially dissolve the solid. Dimethyl maleate is very rapidly absorbed by the polymer to form a white sludge, but again only slight dissolution occurs.

Some Russian workers⁵⁷ have found polychloroalkanes to be susceptible to attack by fuming nitric acid, oxidative-hydrolytic splitting of the carbon-carbon bonds occurring. The solid was not appreciably affected by this reagent and it was also resistant to three hours boiling with chromic acid, and to boiling hydrochloric acid. It chars in boiling concentrated sulphuric acid, liberating hydrogen chloride. Boiling concentrated aqueous potassium hydroxide solution causes slight charring.

DICHLOROETHYLENE: POLYMER ANALYSES.

	<u>CIS</u>	<u>TRANS</u>	
DIMER	Cl = 69.5%	Cl. = 69.3%	Cl = 73.1%
	C = 25.7%	C = 24.8%	Calc. for C = 24.8
	H = 2.00%	H = 2.24%	$C_2H_2Cl_2$ H = 2.1%
	<u>97.2%</u>	<u>96.34%</u>	<u>100.0%</u>
TRIMER	Cl = 69.86%	Cl = 71.40%	
	C = 25.2%	C = 26.2%	
	H = 2.00%	H = 2.16%	
	<u>97.06%</u>	<u>99.76%</u>	
TETRAMER	Cl = 70.40%	Cl = 71.00%	
	C = 24.9%	C = 26.2%	
	H = 2.24%	H = 1.97%	
	<u>97.54%</u>	<u>99.17%</u>	
SOLID WHITE POLYMER	Cl = 74.80%	Cl = 71.70%	
	C = 23.2%	C = 25.8%	
	H = 2.16%	H = 2.32%	
	<u>100.16%</u>	<u>99.82%</u>	

A very noticeable feature of this series of polymers is the lack of good analyses. This can no doubt be attributed in part to the difficulties inherent in the handling of liquids, since the analyses for the bromo derivatives are, without exception, good. There are two divisions to be made: in some, the chlorine analyses are extremely low but the carbon and hydrogen are reasonable. It is felt that this is

due to bad chlorine analysis. In others, the total is good but the chlorine is low and the carbon high. This tendency is found in the solid and in the higher polymers. In the trans solid, some loss of HCl is indicated and this is discussed later. In the liquids it is the higher oils which have lost HCl during distillation. A tendency to lose HCl on standing at room temperature has also been observed.

DICHLOROETHYLENE: BROMINATED POLYMER ANALYSES.

	<u>CIS-</u>	<u>TRANS-</u>	<u>CALCULATED</u>
DIMER:	Halogen = 84.7% C = 14.1% H = 1.3 <u>100.1%</u>	Hal=84.9% C =14.0% H = 1.0 <u>99.9%</u>	Hal = 85.3% for $C_4H_4Cl_4Br_2$ C = 13.6% H = 1.1 <u>100.0%</u>
TRIMER	Hal = 82.1% C = 16.5% H = 1.4% <u>100.0%</u>	Hal=82.5% C=16.3% H= 1.4% <u>100.2%</u>	Hal = 82.6% for $C_6H_6Cl_6Br_2$ C = 16.0% H = 1.4% <u>100.0%</u>
TETRAMER	Hal = 80.2% C = 17.9% H = 1.3% <u>99.4%</u>	Hal=80.5% C =18.0% H = 1.7% <u>100.2%</u>	Hal = 81.0% for $C_8H_8Cl_8Br_2$ C = 17.5% H = 1.5% <u>100.0%</u>

MELTING POINTS

	<u>CIS</u>	<u>TRANS</u>
DIMER	102-3°C	102-3°C
TRIMER	115-124°C	121-24°C
TETRAMER	244-48°C	246-249°C
MIXED HIGHER OILS	220-45°C	-
Wax	173-189	-

The low melting points of the higher oil and wax derivatives may be indicative of degradation during the rather drastic molecular distillations.

All these derivatives can be sublimed easily at reduced pressure.

TRICHLOROETHYLENE.

Trichloroethylene supplied by E. Merck A.G. (Darmstadt) was irradiated for 358 hours in a filled stoppered vessel (2630 ml - 3857 gm.) The dose was estimated to be over 4.2×10^6 Roentgen. After Twenty-four hours, (2.9×10^5 R) a network of needle shaped crystals filled the flask and a few were abstracted for examination. At the end of Three hundred and fifty-eight hours, very few of these crystals remained, and only where the intensity of radiation was least. The crystals (A) were filtered off (1 gm).

The solution was a golden yellow colour and HCl was present. Unchanged monomer was ~~distilled off~~ ^{removed by distillation} leaving a dark brown rather viscous oil (64 gm) containing some crystals. This residue was fractionated ^{employing} on a high vacuum pump, yielding oil (21 gm: $n_D^{20} = 1.5382$) which was fuming with HCl. The black charred residue (43 gm) was taken up in 60-80° petrol-ether and percolated through an alumina column. A white crystalline material (designated Solid B) was obtained on evaporating off the ^{eluted} solvent.

A further irradiation of trichloroethylene yielded the same products. After removal of unchanged monomer, the oils were taken up in ethanol and the insoluble crystals (B) filtered off (4.1gm). The ethanol was then removed and the residual oils fractionated:

These polymers do not react with bromine in carbon tetrachloride solution to form derivatives, presumably *due to hindrance* for steric considerations.

Solid material A: These colourless needle shaped crystals have a melting point of $224-9^{\circ}\text{C}$ with sublimation. Initially they were thought to be hexachlorobenzene (MP = 228°C) and a mixed melting point was over the same range. X-ray powder photographs of the two were, however, completely different.

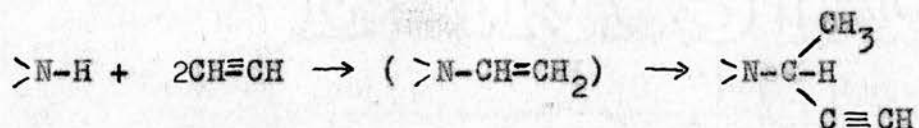
The crystals were instantly soluble in cold chloroform, cold water (the solution being neutral to litmus) and very soluble in ethanol, unlike hexachlorobenzene. On adding silver nitrate solution to an aqueous solution of the crystals, a white precipitate was formed. The crystals were also soluble in glacial acetic acid, but insoluble in boiling carbon tetrachloride, benzene and acetone. The action of aqueous sodium hydroxide produced an oil with an ammoniacal smell. A picrate was formed. (M.P. = $167-70^{\circ}\text{C}$). Analysis of the original material gave: - C;52.3%: Cl;24.5%: H;11.5%: N;7.0%.

Initially this was thought to be an amine hydrochloride formed by the interaction of stabiliser with HCl produced during the irradiation. When a 0.5% solution of benzylamine in trans dichloroethylene was irradiated for a short time, there was no detectable HCl and a slight precipitate was

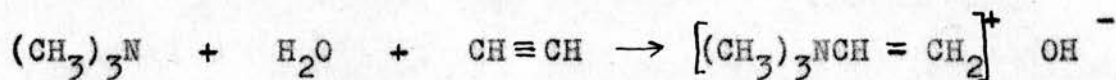
noticeable. This was filtered off. M.P. = 252 - 8°C
 (Lit. M.P. for benzylamine hydrochloride = 248°C with
 rapid heating.) Collins⁵⁸ has found a similar effect
 when carbon tetrachloride solutions of basic nitrogenous
 compounds are exposed to light.

However, in view of the later work involving stabiliser-
 free trichloroethylene, it was realised that the stabiliser
 must also be reacting with the explosive gases produced
 from the trichloroethylene. Newton⁵⁹ identified these
 gases as mono- and dichloroacetylene.

The reaction of primary and secondary amines with mono-
 substituted acetylenes in the presence of copper acetylides⁵⁵
 yields vinylamines which react with a further molecule of
 acetylene to produce substituted 3-aminobut-1-yne.

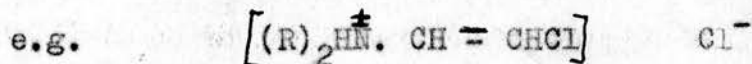


Tertiary amines react under pressure to give salts of the
 following type:



These additions are enormously facilitated if the triple bond
 is conjugated with an electron attracting group, no catalyst
 being required, and chlorine is strongly electron attracting.

The infra red analysis of this material is included and discussed in the IR section. It seems likely that a molecule of the latter type has been produced:



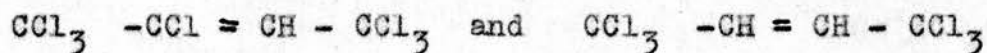
Solid material B: Recrystallisation from chloroform yielded shimmering crystalline platelets (MP = 216-7°C without sublimation). The compound was insoluble in ethanol, but soluble in benzene, ether and chloroform. An X-ray powder photograph, infra red spectra and elementary analysis was obtained.

ANALYSIS:

Found.	Calculated for dimer, $C_4H_2Cl_6$	Calculated for $C_4H_2Cl_6 + Cl_2$	Calculated for $C_4H_2Cl_6 + HCl$
Cl=82.1%	Cl=81.0%	Cl=85.0%	Cl=82.9%
C=16.7%	C=18.3%	C=14.4%	C=16.0%
H= 1.0%	H= 0.7%	H= 0.6%	H= 1.1%
<u>99.8%</u>	<u>100.0%</u>	<u>100.0%</u>	<u>100.0%</u>

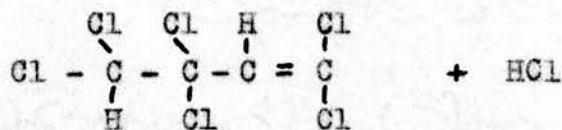
The infra red analysis (see infra red section) indicates that the molecule is either a butane or a trans but-2-ene. A saturated molecule may well result from the addition of chlorine or HCl across a double bond and from the analyses above the latter seems more likely.

The two possible unsaturated structures are:



The second seems less likely as no addition of bromine takes place and it is incompatible with the analysis. The first, on the other hand, would not be expected to add bromine and only the hydrogen analysis would be significantly different from that obtained. A third compound, $\text{CHCl}_2 - \text{CCl} = \text{CCl} - \text{CHCl}_2$, is also structurally although not analytically feasible, but the cis- and trans- forms have been identified and do not compare with our material.

Our conclusion is that the substance is probably



with $\text{CCl}_3 - \text{CCl} = \text{CH} - \text{CCl}_3$ as an outside possibility.

Ampoules were now prepared as in previous experiments. Two sets of three ampoules were irradiated for varying times.

FIRST SET.

The trichloroethylene was dried and distilled before use.

AMPOULE	DOSE. R	CONTENTS (gms)	HCl (moles)	TOTAL POLYMER (Moles)	CRYSTALLINE SOLID B. (gms)
I	15×10^6	50.5712	0.00089	0.0189	0.113
II	15×10^6	50.7646	0.00087	0.0191	0.108
III	30×10^6	49.5654	0.00143	0.0371	0.237

I	2.59×10^{-5}	54.6×10^{-5}
II	2.50×10^{-5}	55.0×10^{-5}
III	4.22×10^{-5}	110.1×10^{-5}

In the lower table, the quantities of product are reduced to moles/ml of monomer irradiated, assuming MW = 131.4 and $D_4^{20} = 1.4655$.

Using the method of least squares, $G(\text{HCl}) = 0.92$ and $G(\text{Polymer}) = 30.3$.

It was noticed that the organic layer turned a golden brown colour after being shaken with the aqueous sodium hydroxide solution for a few seconds. (Trichloroethylene before irradiation is unaffected by this treatment). After removal of monomer, the oil was separated from the crystalline residue by dissolving it in ethanol and filtering off the crystals.

Ampoules I and II were given the same total dose in order to test the reproducibility of the methods used.

SECOND SET.

The trichloroethylene was pre-treated by successive washings with dilute aqueous HCl, water, aqueous sodium carbonate solution and finally two lots of water. ^(twice) Careful fractionation followed, the middle cut being dried for two days over calcium chloride and finally distilled before use. The distillate was discarded until sweet smelling material was obtained. $n_D^{20} = 1.4772$ (lit $n_D^{20} = 1.4776$). The dose rate was 6680 R/min.

AMPOULE	DOSE. R	CONTENTS (gms)	HCl (moles)	TOTAL POLYMER (moles)	CRYSTALLINE SOLID (gms)
I	7.5×10^6	61.5347	0.00169	0.0116	0.105
II	15.0×10^6	56.8636	0.00320	0.0237	0.183
III	30.0×10^6	61.3088	0.00553	0.0519	0.332
I			3.97×10^{-5}	27.8×10^{-5}	
II			8.24×10^{-5}	61.2×10^{-5}	
III			13.2×10^{-5}	124.0×10^{-5}	

This gives $G(HCl) = 3.3$ and $G(Polymer) = 35.2$.

With this set of ampoules, there was no change in colouration when the HCl was extracted with aqueous NaOH solution. ^{for titration.}
As the solutions were being warmed up, preparatory to dis-

tilling off monomer, quite vigorous degassing occurred while the solution was between 20-40°C. This culminated in a flash which filled the Vigreux column, particularly when the last ampoule was concerned. A considerable quantity of carbon was left in the column. This occurrence is attributed to the presence of monochloroacetylene, and probably dichloroacetylene⁵⁹. It is certainly fortunate that stabiliser was present in the large scale irradiations.

In all these irradiations involving ampoules, the final polymer content reached a maximum of 12% by weight and at this concentration no significant^t drop in yield due to reduced monomer concentration is observed. The third ampoule of unstabilised trichloroethylene shows a lower HCl content than is expected due, probably, to the commencement of a secondary reaction involving the HCl,

The apparently lower production of HCl from the stabilised trichloroethylene must be due to interaction with the stabiliser. This results firstly in the production of solid material (A) which in turn reacts. The persistent orange colour of the oil residues must be associated with this process.

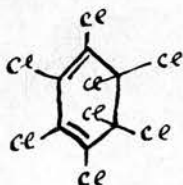
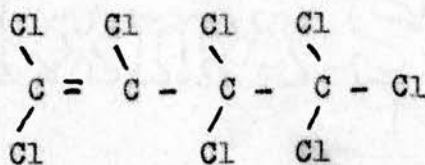
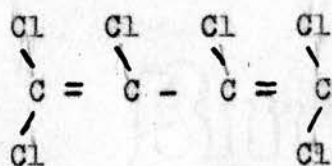
The presence of stabiliser has much less effect in the polymerisation, as is to be expected.

*or less on open the tube
due to
solubility
limitations*

VINYLDENE CHLORIDE AND TETRACHLOROETHYLENE.

In association with the present work, Miller and Stafford have been investigating the effects of gamma radiation on vinylidene chloride and tetrachloroethylene. The former has been found to polymerise readily with a G value of the order of thousands, a solid polymer similar to that obtained by other methods being formed.

Tetrachloroethylene has yielded several products, including hexachlorobutadiene, octachlorobutene-1 and possibly -2, and octachlorocyclohexadiene-1:3. The G value was about 12 for monomer conversion to polymer.



INFRA RED SECTION.

I Dichloroethylene Polymers.

All the spectra were obtained using a Hilger H 800 Spectrophotometer with a sodium chloride prism and the instrument was not calibrated for the following spectra, the values given being exactly comparable only with other spectra obtained from the same machine.

The polymers of dichloroethylene show an overall similarity whether they are derived from the cis- or the trans- isomer. The stretching frequency of -C-H groups appears at 3000 cm^{-1} and =C-H stretching at 3095 cm^{-1} in the dimer. The former resolves into two vibrations with the same mean value and the latter drops a little to about 3080 cm^{-1} with the trimer and higher polymers. A C=C stretching vibration (1635 cm^{-1}) is quite strong in all the polymers but again drops by about 5 wave numbers in the higher polymers.

A =C-H (trans) in-plane deformation is shown at 1294 cm^{-1} in the dimer dropping to 1275 in the trimer, but the out-of-plane deformation seems to remain fairly constant at about 937 cm^{-1} for all the polymers. Bellamy⁶⁰ says that "trans ethylenic double bonds give rise to a medium to strong band at $990-965\text{ cm}^{-1}$ due to the hydrogen atoms which are out of plane at the double bond." A chlorine atom on the same carbon atom has the effect of displacing the vibration to lower frequencies and Haszeldine⁸⁷ quotes 935 for this vibration in the group

-CH=CHCl. Bellamy continues that the weight of substituent atoms should have little effect on the intensity, which should, therefore, be inversely proportional to the molecular weight of the molecule. Thus the opportunity arises of making quantitative estimations of the amount of double bonding present in the molecule. Unless the film thicknesses are identical, a constant reference peak is necessary for calibration purposes. The strong vibration at 983 or 967 cm^{-1} is fairly constant and has been assumed to have the same intensity regardless of molecular size. The ratio of the two peak heights in a trans dimer spectrum is about 3.2 and the ratio for the solid polymer is about 0.66, the ratio of these two values being about 5.

This suggests that the solid polymer has one double bond for each ten monomer units and this may be an indication of the unit if not the molecule size. Comparing the C=C vibration at 1635 with the same reference peak, the ratios are 3.6 and 0.53 respectively, indicating fourteen monomer units per double bond. However, the intensity of the C=C vibration would be expected to increase as the molecular symmetry decreases due to extension of the saturated chain from the terminal double bond, and this is not a reliable measure.

From 600 to 850 cm^{-1} there are several very strong bands due, probably, to the C-Cl bonds but these vibra-

tions have never been identified with any certainty.

Stereoisomerism.

Geometrical isomerism has not been found. Both cis- and trans- monomers appear to produce polymers with substantially a trans- configuration about the double bond. If material with the cis- configuration were present in minor quantity, it would not be easily detected by infra red analysis of the mixture, but could be expected to differ in chemical properties and no different fractions have been found.

The possibilities of geometrical isomerism due to the accumulation of asymmetric centres are, however, numerous.

The dimer, if the double bond is purely trans, will be a homogenous racemate whether it is derived from the cis- or the trans- monomer. The trimer, with two centres of asymmetry, is capable of forming two analogous racemates which we may designate "erythro and threo". As the trimers from both cis- and trans- monomer seem identical in properties, it is likely that the mixture, if it exists, is the same in both instances. The theoretical importance of this in the polymerisation will be discussed later.

The bromo compounds introduce new asymmetric centres but the dimer appeared to yield only a single compound in

quantity. This appears surprising because selectivity with respect to both new asymmetric centres is improbable. It was however, a fact and it seems reasonable to assume that similar homogeneity with respect to bromination will occur in the higher members of the series. If both erythro and threo trimer are present then two bromo compounds might be expected. However, apart from the observation that after the initial rapid precipitation further deposition of solid bromo compound took place slowly, no indication of different products was apparent and indeed, despite efforts to prove the contrary, the bromo compound rapidly produced could not be differentiated from that slowly produced.

The infra red spectra of the bromo derivatives show the same features as the oil polymers except for the lack of unsaturation. The C-Br stretching occurs below 600 cm^{-1} and therefore, apart from weak harmonics at 1100 to 1200 cm^{-1} , is not observed. Some influence is to be expected on the C-H bending vibrations at the particular carbon atom to which the bromine is attached and this is observed.

II Trichloroethylene Polymers.

The absorption of the oil dimer is very similar to that of the dichloroethylene dimer but the reduced C-H content is apparent, and is consistent with the structure

$\text{CHCl}_2 \cdot \text{CCl}_2 \cdot \text{CH}=\text{CCl}_2$ proposed by Frank and Blackham⁵¹ or the alternative structure $\text{CHCl}_2 \cdot \text{CCl}_2 \cdot \text{CCl}=\text{CHCl}$. The 3062 cm^{-1} vibration indicates the $=\text{C}-\text{H}$ stretching; no question of cis or trans configuration arises in this case.

Solid Material A: The spectrum is relatively simple compared with some of the others recorded in this section. The most striking feature is the broad strong absorption band over the range 2800 to 2500 cm^{-1} . This is too low for the NH_4^+ group, but is very similar to the broad band shown by amino acid hydrochlorides, $\text{NH}_3^+ \text{CHRCOOH}$. It is conceivable that this might also result from a group of the type $(\text{R}_1\text{R}_2\text{HN}^+\text{CH})$ as found in a primary or a secondary amine, and there are no other groups which would be expected to produce this type of absorption. At higher wave numbers 2976 and 3000 cm^{-1} , the presence of methyl and perhaps methylene groups is indicated. The 1192 , 1174 and 809 cm^{-1} absorptions may indicate the skeletal vibrations of $(\text{CH}_3)_2-\text{C}$ or $(\text{CH}_3)_2-\text{N}$, but the last value might alternatively be due to $\text{C}-\text{Cl}$ bond stretching. There is no indication of the $\text{C}=\text{C}$ group although a little $\text{C}=\text{N}$ may be present, as shown by the 1534 peak.

It is much easier to say conclusively that a certain functional group is present or absent if the type of molecule being examined conforms to the general pattern of simple organic molecules discussed in the literature. No substances of a structure resembling $(\text{R}_1\text{R}_2\text{HN}^+\text{CH}=\text{CHCl}) \text{Cl}^-$ have ever been

investigated. With such a structure, the electron displacement is certain to be very large and, if a primary or secondary amine is involved, a tautomeric form exists: $(R_1R_2\overset{+}{N}=CH-CH_2Cl) Cl^-$. Under these circumstances, the absorption of the molecule in the infra red will be considerably different from the overall picture obtained by considering the absorptions of the various uninfluenced groups, and the postulated structure can be neither confirmed or refuted.

Solid Material B: The residual solid (B) obtained from trichloroethylene shown similarities to the oil dimer. It also absorbs at 3039 cm^{-1} , which is rather higher than C-H stretching vibrations unless the carbon atom has a double bond. No C=C is indicated, but if this were in the 2-position of a trans butene, the molecule would be symmetrical and no dipole moment change would occur in the C=C vibration, thus prohibiting the associated frequency in the infra red. Thus, once more, no definite conclusion can be drawn from examination of the spectrum.

INFRA RED SPECTRA.

The oils were examined as thin films and the solids as mulls with hexachlorobutadiene (4000-2000 cm^{-1}) and Nujol (2000-750 cm^{-1}).

<u>CDE DIMER</u>	<u>TDE DIMER</u>	<u>CDE TRIMER</u>	<u>TDE TRIMER</u>
3095 s	3095 s	3089 s	3094 s
		3014 s	3016 s
3000 s	2995 s	2976 s	2983 s
2430 w	2439 w	2519 w	
2400 w	2412 w	2410 w	
1745 m	1752 s	1746 m	1745 m
1678 m	1675 m	1629 vs	1631 vs
1348 s		1350 s	1350 s
1334 s	1335 s	1340 s	1338 s
1317 s	1317 s	1314 s	1313 s
1294 s	1295 s	1275 s	1279 s
1285 s	1281 ss	1260 s	1265 s
1254 s	1256 s	1244 s	1244 s
1231 s	1234 s		
	1223 s	1219 s	1217 s
1212 s	1213 s	1200 s	1201 s
1192 s	1213 s	1187 s	1188 s
	1194 s		
1121 m	1123 s	1119 m	1117 m
1100 s	1102 s	1102 m	
1071 m	1069 m	1063 m	
1044 m	1046 m	1029 s	1031 s
1012 s	1013 s		
983 s	986 s	985 s	987 s
	959 s	967 s	967 s
937 vs	934 vs	940 s	940 s
858 s	858 s	865 s	864 s
819 s	813 s		
	792 s		
767 vs	779 s	788 s	785 s
		754 s	753 s
748 vs	744 s	734 s	733 s
718 s	702 s		
	654 s	656 s	

All values are given in wave numbers (cm^{-1}), and the intensity of vibration is indicated by very strong (vs), strong (s), medium (m) or weak (w).

CDE TETRAMER

TDE TETRAMER

TDE SOLID POLYMER

3827 vw		
3689 vw		
3609 vw		
3255 vw		
3080 m	3085 m	3099 w
3005 s	3019 s	3000 s
2991 s	2991 s	
2859 w		2897 w
2608 w		
2528 w		
2411 w		2420 w
1744 m		
1627 vs	1630 vs	1629 w
1425 w		
1342 s	1343 s	
1331 s	1333 s	1319 vw
1273 vs	1273 vs	1273 s
	1248 m	
1219 vs	1219 vs	1206 m
1200 vs	1203 vs	
1185 vs	1188 vs	1186 m
1105 s	1117 s	
1148 s		
967 s	972 s	971 m
935 s	938 s	936 w to m
	837 s	
	813 s	
790 vs	791 vs	783 ms
752 vs	752 vs	743 s
	732 vs	729 s
		706 s
	686 s	



BROMO DERIVATIVES.

CDE DIMER

CDE TRIMER

TDE TRIMER

		3009 m
		2980 m
1313 w		1323 w
	1276 m	1283 m
1267 w	1269 m	1265 m
1254 w	1252 m	1249 m
1244 w	1233 m	1229 m
1215 w	1213 m	1211 m
	1194 m	1193 m
1173 w	1174 m	1174 m
1158 w	1154 m	1147 m
	1092 w	
	1070 w	1067 w
1017 w	1049 w	1045 w
992 m	992 m	
	982 m	981 m
		970 m
	827 m	825 m
	804 s	799 s
777 s	773 s	771 s
735 s	742 s	742 s
712 s	712 s	712 s
	667 s	
	650 s	

TRICHLOROETHYLENE.

<u>OIL DIMER.</u>	<u>RESIDUAL SOLID B</u>	<u>INITIAL SOLID A</u>	
3062 m-w	3039	3000 s	
3004 w-m	3000	2976 s	
	2953	<hr/>	
		2780 s	These three form a very broad band.
	2330	2605 s	
		2500 s	
1612 s		<hr/>	
		1534 w	
		1402 s	
	1323 w	1333 m	
1304 w-m			
1273 w		1192 w	
1215 m	1214 m	1174 ms	
	1171 w	1079 wm	
	1161 w	1042 ms	
1109 m			
1084 w-m		854 m	
1025 s	1041 w	809 m	
994 w	1005 w		
963 w	972 w		
929 s	923 m		
898 s			
838 s	854 s		
817 s	816 s		
789 s	791 s		
742 s	761 s		
721 s	728 s		
	705 s		

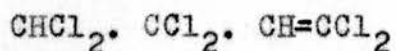
OZONISATIONS.

Some of the oil polymers of both di- and trichloroethylene were ozonised, in an endeavour to differentiate between alternative structures. In most of the experiments the ozone-oxygen mixture was bubbled through a 1% solution of the oil in glacial acetic acid at room temperature for about four hours. In no case was the ozone completely absorbed initially and continuous production of HCl occurred.

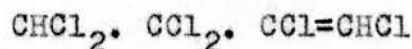
A little water was added at the end of the ozonisations, the solutions boiled for five minutes and then diluted with water and extracted with ether. The ethereal solution was washed with water and then evaporated off. In a few cases crystallisation occurred, although usually a heavy oil was obtained.

Trichloroethylene Dimer.

An oil was obtained with $n_D^{20} = 1.5080$ and this solidified after a few days to a mass of colourless crystals (MP=46-54°C). Attempts to purify this led to considerable reduction in yield and sufficient for infra red analysis only was obtained. There are two structures for the dimer to be considered.



I



II

I would yield a chloroaldehyde which would be expected to be of considerable stability and to form a hydrate due to the alpha dichloro groups.

II would yield an acid chloride and eventually an acid. The infra red analysis indicated that the product was a carboxylic acid containing water either of crystallisation or occluded in some manner. This would favour II.

The melting point is low for the known $\alpha:\alpha:\beta:\beta$ - tetra-chloropropionic acid (MP = 76°C) and conforms rather with that of trichloropropionic acid which is known to have a variable melting point of the same order. More work on the conditions of ozonisation and isolation are patently required to provide adequate material for future study.

Dichloroethylene Dimer.

A crystalline material was obtained and recrystallised twice from benzene, and dried for one hour at about 60°C in a vacuum pistol.

The substance still presented a broad melting range ($133\text{-}143^{\circ}\text{C}$) and an analysis gave: C=48.0% Cl=28.0% H=7.5% O=16.5%. The only method of accommodating this is to assume the presence of solvent of crystallisation. It is inviting to assume the presence of benzene of crystallisation with additional water to account for the C_{15}Cl_3 ratio. An attempt was made to confirm this by dissolving a sample in spectroscopic ethanol and determining its absorption. An absorption of 275 μ rather than 255 μ was obtained with an $E_{1\text{ cm}}^{1\%}$ of about 161 (assuming $\text{C}_3\text{Cl}_3\text{H}_3\text{O}_2$).

The wavelength of absorption was inconsistent with the presence of benzene and the matter rests at the moment, although no alternative explanation of the absorption based on the expected product types is forthcoming.

Dichloroethylene Trimer.

Ozonisation of a 1% solution yielded a crystalline solid, (MP:159-161°C) from acetic acid (Found: C;21.5% Cl;48.2% H;1.8% O;28.5%). Infra red analysis showed this to be an acid and the analysis indicates possible association with acetic acid.

Ozonisation of a 5% solution yielded a little solid (MP = 115-8°C) and a considerable amount of starting material. This was not further examined.

It is apparent that ozonisation may be proceeding normally but that the character of the products with possible high capacities for solvation in the crystals is complicating the issue. Until the whole matter of the ozonolysis of much simpler chloro compounds is investigated, little additional value would emerge from a study of these more complex systems. The ozonisation studies have been taken over by another worker as they are not directly associated with the fundamental problem of the effects of gamma rays on chloro compounds.

COPOLYMERISATIONS.

A few copolymerisations were attempted. In the first series of four, a number of different monomers were mixed in different proportions with vinylidene chloride and irradiated. The solutions either emulsified and then showed little further change or they solidified completely. This seems to be more a measure of the swelling of polyvinylidene chloride in the various monomers rather than an indication of the extent of polymerisation. In all cases a large amount of HCl was produced, and the weight of solid polymer obtained was about the same as the weight of vinylidene chloride employed. Infra red spectra of the polymers did not differ noticeably from the spectrum of polyvinylidene chloride prepared by gamma ray initiation.

The following list indicates the principal features of these experiments, the heading indicating the other monomer and the percentage of the other monomer present in the solution with vinylidene chloride. The dose was approximately the same for all four (9×10^8 R)

1 Trans dichloroethylene: 49%

After two days the solution had emulsified and after five days it was solid. Irradiation was stopped after fourteen days. Solid polymer yield = 50%

2 Trans dichloroethylene: 77%

This solution remained an emulsion. Solid polymer yield = 24%. The supernatant liquid contained less than 0.5% vinylidene chloride.

3 Trichloroethylene: 75%

The trichloroethylene was free of stabiliser. The solution emulsified, yielding 17% of solid polymer, and a surprising amount of vinylidene chloride (5%) was found in the supernatant liquid, thus accounting for ~~all~~ ^{the bulk of} the vinylidene chloride. Oil polymer (10 gm) was also obtained: two fractions (1.2 gm) with $n_D^{20} = 1.5450$ and 1.5622 respectively, and black charred residue (8.2 gm) fuming with HCl. These oils resemble the dimer and trimer of trichloroethylene.

4 Tetrachloroethylene: 80%

The solution polymerised to a solid, but on drying the polymer, the weight obtained was equivalent to 25% yield only.

5 Trans- dichloroethylene (46%) was copolymerised with trichloroethylene (54%). Considerable HCl was produced, but no insoluble polymer. An oil polymer resulted (5% yield) but on trying to fractionate it at a high vacuum pump, it charred with evolution of very large quantities of HCl. To safeguard the pump this fractionation was discontinued.

6 One Block Copolymerisation, namely the irradiation of trans dichloroethylene solid polymer swollen with dimethyl maleate, was attempted. On extracting the resultant material for Twenty-four hours with ether, the residue was dried and examined by infra red analysis. A strong vibration attributable to the C=O group was present.

In mixtures, each monomer polymerises at a rate rather lower than its polymerisation rate in the pure state. If the rates of the two monomers in the mixture are widely different, then a polymer containing a preponderance of the material which polymerises more quickly must be expected. A second factor, given by the monomer reactivity ratios, determines the tendencies of radicals to combine with their own monomer molecules or the other monomer molecules preferentially. The rates of polymerisation in experiments 1-4 are so different as to render any useful observations difficult. Certainly the situation appears to be similar to that found using conventional methods of polymerisation. In system 3, there is some tendency to avoid copolymerisation if the oils found are indeed trichloroethylene dimer and trimer. In 5, interaction must have occurred as the production of solid polymer was inhibited. The block copolymerisation 6, was originally planned in order to try to solubilise the insoluble solid polymer by "attaching" soluble groups. If this is to be successful, either much longer irradiation will be necessary, or the source of

these soluble groups (dimethyl maleate in this case) should be better chosen.

DISCUSSION

Polymerisation reactions may be classified into three types: condensation, ionic and addition polymerisation. The first type usually involves amino or carboxylic groups and ammonia or water are eliminated as the polymerisation proceeds.

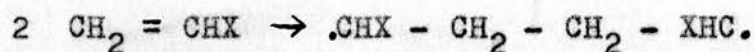
When certain unsaturated compounds are treated with Friedel-Crafts type catalysts in the presence of traces of water, ionic polymerisation occurs. Isobutene, for example, although completely stable in the presence of free radicals, polymerises in the presence of boron trifluoride even at temperatures below -100°C . The outstanding feature of this type is the relative independence of the rate on temperature.

The gamma radiation initiated polymerisation of isobutene⁶¹ has been found to possess a negative temperature coefficient and to be independent of radiation intensity, showing the ionic character of the reaction. The addition of carbon tetrachloride under suitable conditions increases the yield by 50%. None of those characteristics pertain to the dichloroethylene and trichloroethylene polymerisations. Addition of carbon tetrachloride (10%) to the former does not affect the yield appreciably, and the addition of iodine to dichloroethylene and vinylidene chloride before irradiation has been found to inhibit both polymerisations completely. Lastly, the positive

temperature coefficient of the dichloroethylene polymerisation and the close resemblance of the products to those obtained using more conventional initiators points to the occurrence of a free radical mechanism. Many other polymerisations utilising gamma radiation have also been shown to be free radical in nature, isobutene being the one exception.

This addition polymerisation is a common property of ethylenic materials when heat photochemical excitation or free radicals derived from the thermal breakdown of organic peroxides are used as initiators.

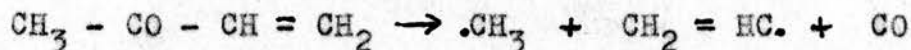
Thermal initiation is thought to be due to the formation of a dimeric diradical^{62,63}.



The results of photochemical polymerisation are similar, and many workers have suggested that the initial step is the excitation and uncoupling of the electrons of the double bond⁶⁴⁻⁶. Free radical initiation utilising the thermally produced free radicals from organic peroxides, the third type of addition polymerisation, is well known and will not be further discussed at this point.

Under certain conditions in these addition reactions, the monomer molecule may split into monoradicals. In the vapour phase polymerisation of methyl vinyl ketone, normal ketonic photolysis with the production of carbon monoxide

methyl and vinyl radicals initiates the polymerisation⁶⁷.
A similar type of reaction is thought to occur with
styrene and methyl methacrylate⁶⁸⁻⁹.



The vinyl radicals take no part in the polymerisation
and dimerise to butadiene.



Propagation:

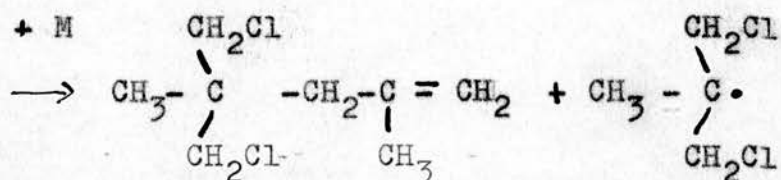
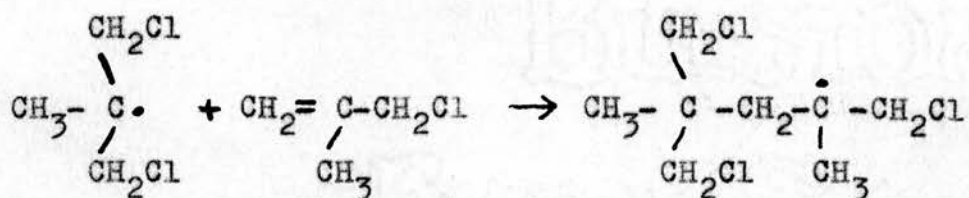
The propagation steps are relatively simple, consisting simply of successive additions of a radical to a monomer molecule.

Termination:

The destruction of free radicals, including the growing polymer radical, nearly always occurs by interaction of pairs of these radicals, although a termination step of first order with respect to the propagating radicals, has been found for allyl compounds⁷⁰⁻¹, and vinyl benzoate⁷². Thus, if a radical interacts with a molecule, a new free radical is formed, and this free radical will produce further polymerisation chains (chain transfer). If two radicals interact, either a single molecule is formed, (termination by combination), or

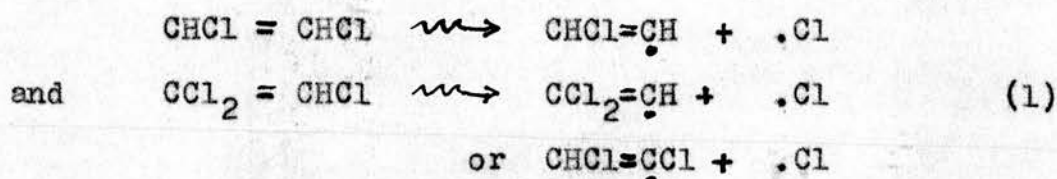
an atom is transferred with the formation of two molecules, one saturated, the other unsaturated (disproportionation).

The structure of methallyl chloride polymer (dimer) has been determined⁷⁵ and a mechanism proposed in which a chlorine radical initiates polymerisation by adding to a monomer molecule. After a further addition, the dimeric radical terminates by losing a chlorine atom to a monomer molecule, this new radical continuing the chain.

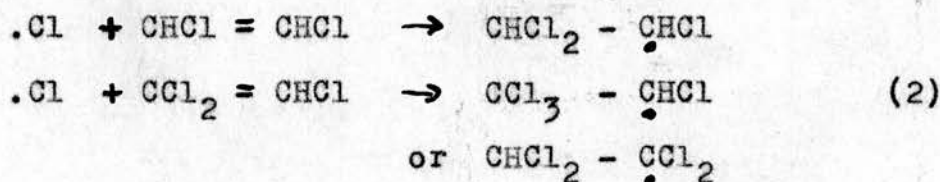


Several workers have applied this mechanism to the polymerisations of both di- and trichloroethylene^{51,76} when conventional initiators are used.

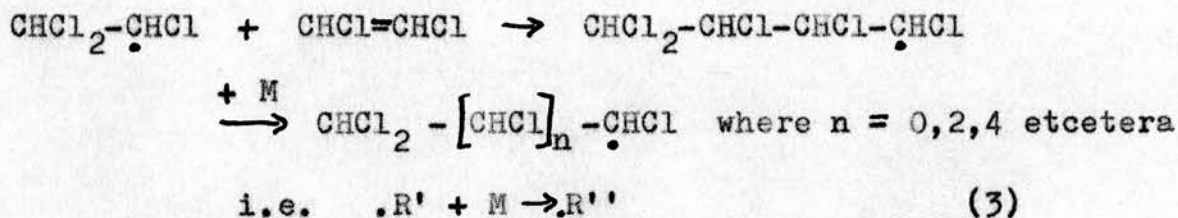
The comparative bond dissociation energies of C-H, C-C and C-Cl indicate that the C-Cl is the weakest. Therefore, it seems reasonable to postulate initiation as follows:-



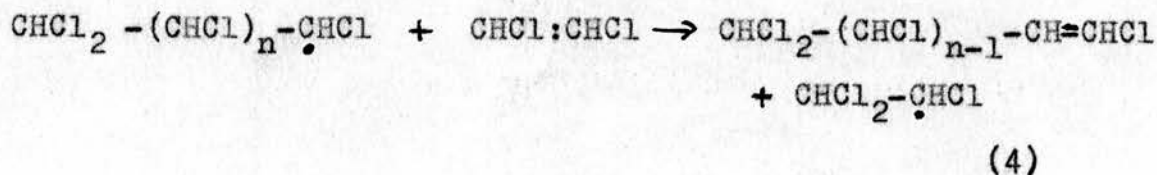
The chlorine radical then adds to a monomer molecule.



The activated complexes so formed have two possible further reactions. Either the radical adds to a further monomer forming a dimeric and eventually a polymeric radical:

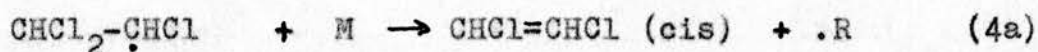
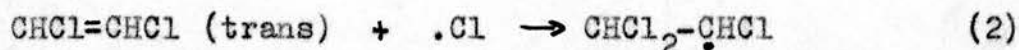


or it loses a chlorine atom which continues the chain reaction.



As a result of a suggestion by Kistiakowsky⁷⁸ that radicals are non-planar, Mayo and Wilzbach⁷⁹ investigated such radicals from cis- and trans- dichloroethylene in their addition to vinyl acetate. They concluded that the radicals were either planar or, if pyramidal, that rotation occurs before addition, that is, that the frequency of rotation is greater than the frequency of addition.

As the isomers used in the present work were almost pure and the equilibrium ratio at room temperature is trans/cis-1/4, the fact that little isomerisation occurred even when considerable polymerisation was achieved indicates that reaction (3) is very much more efficient than reaction (4a)



This mechanism has been suggested by Ewald and his co-workers⁷⁶ for the iodine catalysed isomerisation of dichloroethylene.

The corresponding reaction (3) for tri- and tetrachloroethylene will be much less efficient due to the increasing significance of steric and charge factors. This is reflected in the decreasing G value of polymer production in the sequence dichloroethylene, tri- and tetrachloroethylene. It is of interest to note in this context that some Russian workers⁸³ have reviewed the polymerisation of ethylene and butadiene derivatives and have come to the conclusion that

only the stereochemical factor is operative in hindering the formation of high polymer molecules: the electronegativity of the substituted atoms is irrelevant.

Pauling⁸⁰ has found that the lengths of the C-Cl bonds in tetra, tri and dichloroethylenes are respectively 0.03Å, 0.05Å and 0.08Å shorter than the normal C-Cl bond length in a saturated molecule. This can be expressed alternatively by saying that a chlorine atom adjacent to a double bond assumes some double bond character, and that if several chlorine atoms are present each will assume this character to a lesser extent than if only one were present. Hence the ease of C-Cl bond fission of the chloroethylenes increases as we progress from two to four-fold substitution. The HCl yield reflects this and reaction (1) increases in significance while reaction (2) diminishes. At this point, it should be noted that although trans isomers are normally the more stable because the configuration permits higher double bond character, in this case the cis isomer is more stable. (At 0°K in the gaseous phase, the cis form is more stable than the trans form by about 530 calories per mole⁸¹).

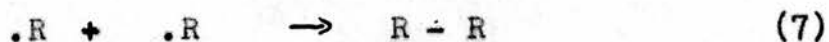
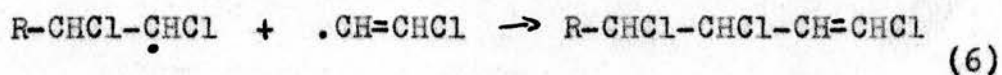
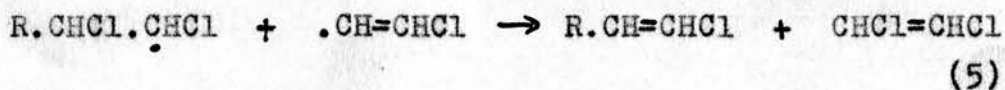
	<u>G(HCl)</u>	<u>G(Polymer)</u> [*]
TRANS dichloroethylene	0.91	224
CIS dichloroethylene	1.48	142
Trichloroethylene	3.30	35.2
(Trichloroethylene-stabilised)	(0.92)	(30.3)
Tetrachloroethylene	-	approx 12 ¹⁰

* Calculated as moles of monomer changed to polymer.

CHAIN TERMINATION

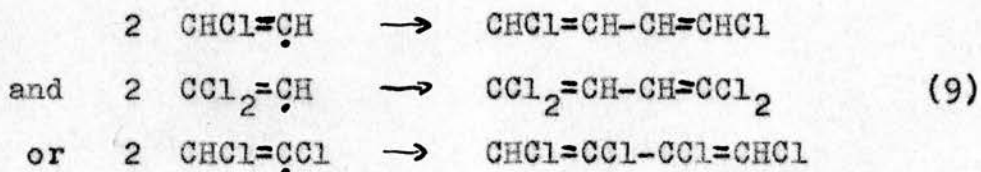
Termination.

The destruction of a growing radical can occur in several ways: by interaction with a monomer molecule and transference of the polymerisation chain, as in reaction (4), or by interaction with another radical and termination of the chain. The latter process may happen in three different ways.



Reaction (7) m is not likely to be very significant as no fully saturated products have been found with the possible exception of the dimeric solid from trichloroethylene. Reaction (5) would be expected to result in the production of a mixture of cis- and trans- monomer with the cis- predominating, and therefore cannot be very important as little isomerisation occurs with either pure isomer. The fact that all the oil polymers have a trans- configuration about the double bond implies that this is more stable than the corresponding cis- configuration, as is normally the case.

Dimerisation of the ethylenic radicals to form a butadiene is feasible as previously suggested (butadiene from vinyl polymerisations). Hexachlorobutadiene is a product of the gamma irradiation of tetrachloroethylene.



Since the butadiene to be expected from trichloroethylene would be 1;1;4;4- or 1;2;3;4;-tetrachlorobutadiene and the latter is a solid with a melting point of 50°C⁸², the residual materials were investigated after removal of monomer. The UV spectra showed no signs of dienic conjugation. Dichloroethylene residues were not examined in

this way.

The negligible yield of polymer in the low temperature irradiation of the trans isomer implies that the initiation reaction (1) requires a small activation energy and has been slowed down considerably. Comparing the room temperature and high temperature irradiations, we find that although there is an overall increase in yield when the temperature is raised (implying an increased rate of initiation), nevertheless the average degree of polymerisation is lower. By far the major product in the high temperature irradiation is wax which could not be distilled. Obviously there must be an optimum temperature at which a high initiation rate is combined with sufficient stability of the attacking radicals. If the temperature is too high, the radicals become unstable, and disproportionate or terminate with chain transfer instead of continuing growth.

Dichloroethylene dimer shown marked stability to gamma radiation confirming Weales observation of high stability. Bauer⁸⁴ claims, however, to have proved the active participation of the dimer obtained by continuous polymerisation of dichloroethylene, polymers as high as hexamer being formed. In view of the polymerisability of 1-butenes in general, this stability towards gamma radiation must be attributed to resonance stabilisation of the double bond and steric factors. The lability of some of the chlorine atoms is revealed by the copious HCl production. An attempt to

hydrogenate the trimer resulted in HYDROGENOLYSIS.

Almost the entire uptake of hydrogen was accounted for in the form of HCl, of which almost three molecules were formed per molecule of trimer. (Hydrogenation using Adam's catalyst in ethyl acetate: resulting oil had $n_D^{20} = 1.51111$)

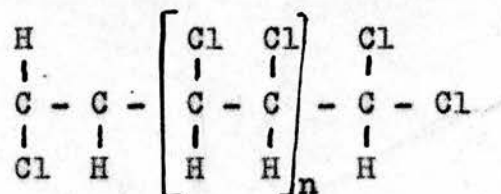
SOLID POLYMER

Only one case of a polymer insoluble in its own monomer has been investigated⁷⁴. This polymer, polyvinylidene chloride, is markedly crystalline, but otherwise little is known about its constitution or the kinetics of its formation.

The solid polymer obtained from trans dichloroethylene is most difficult to study on account of its insolubility. The fact that small amounts can be separated by prolonged extraction, and that such fractions have lower melting point ranges than the residual material, indicates a considerable molecular weight distribution. All samples examined by infra red spectroscopy showed considerable unsaturation with trans configuration, and an overall similarity to the oil polymers. After small doses of radiation the monomer becomes opalescent, indicating that initially, at least, the solid is the result of a rapid chain reaction. As the dose is increased, flakes of polymer appear, gradually

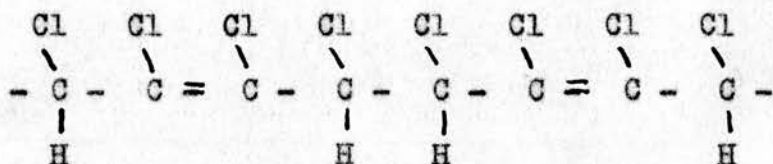
increasing in size and quantity. The approximate figures for solid polymer production show a tendency to increase rapidly as the dose is increased. These observations indicate an autocatalytic effect, or interaction of growing radicals with the polymer. Burnett⁸⁵ states that many polymerisations increase sharply in rate after the viscosity of the solution has increased to a certain point (the gel stage), and that this increase is accompanied by an increase in the mean molecular weight. Cross-linking must, nevertheless, be present to some considerable extent as a swelling equilibrium is set up. If the polymer consisted purely of long chains, it would presumably continue to absorb solvent until it was effectively in suspension or solution. Alternatively, some crystallinity may be present to obstruct solvent penetration, although this state would not be expected to continue in boiling dimethyl formamide (BP = 153°C) or boiling tetrahydrofuran (BP = 65°C). An X-ray powder photograph of a sample was completely diffuse and therefore little, if any, crystallinity can be present.

If this polymer is assumed to consist mainly of straight chain molecules



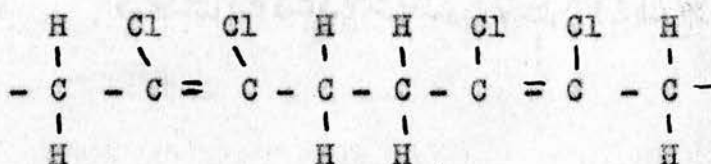
where n = 1,2,3 etcetera.

it is very similar to the theoretical polymer of 1:2:3:4-tetrachlorobutadiene which has never been polymerised.



(Assuming 1:4 polymerisation)

However, 2;3-dichlorobutadiene has been polymerised⁸⁶ and yielded a polymer described as a white hard mass, opaque, tough and only partially soluble in chloroform.



It slowly precipitates as it forms in the monomer and is very swollen. This description could apply to the trans dichloroethylene polymer. The outstanding features of dienic polymerisations are the considerable side-chain production resulting from 2;3 and 1;3 additions and cross linking, which is facilitated by the large residual unsaturation. That cross linking is facilitated under such conditions is supported also by Charlesby's findings mentioned previously. Cross linking is greatest in the trans octadec-1-ene, decreasing as the double bond moves towards

the centre of the molecule: the cis isomers do not cross link to the same extent.

The trans terminal double bond of the oil polymers from both cis and trans dichloroethylenes is such, then, that appreciable cross-linking must be expected by its participation. Similarly, since they are all unsaturated, growing radicals may attack them. The HCl loss must produce further unsaturation, enhancing this effect. From the G values, we see that about one molecule of HCl is present for every 18 monomer units in the solid polymer, or one for every 180 of oil monomer units at low dose rates. (About one molecule of HCl is formed per 90 oil monomer units of the cis isomer). It is still quite legitimate to ask, however, why solid polymer is obtained only from the trans isomer since all the effects mentioned apply to both isomers in the course of polymerisation.

During the course of the present work, no solid polymer has been obtained even in trace from purified cis isomer, this corroborating the results of some previous workers.

The considerably higher energy of the trans isomer would allow of a much faster rate of reaction, and steric influences would also be significant. A difference in degree and not a difference in mechanism is the distinguishing feature of the two polymerisations. Weale has

obtained solid from cis dichloroethylene with drastic treatment and this appears to confirm the argument.

The significance of the much larger yield of solid obtained in the gamma initiated polymerisation of trans isomer may depend on two factors. Firstly, the temperature at which the irradiation occurs is much lower than the minimum temperature at which free radicals can be obtained from peroxide initiators (usually about 80°C), and low temperatures seem to favour the growth of the radical. Secondly, the possibility of the influence of excited molecules, that is, molecules which have received energy below the ionisation potential but above the various electronic excitation levels, must not be ignored. Such molecules would have a much greater frequency of addition than the other molecules. In this context, it is as well to point out that the G values for the ampoule polymerisations are not comparable with yields in the initial large scale irradiations where the dose rate was very much lower, and where the yields will probably, therefore, be higher.

TRICHLOROETHYLENE

The products of the irradiation have not been sufficiently elucidated to warrant further separate discussion: Newton⁵⁹ has irradiated trichloroethylene with alpha particles to a total dose of 10^{21} ev/ml (5×10^7 R/ml) with the following results:

	<u>α particles.</u>	<u>γ radn. (this work)</u>
HCl	G value = 0.60 - 0.80	0.9
HC \equiv CCl	1.8 - 1.6	?
ClC \equiv CCl	0.59 - 0.65	?
CHCl ₃	trace	-
Polymer	10.1 - 11.7	30.3

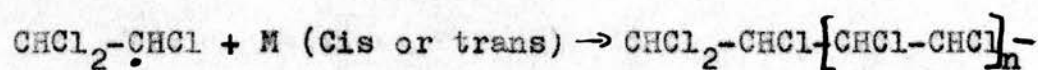
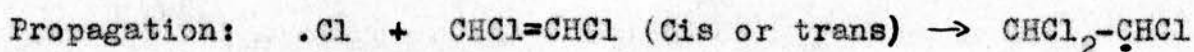
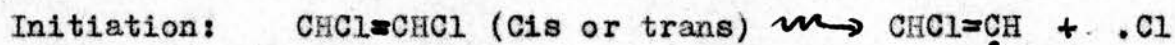
The production of acetylenes must be due to an abstraction reaction such as:-



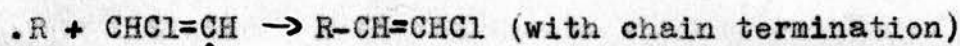
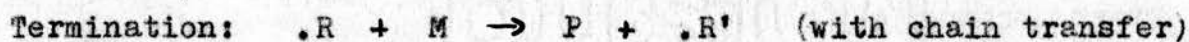
The difference in polymer yields obtained using the two different ionising radiations is explained later.

To summarise, it is our opinion that the polymerisation processes are as follows:-

DICHLOROETHYLENE

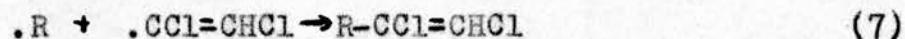
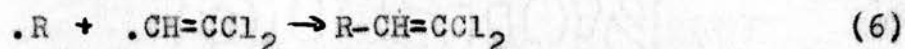
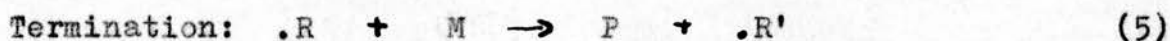
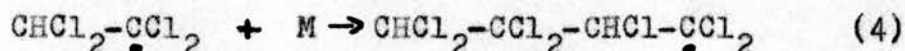
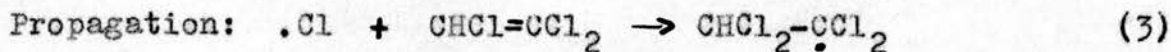
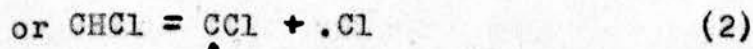
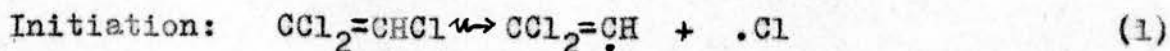


where $n = 1, 2, 3, \text{ etcetera}$



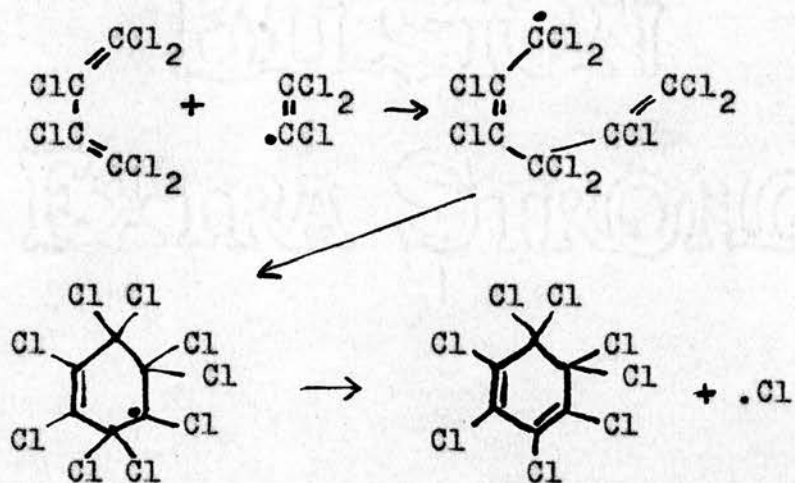
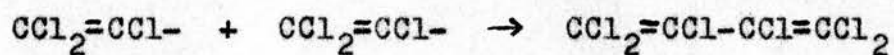
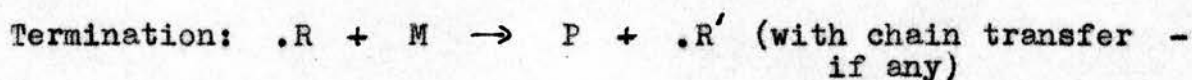
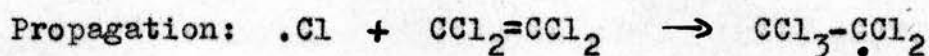
The production of HCl is an independent process except in so far as it facilitates cross-linking and therefore the production of solid polymer.

TRICHLOROETHYLENE.



Whether both of reactions (1) and (2) occur or not cannot be said definitely as intramolecular energy transfer may lead to only one mode of dissociation. Certainly the radical obtained in reaction (2) appears the more probable. However the possibilities of reactions (6) and (7) cannot be discounted, because the products would not be distinguishable by our methods. A reaction such as (8) must be postulated for the production of monochlor- and dichloroacetylenes. The stability of these vinyl ions must be very dependent on the influence of degree of substitution as no acetylenes have been observed in the irradiation of the other chloroethylenes.

TETRACHLOROETHYLENE.

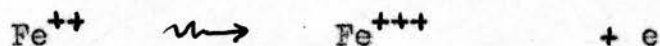


CARBON TETRACHLORIDE

SYSTEMS

DOSE RATE DETERMINATIONS.

Dose rates were determined by measuring the rate of increase of ferric ion in the reaction



which occurs in oxygenated aqueous acid solutions of ferrous ion. This "dosimeter", suggested by Fricke and Morse⁴⁰, has been shown to be very reliable provided the concentration of ferric ion is about 10^{-3} to 10^{-4} molar and the solution is between 0.5 and 1N with respect to sulphuric acid. If the solution is saturated with air, total doses of up to 50,000 Roentgen are permissible, after which further aeration or oxygenation is required or the rate of oxidation falls off. In this permissible range, the G value for the oxidation of ferrous ion to ferric is 15.6 ± 0.4

In the present work the solutions were made up in the following way:

Water: Water was prepared by subjecting tap water to a three stage distillation process, the first stage being an acid potassium dichromate solution, the second a sodium carbonate solution and the third being simply a redistillation of the water so obtained. The entire apparatus was made of Pyrex glass and the water was stored in a silica container.

Reagents: Concentrated sulphuric acid and ferrous ammonium sulphate, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, both of Analar

grade were used and solutions were made 0.8 N with respect to sulphuric acid and M/100 with respect to ferrous ion.

Vessel; The vessel for which the dose rate was required was cleaned with benzene/concentrated sulphuric acid, washed several times with distilled water and dried for at least Twenty-four hours at 100°C.

The vessel was then filled with solution and irradiation commenced.

At approximately fifteen minute intervals, samples were abstracted and their transmission of light at 304 mμ compared with that of the original solution. As the molar extinction coefficient of the ferric ion in solution is accurately known (Table I) the concentration can be determined by the equation.

$$\text{Log} \frac{I_0}{I} = e c d$$

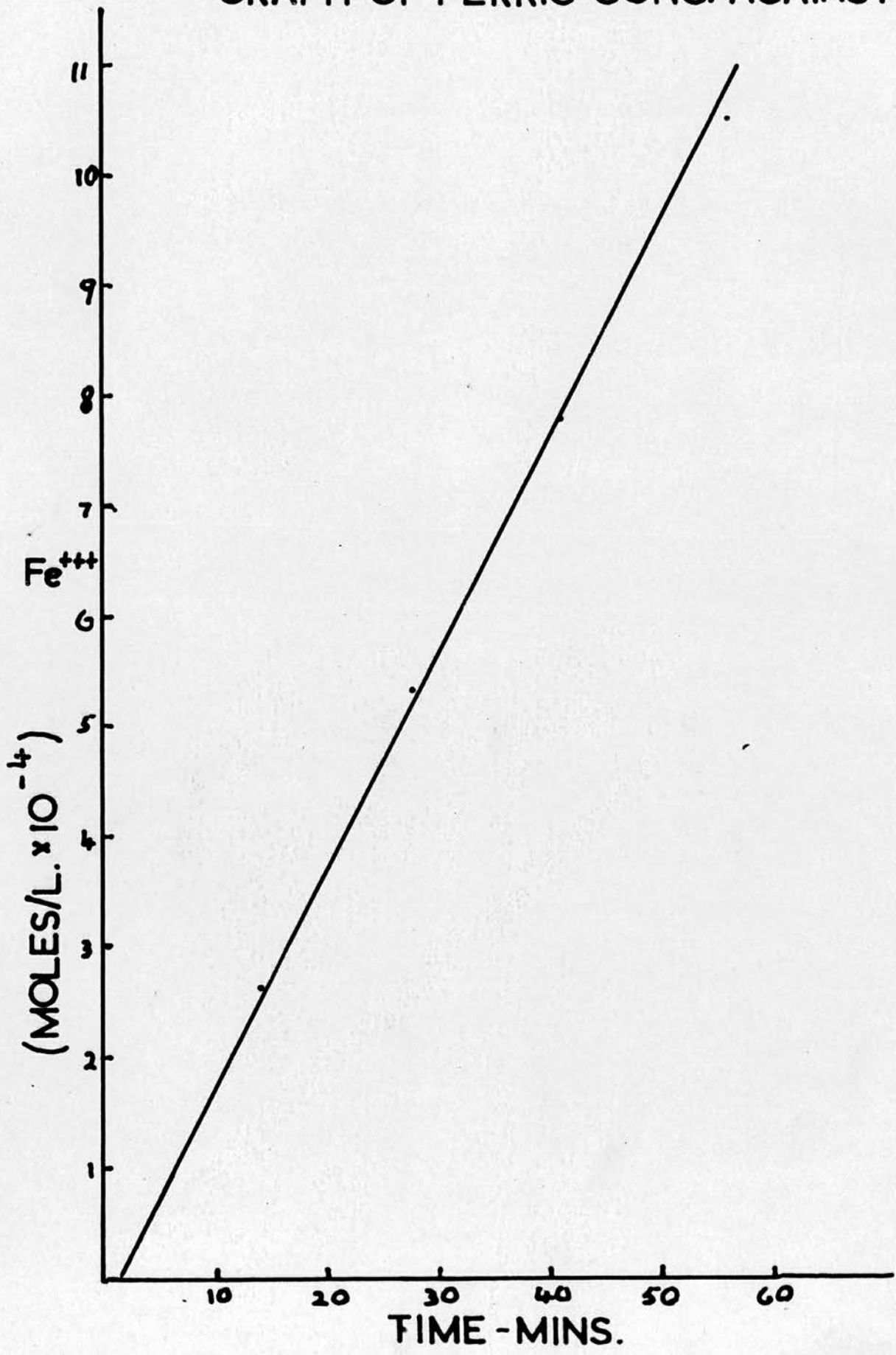
where e = the molar extinction coefficient
 c = concentration in moles/litre
 d = cell thickness (cm.)

A typical determination is as follows:

<u>Time irradiated.</u> (mins)	<u>Transmission</u> Log I_0/I	<u>Ferric concentration.</u> (moles/litre x 10 ⁻⁴)
14.5	0.110	2.60
28.0	0.224	5.29
41.0	0.328	7.75
56.0	0.465	10.99

DIAGRAM V

GRAPH OF FERRIC CONC. AGAINST TIME.



From these figures and using the centre of gravity method, the best gradient is given by 0.20×10^{-4} moles/litre/minute (diagram V) which is the rate of increase of ferric ion. This is equivalent to $0.20 \times 10^{-7} \times 6.025 \times 10^{23}$ atoms of Fe^{++} oxidised per ml. per minute. In all these calculations, the G value for the oxidation of ferrous ion has been taken as 16 and hence the energy absorption in ev can be calculated.

$$\text{Energy absorption} = 7.5 \times 10^{16} \text{ ev/ml/min.}$$

As has already been indicated in the introduction, the energy of gamma radiation produced by Co^{60} is absorbed by matter almost entirely by Compton scattering. Hence the ability of the material being irradiated to absorb energy depends on its electron concentration and a correction must be made for the relative electron density of the material being irradiated relative to the density in the acid Fe^{++} solution used to determine the dose rate.

The energy absorbed per unit volume (E ergs/cm³) is related to the flux of radiation (I ergs/cm²) by the relation⁹⁹:

$$E = I u$$

where u is the absorption coefficient of the material

$$\text{and } u = n_e \cdot e \sigma_a$$

where n_e is the number of electrons per unit volume (i.e. the electron density)

and $e \sigma_a$ is the electronic absorption cross-section for Compton scattering.

As $e\sigma_a$ is a constant for radiation of a given frequency and the geometry of the systems is identical, the ratio of the electron densities gives the ratio of energy absorption of the two systems where the electron density is given by:

$$\frac{n_e}{e\sigma_a} = \frac{d}{M} \times N \times A$$

and d = the density of the material

M = its molecular weight

N = Avogadro's number (6.025×10^{23})

A = the sum of the atomic numbers of the constituent atoms composing a molecule of the material.

This ratio has been calculated for each organic system irradiated, the electronic density for the ferrous solution being obtained by treating it as pure water with a density of 1.023 gm/cm^3 .

The determined energy absorption is then modified by this ratio.

TABLE I

Molar Extinction Coefficient of Ferric Ion in 0.8 N Sul-
phuric Acid at 304 m μ ⁸⁸

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

e = Molar Extinction Coefficient at a temperature of T^oC.

HYDROCARBON/CARBON TETRACHLORIDE SOLUTIONS.

Carbon tetrachloride and solutions of various hydrocarbons from methane to hexadecane in carbon tetrachloride have been irradiated.

In all cases the irradiation vessel was an annular Pyrex glass vessel, which had been browned by previous exposure to radiation. Before each run the vessels were treated with benzene/concentrated sulphuric acid and then washed several times with distilled water before drying in an oven at 100°C for several hours. The carbon tetrachloride was dried for several days over phosphorous pentoxide and then rapidly distilled at atmospheric pressure, the first 10% being rejected.

Purification of the gaseous hydrocarbons varied considerably and is specified in each experiment. The liquid hydrocarbons (Messrs. Light & Co.) were originally dried before use. But latterly the work was repeated using materials purified by the method of Vogel⁹⁷ as follows: The hydrocarbons were shaken with 10% by volume of concentrated sulphuric acid, the process being repeated with fresh acid until it remained almost colourless. The organic layer was then washed with water, 10% sodium carbonate solution and water (twice), dried over phosphorous pentoxide and fractionated twice using a Widmer column. Immediately before use the hydrocarbon was fractionated

using a Vigreux column, and the refractive index compared with the literature value.

SERIES I

(1) Propane/CCl₄

The propane was purified by passing it through two concentrated sulphuric acid bubblers followed by a bubbler of saturated aqueous potassium hydroxide solution and a phosphorous pentoxide tube. The propane was then passed into purified carbon tetrachloride until a saturated solution (at room temperature) was obtained and irradiation was usually of about One hundred and fifty hours duration. The method of analysis was gradually developed in a series of experiments and finally assumed the following form.

(i) Two portions were removed and shaken with standard sodium hydroxide solution, (0.1 N). From the back-titration with standard HCl (0.1 N), the hydrogen chloride in the organic solution was calculated.

(ii) The remainder of the solution was then distilled using a Podbielniack type column with a silver spiral packing. The vapour initially obtained was always unchanged propane which, as it boiled out, entrained carbon tetrachloride, propyl halides and a little chloroform. These were condensed in a cardice/acetone trap and analysed by vapour phase chromatography. Subsequent fractions con-

tained the same constituents but in different and diminishing proportions. Fractionation in this manner was continued until there was no evidence of chloroform, the last component to disappear, in the distilling carbon tetrachloride and the fractions were combined and analysed. By use of standard mixtures, exact reproduction of the chart was obtained and the ratios present in the standard were then assumed to be present in the combined fractions.

In a typical early experiment, the following ratios were obtained. A solution of 200 ml. irradiated for 137.5 hours yielded 0.0067 moles iso-propyl chloride, 0.0012 moles n-propyl chloride, 0.0033 moles chloroform and 0.01 moles HCl that is 5.5 parts iso: 1 part n: 2.7 parts chloroform: 8.3 parts HCl.

In experiments in this department on the halogenation of propane in the vapour phase⁹⁵, using photochemically produced chlorine atoms, the ratio of iso/n was found to be approximately unity over a large range of temperature. It was decided, therefore, to investigate the photochemical chlorination of propane in the liquid phase. Using essentially the techniques described above, a propane saturated solution of carbon tetrachloride, containing some dissolved chlorine, was irradiated for about an hour with ultra violet light. The ratio of n/iso was again found to be approximately unity and no chloroform was detected.

Subsequent work showed that there was still some propy-

lene present in the propane and a more elaborate purification process was adopted. The propane was passed through three bubblers of concentrated sulphuric acid followed by one of saturated aqueous sodium hydroxide solution. To remove residual propylene, it was then passed over a column of coarse wood charcoal on which bromine had been absorbed and then over a clean charcoal column. Finally, the propane was passed through a drying tube of phosphorous pentoxide. The propylene content was now determined chromatographically to be less than 0.1%.

Using this propane, and irradiating the 395 ml solution for 136.5 hours, the yields were as follows:

HCl	0.02 moles	13 parts	G=4.9
iso-propyl chloride	0.011	7	
n-propyl chloride	0.0015	1	
chloroform	0.0026	2	
hexachloroethane	0.017	11	

The hexachloroethane was obtained by careful distillation of the carbon tetrachloride using a Vigreux column and drying and weighing the residue.

It should be observed that the HCl determination is much more reliable than the hexachloroethane. After removal of most of the carbon tetrachloride, the few mls. of solution was cooled to precipitate the hexachloroethane. An optimum weighing requires that the crystals be dried quickly and weighed before an appreciable quantity of

material is lost due to its exceedingly high volatility.

Hence, although this determination is quoted, it should be treated with the reservation that the error may be \pm 10%.

(2) CYCLOpropane/CCl₄

Anaesthetically pure CYCLOpropane containing no propylene was used without further purification. A 435 ml saturated solution was irradiated for 162.5 hours and then analysed by the previous procedure.

Three substances were detected in considerable quantity with volatilities between those of the large quantity of unchanged propane and the chloroform and carbon tetrachloride present. The times of elution were (i) 3.5 mins. (ii) 7, (iii) 11, (iv) 15.5 (v) 27.5 followed by CCl₄ (vi). (i) was very large (unchanged cyclopropane) and (v) was chloroform.

HCl	0.0114 moles	8 parts
Chloroform	0.0014	1
Hexachloroethane	0.0178	12.7

As this complexity was rather unexpected, a similar solution containing some added chlorine and a trace of iodine catalyst was exposed to ultra violet radiation.

The only materials present were a large quantity of unchanged cyclopropane, corresponding to (i) above and a second peak corresponding to (iv). Carbon tetrachloride (vi) was present of course.

No further investigations of this system were made.

(3) n-Hexane/CCl₄

A DSIR Standard Sample of pure n-hexane was obtained. Exactly 4 ml was made up to 395 ml of solution with carbon tetrachloride and irradiated for 185.5 hours.

No volatile material was found in the cardice-acetone trap. The first few fractions contained three minor constituents: (i) 8 mins, (ii) 19 mins. and (iii) 33 mins. Peak (ii) corresponds to unchanged hexane and peak (iii) is chloroform. The first peak was not identified.

Carbon tetrachloride was now fractionated leaving a small residue of amber coloured liquid. This was chilled, the crystalline precipitate filtered off, and the liquid fractionated to yield an oil (0.6 gm: BP = 121°C). This gave one peak only, by chromatography, and was assumed to consist of hexyl chlorides.

(lit. B.P. : 1-chlorohexane, BP = 136°C: 2-chlorohexane, BP = 123°C: 3-chlorohexane = 123°C)

HCl	0.0312 moles	8 parts
CHCl ₃	0.0039	1
hexyl chloride	(0.005)	(1.3)
hexachloroethane	(0.0204)	(5.2)

The figures for hexyl chloride and hexachloroethane should be considered as minimal values only.

(4) Methane/CCl₄

395 mls of a saturated solution of methane in carbon tetrachloride was irradiated 113.5 hours. The products were identified chromatographically as methyl chloride ethyl chloride and chloroform.

HCl	0.0143 moles	16-18 parts
Ethyl chloride	0.0009	1
methyl chloride	of the same order as ethyl chloride	
chloroform	0.0008	1
hexachloroethane	0.0074	8-9

(5) n-Decane/CCl₄

A solution (435 ml) of n-decane (4 ml) in CCl₄ was irradiated for 114 hours. Only the HCl was determined (0.0238 moles).

The dose rate for the methane, propane and hexane experiments was 4.86×10^{16} ev/ml/minute, and the rate for the decane and cyclopropane experiments was 4.80 ev/ml/minute. The G values for HCl production are listed.

If it is assumed that the amount of carbon tetrachloride reacted is given by the total of hexachloroethane and chloroform, then the second column of G values holds. The value for n-hexane is a minimum only, and should not be given the same weight as the others.

	<u>G(HCl)</u>	<u>G(-CCl₄)</u>
Methane	4.9	5.3
Propane	5.7	10.4
n-Hexane	6.5	(9.4)
n-Decane	7.4	-
CYCLOpropane	2.5	8.1

SERIES II

(1) Pure Carbon Tetrachloride

With similar procedure, pure carbon tetrachloride (48 ml) was irradiated (65 hours) at a dose rate of 7.53×10^{16} ev/ml/min. The chlorine produced was determined by abstracting a sample, adding it to excess of a 5% potassium iodide solution and titrating the liberated iodine with standard potassium thiosulphate solution and starch solution as indicator. The residual solution was then fractionated using an 8" Vigreux column and the residual solid crystalline material dried and weighed.

The total yield of chlorine and hexachloroethane was 0.000244 moles and 0.000248 moles respectively. Taking the chlorine as the more accurate, the total carbon tetrachloride reacted is 0.000488 moles. A mean of two determinations (1.62, 1.55) gave $G(-CCl_4) = 1.6$ up to total doses of 3×10^{20} ev/ml.

(2) Carbon tetrachloride/n-Octane, n-Decane, n-Tetradecane.

These solutions were prepared by making 0.5 ml exactly of hydrocarbon up to 48 ml. of solution with carbon tetrachloride, and irradiating for 65.5 hours. (Dose rate = 8.0×10^{16} ev/ml/min. to a maximum dose of 3.2×10^{20} ev/ml)

	<u>Time irradiated</u> <u>(hours)</u>	<u>HCl Produced</u> <u>(moles)</u>	<u>G(HCl)</u>
n-Octane	65.5	0.00188	5.6
n-Decane	65.6	0.00133	3.9
n-tetradecane	65.4	0.00132	3.9

Before and after the purification of the n-octane it yielded the same high value for HCl. Although the physical constants of these hydrocarbons all compared favourably with the literature values, it was noticed that the octane had a very sweet smell, unlike the others which were without odour. For this reason the sample of octane was adjudged to have some impurity present, to cause the abnormally high values.

It was hoped to measure the hexachloroethane concentration by making the residual material after removal of CCl_4 up to a known volume with CCl_4 and determining the refractive index of the solution. Comparison with a series of standards would have allowed considerable accuracy. Due, however, to the presence of chlorinated hydrocarbons and pure hydrocarbon this was found to be impracticable and hexachloroethane was not determined.

This constancy of HCl production led to speculation as to the critical concentration at which the HCl production would begin to decrease. A series of experiments were therefore carried out to test the effect of concentration on HCl yield.

The dose rate was rather higher than that used in the experiments in series II by a factor of about 2 but cannot be given exactly as the magnitude of dose in relation to the capacity of the ferrous/ferric system had been overlooked and dose rates were being obtained from oxygen depleted systems. As the increase in dose rate is relatively small, it is felt that G values can be assumed to be approximately the same, and that Series II and series III are directly comparable.

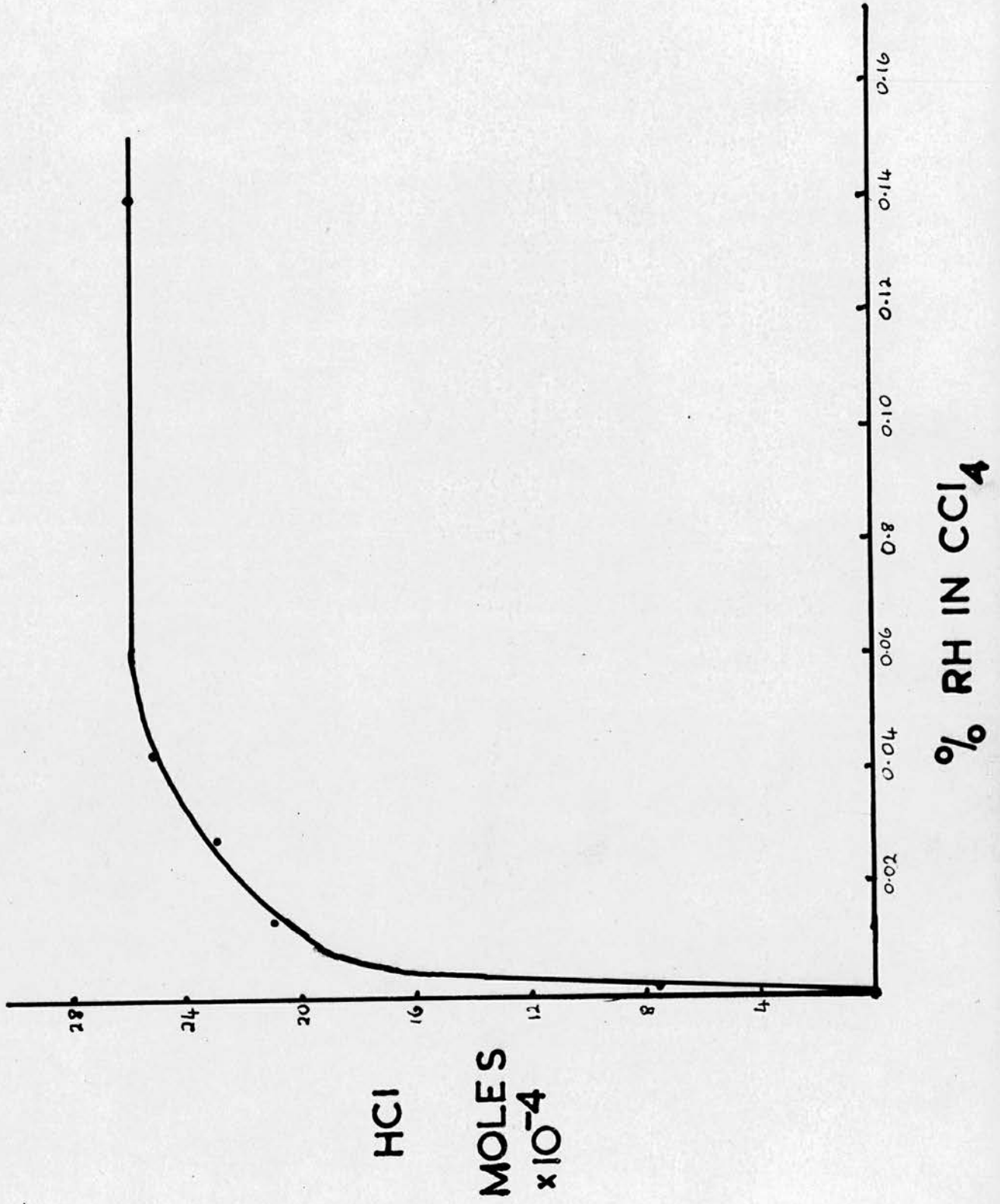
SERIES III

Using an annular 55 ml vessel, carbon tetrachloride solutions of n-hexadecane ranging from 0.014% to 6.5% by weight were examined for HCl content. (Irradiation time = 40 hours.)

As the end approximately 1% solutions of three other hydrocarbons were irradiated to confirm the consistency of HCl production at the higher concentrations.

<u>HEXADECANE</u> <u>(Wt. in gms)</u>	<u>HYDROCARBON</u> <u>(% in soln.)</u>	<u>HCl yield.</u> <u>(Moles)</u>
0.0125	0.014	0.0021
0.0250	0.028	0.0023
0.0375	0.043	0.0025
0.1252	0.14	0.0026
0.2500	0.29	0.0026
0.5000	0.58	0.0026
0.9996	1.2	0.0026
2.5001	3.0	0.0026
5.0007	6.5	0.0026
<hr/>		
n-dodecane	0.58	0.0026
n-decane	0.58	0.0025
CYCLOpropane	0.15	0.0026

DIAGRAM VI
HCl PRODUCTION



DISCUSSION.

The solutions of the more volatile hydrocarbons in carbon tetrachloride will be discussed first.

SERIES I

(1) Propane/Carbon Tetrachloride.

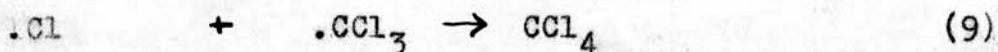
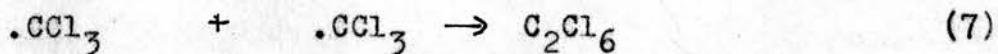
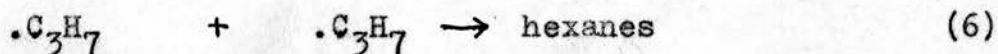
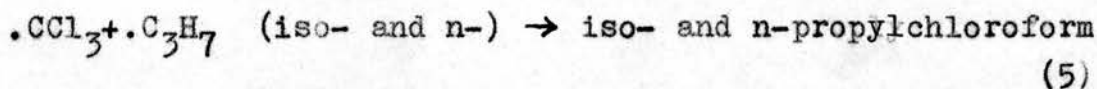
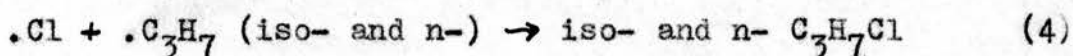
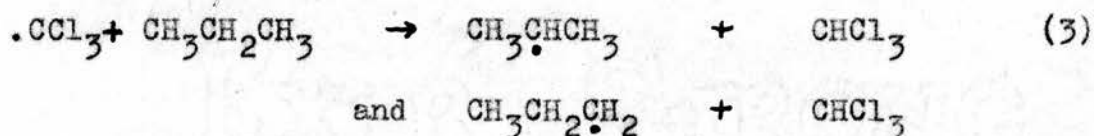
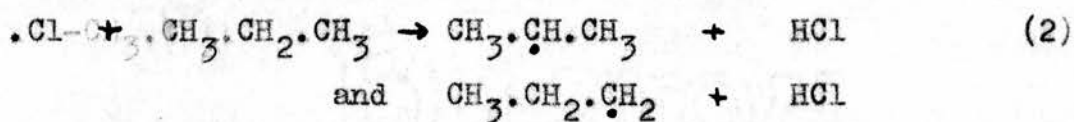
The determined products from the system are as follows:

HCl	13	molecular proportions.	$G = 4.9$
iso-propyl chloride	7		
n-propyl chloride	1		
Chloroform	2		
hexachloroethane	11		

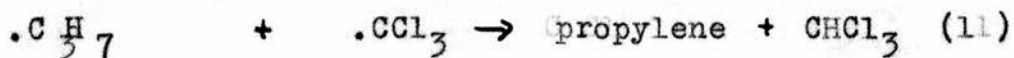
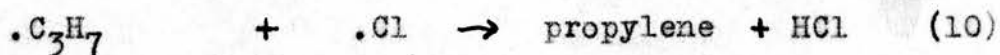
On the basis of the combined hexachloroethane and chloroform production, 24 molecular proportions of carbon tetrachloride are involved. Of the complementary chlorine atoms (24), some are accounted for as propyl chlorides (8) and the majority as hydrogen chloride (13). The residue (3) is more likely to arise from over estimation of the hexachloroethane than from under estimation of the propyl halides. (The HCl determination is the most reliable). The 15 hydrogen atoms forming the HCl and chloroform must have been abstracted from the hydrocarbon, but only 8 proportions of propyl radical are evident. This leaves 7 propyl radicals to be accounted for and there are several

possible reactions.

Assuming that the initial reaction is the fraction of the carbon tetrachloride molecule as previously postulated, we can develop the following reaction mechanism.



Termination by disproportionation is also feasible and must be considered:





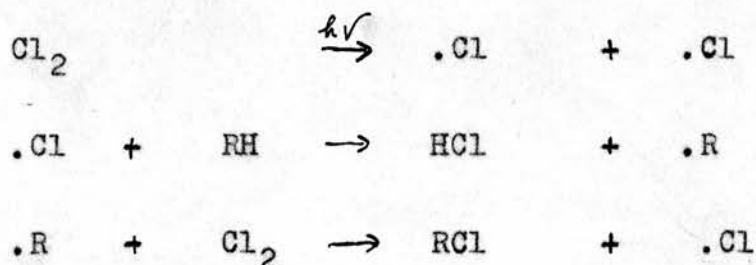
Also hydrocarbon radicals may be abstracting chlorine from the carbon tetrachloride.



Although the C-H bond in methylene group is slightly weaker than the same bond in methyl group, reaction (2), which is identical with the photochemical hydrogen abstraction by $\cdot\text{Cl}$, probably produces about equal amount of n- and iso-propyl radicals. However, the generally presumed low reactivity of the trichloromethyl radical compared with the others in the system makes it probable that reaction (3) if it occurs, will yield mainly iso-propyl radical. Reaction (4) is the source of the halides rather than (13) which would require appreciable activation energy and as trichloropropane has not been found, (5) is negligible. The indications are that the $\cdot\text{CCl}_3$ radicals are found almost entirely in the dimerisation (7). Molecular chlorine has never been found in any of these CCl_4 solutions and any chlorine which dimerises would certainly react with propyl radicals with great rapidity as this is the second stage in the photochemical reaction. The loss of propyl radicals may occur by (6) or by one of the disproportionation reactions. Szwarc⁹⁴ observes that no definite statement can be made about the relative rate of disproportionation of hydrocarbon radicals as compared with

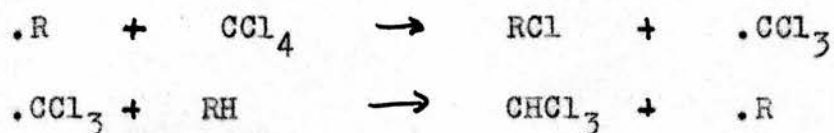
dimerisation, although disproportionation seems much more likely from general considerations. No hexanes have been detected in this system and the loss of propyl radicals is probably due to one of the disproportionation reactions such as (10) and (12), resulting in the formation of propylene.

Apart from the loss of propyl radicals the balance of products is reasonable. The feature in which these results differ from normal hydrocarbon chlorinations is in the ratio of n- to iso- propyl chloride produced. Knox⁹⁵ found the iso- and n- propyl chlorides in roughly equal quantities in the gas phase chlorination of propane and in the present series of experiments some liquid phase chlorinations using chlorine atoms were investigated. A solution of chlorine and propane in carbon tetrachloride was irradiated with ultra violet light for an hour. In addition to copious HCl, the chlorides were present in large quantity and in approximately equal amounts indicating that the solvent had no great effect. The photo mechanism is as follows:



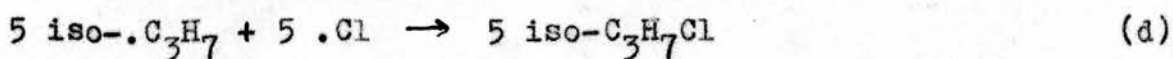
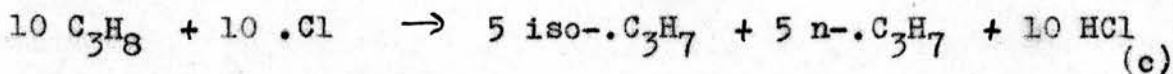
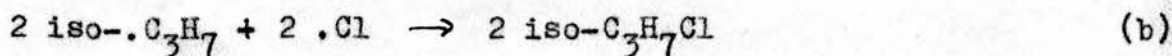
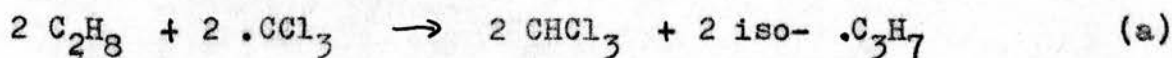
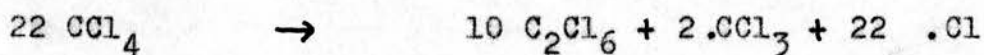
The fact that no chloroform is produced discounts any suggestion that it is a side product of this chain reaction in

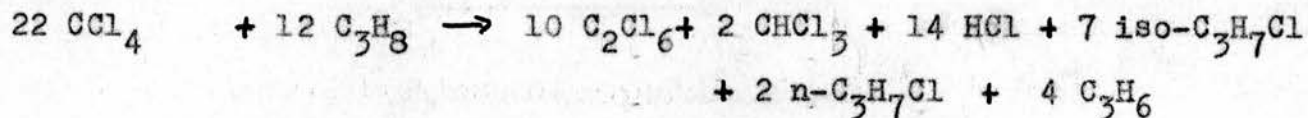
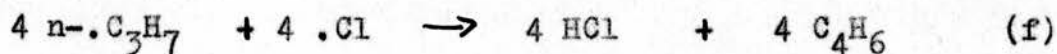
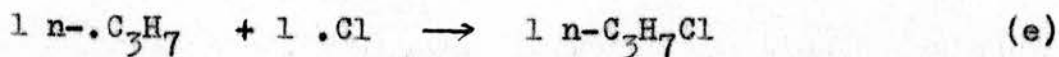
the following way:



Also, the low G value of the gamma irradiated system excludes the possibility of a chain reaction. By comparison, the addition of chlorine to aromatic hydrocarbons containing dissolved chlorine under the influence of gamma radiation⁹⁶ results in chain reactions with G values of thousands.

Summarising, we can write out a tentative reaction mechanism as follows by consideration of the relative yields found.





It must be remembered that many other processes are possible. Considering the system on an energetic basis, a reaction with a G value of unity implies that one mole of material has been reacted for an energy input of 2300 Kilocalories. Assuming the $\text{Cl}_3\text{C-Cl}$ bond dissociation energy to be 70-80 Kcals/mole, 29-33 of such bonds may be broken leading to a G(Rad) of 58 to 66. This allows for no loss of energy in other processes such as molecular excitation, heat production and so forth and can, therefore, be taken only as a theoretical maximum for radical production. The importance of considering the possible participation of excited molecules is obvious. Excited hydrocarbon molecules would be expected to dissociate least in the terminal positions⁹¹, and intermolecular energy transfer could conceivably make this an important process.

The earlier experiments with this system containing propylene in appreciable quantity indicate that the propylene may be playing an important part in the reaction but little more can advantageously be said at the moment in the light of the present information.

(4) Methane/carbon tetrachloride.

The products are listed:

HCl	16-18 parts
Ethyl chloride	1
Methyl chloride	1 (approx).
Chloroform	1
Hexachloroethane	8-9

As expected, this reaction appears to be much more simple than the previous one. The products balance reasonably well except once more, for the big loss of hydrocarbon radicals. The presence of a little ethane in the methane was unfortunate as a likely process is $2 \cdot \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$ eventually yielding competitive quantities. Even so the considerable production of ethyl chloride reflects the lower bond dissociation energy of the C-H bond in ethane.

Technically this was the most difficult experiment due to the high volatility of both methyl chloride and methane. Isotope dilution is suggested as a suitable means of determining the true methyl chloride concentration.

(2), (3) and (5)

The hexane irradiation shows the same general features as the others but the hexyl chloride and hexachloroethane determinations are to be taken as minimal values only.

A comparison of the cyclopropane irradiations with both ultra violet light and gamma radiation again emphasises the fundamental difference of the two processes. Considerable chlorination of the hydrocarbon occurs as in the propane runs and it is suggested that the reason for the complexity of products from the radiolysis is the relatively longer life of the cyclopropyl radical which has opportunity to rearrange. Three propylene chlorides are possible but it was found that allyl chloride was not present, leaving two possibilities for the unidentified products.

The distinction between the often confused concepts of "reactivity" and "stability" as applied to free radicals is forcibly emphasised here.

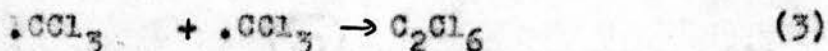
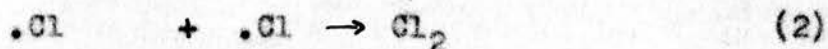
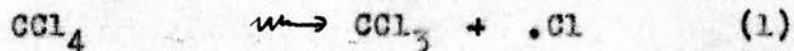
In all these experiments there was a large excess of unreacted hydrocarbon after the irradiation and therefore the HCl yields may be a measure of the rates of attack of CCl_4 fragments on the hydrocarbon. Thus a rise in HCl formation from methane to propane is to be expected and the high HCl value from decane is unexpected.

In none of these systems is there any evidence of trichloromethylation of the hydrocarbon.

SERIES II

(1) Carbon Tetrachloride.

The production of hexachloroethane and chlorine from carbon tetrachloride has been observed by several workers using X-rays or radium radiation⁸⁹ and both of these products have been obtained in the present work. A simple free radical mechanism immediately suggests itself.



Magat and his co-workers⁷ investigated the radiolysis of carbon tetrachloride using DPPH and suggested a G value of 70 for radical production with some reservations. Recently, however, Chapiro⁹⁰ has placed this value at 20. In our determinations the G value for the removal of carbon tetrachloride as chlorine and hexachloroethane is about 1.6. To reconcile these two values a reverse reaction must be postulated:



If we consider a molecule AB which is ruptured to form two free radicals and assuming that these free radicals can diffuse away from one another through the surrounding medium, then these radicals A and B might be expected to recombine on a statistical basis to form stable molecules AA, BB and AB. This also assumes that there is no preferential combination on energetic or steric grounds. Thus the measurable quantities AA and BB will indicate the production of AB. Considering the results for carbon tetrachloride on this basis, we would expect that $G(-CCl_4) = 3.2$ and $G(\text{Rad}) = 6.4$. This simple theory fails conspicuously to reconcile the two values for $G(\text{Rad})$.

There are two other considerations which we have ignored. Firstly: Magat suggests that his results can be explained only by postulating processes other than the above, resulting in the production of fragments such as CCl_2^+ , CCl_3^+ ions and CCl radicals. Thus the issue is considerably complicated. If these fragments are produced, the products measured from the irradiation of pure carbon tetrachloride may still be measures of the radical production as indicated above, but equally they may be measures of which fragments can ultimately react with one another to form these products. It is important to consider the significance of the DPPH experiment. The use of DPPH in such work depends on two premises: (i) that DPPH will trap all the radicals produced and that the only fragments which are trapped are radicals, (ii) that the DPPH is assumed

to be stable to the radiation doses it receives and this is debatable⁹².

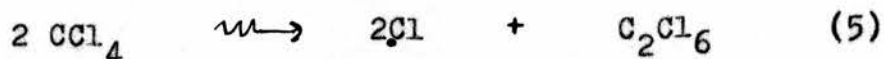
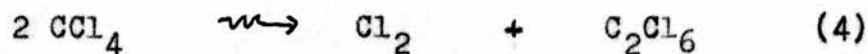
Secondly: The dose rates employed by Magat in his experiments are of the order of 1.7 Roentgen/per minute. In our work the dose rate was about 1390 R/min. The possible significance of the difference is very great and will be discussed again.

Very recently Schulte⁹³ has published a paper dealing with the gamma radiation induced exchange of labelled chlorine with carbon tetrachloride and comes to some very interesting conclusions. His dose rates are over a range comparable to ours.

<u>Dose Rate†</u> <u>ev/ml/min x 10¹⁶</u>	<u>G_{Cl₂} exchange</u>	<u>G_{Cl₂} formation</u>
0.197	3.91	0.74
0.530	3.68	0.80
2.08	3.25	0.84
11.1	3.32	0.84

† Assuming G (Fe⁺⁺⁺) = 15.8

Schulte interprets his results as indicating the simultaneous occurrence of two independent processes, the first a free radical process such as we have already suggested, and the second a bimolecular process:



He suggests that $G(-\text{CCl}_4) = 3.5 \pm 0.35$ for radical production by the first mechanism, that is $G(\text{Rad}) = 7$; and the bimolecular mechanism gives $G(-\text{CCl}_4) = 1.6$

Schulte's interpretation of his results is open to query, but his experimental determination of the G value for Cl_2 production from pure carbon tetrachloride is in good agreement with ours.

The Effect of Solutes in CCl_4 (series II and III)

The irradiation of approximately 1% solutions of n-decane and n-tetradecane in carbon tetrachloride under exactly the same conditions yielded HCl such that $G(\text{HCl}) = 3.9$. If we assume that for each hydrogen abstracted a chlorine is substituted, a dubious procedure in view of the results obtained from the experiments with gaseous hydrocarbons, we can say nevertheless that the MAXIMUM removal of CCl_4 as product is 7.8 although probably somewhat less. Obviously the postulated reverse reaction for pure CCl_4

$$\cdot\text{Cl} + \cdot\text{CCl}_3 \rightarrow \text{CCl}_4$$

occurs to a much greater extent than our simple reaction mechanism suggests. If we can assume that the solute acts simply as a radical trap it follows that the irradiation of solutions of n-hexadecane in varying concentrations should result in constant HCl production and this has been found. In 1930 Cronheim and Gunther⁸⁹ irradiated solutions of n-octane in carbon tetrachloride at four different concentrations, the lowest being 0.4% by weight and the highest 44% by weight,

using hard X-rays (0.8\AA). They claim a higher yield of HCl from the least concentrated solution but inspection of their figures shown the variations to be of the same order as their experimental error. Schulte has found that the rate of exchange of radioactive chlorine with carbon tetrachloride is independent of chlorine concentration over similar concentrations. This independence of solute concentration appears to be a general feature and it was of interest to find at what point the HCl yield started to drop. This occurs under our conditions when the n-hexadecane concentration drops below about 0.06% by weight (or about 0.04% in moles.) Thus the ratio of hydrocarbon to carbon tetrachloride molecules is about 1/2500 and about 11.7 molecules of HCl result.

Ehrlich¹⁰⁰ has irradiated solutions of acenaphthylene in carbon tetrachloride under the same conditions, following the decrease in hydrocarbon concentration by measuring the absorption of the solution at 324 mu. In preliminary experiments a linear rate of removal followed by a decreasing rate has been observed and this change occurs when the molar percentage of hydrocarbon is about 0.038%. This remarkable concordance with our value is most easily explained by dismissing it as fortuitous.

Experimentally, our results indicate that under the conditions of irradiation the hexadecane or its initial products are unable to contribute further hydrogen atoms to the attacking

radicals at the initially fast rate. To obtain the critical concentration at which there was just sufficient hydrocarbon present to trap the chlorine radicals being slowly produced from the HCl, the concentrations and irradiation times (that is, total doses) would need to be varied and results extrapolated to zero duration of irradiation. Acenaphthylene would be expected to remove relatively far fewer radicals, and the critical concentration should be much higher than when an aliphatic hydrocarbon is used. Very many different factors are involved in these two systems and much more investigation of the variables is required before definite conclusions can be drawn.

It is of interest to note that Dainton¹⁰¹ has deduced an expression for aqueous solutions showing that if the solute concentration decreases below a certain point (dependent on the reactivity of the solute) then the ionic yield will decrease as the concentration decreases and the dose rate increases. Above this critical concentration, the ionic yield will be independent of both concentration and dose rate. It may be that this will also apply to carbon tetrachloride systems although the result of dose rate variation has not been investigated.

GENERAL DISCUSSION

So far, we have tacitly assumed that radiation interaction results in a homogenous medium in which the reactive particles are uniformly dispersed. This is very far from the truth and the use of overall "G values" has been commented on by Dainton⁶. The chemist can measure the products of a system by some method which indicates only the mean value of all the variations inherent to the system. For this reason, care must be taken to reduce all the variables in chemical systems to a minimum and those which the chemist is most likely to overlook due to an incomplete acquaintance with the physical approach to the subject are the quality and quantity of radiation used and the geometry of the system.

Four separate factors must be distinguished: Firstly, the type of ionising radiation is critical. An example occurs in this work, where the yield of polymer from trichloroethylene per unit of energy absorbed is much greater using gamma radiation than using alpha particles. Comparing an alpha particle and a secondary electron of the same order of energy, the alpha particle will leave a short track with a very high density of shattered molecules with the result that there will be a high degree of instantaneous recombination. The secondary electron resulting from gamma irradiation will leave a long and relatively sparsely ionised track and, although some recombination

to form the parent species must be expected, it will occur to a much lesser degree and the fragments will diffuse away to react with other entities thus accounting for the higher energy utilisation.

The other three factors are closely interconnected: radiation flux, radiation dose rate and the total dose. The last two are the quantities which are usually considered. Many reactions are dependent on dose rate, the yield of products decreasing as the dose rate is increased. This can be explained as follows. If the dose rate is very low, a medium can be considered as stable except along a few isolated "columns" where reactive fragments will be clustered. Many of these fragments are at liberty to diffuse away to other parts of the system and react with stable molecules or other reactive particles. As the dose rate increases, however, a situation will be reached where the columns of reactive species will be so close to one another that the medium is effectively homogenous with respect to these particles and their stability, reactivity and ability to diffuse will be of less account. Thus reactions at low dose rates will depend qualitatively and quantitatively on the character of these fragments to a greater extent than when high dose rates are used. Conditions at high dose rates will favour recombination to form the initial species and drops in total product yields must be expected. Hence the danger of

comparing Chapiro's $G(\text{Rad})$ of 20 for carbon tetrachloride at dose rates of 1.7 R/minute with our findings at over 1000 R/minute.

The total dose, on the other hand, is significant only when the concentration of products in the system becomes so great that secondary reactions set in to an appreciable extent. This is not a very difficult problem and is by no means a new concept to chemists. The permissible concentration may be quite high as in the polymerisation of the dichloroethylenes where a concentration of polymer approaching 12% does not appear to alter the rate of polymerisation, but more reactive products would obviously have to be restricted to lower concentrations.

The quantity which probably is misunderstood to some extent is the total flux or intensity of radiation. This is a measure of the radiation incident on an area of surface and not in a volume of material as is the dose rate and the concept is perhaps insignificant using the conventional radiation systems often mentioned in the literature. These consist mainly of series of ampoules placed at fixed positions with respect to the radioactive source and the dose rate can be altered by varying the distance from the source. Alternatively, the ampoules are placed centrally inside a cylindrical source and this method is often used.

In our work, however, cylindrical annular vessels have normally been positioned so as to enclose the source.

Theoretically, the ideal system is that in which a film of liquid is subjected over its whole area to a uniform flux leading to a completely uniform dose rate. The film must not be too thin (i.e. thinner than about 2 mm which is approximately the path length in water of the secondary electrons produced by gamma radiation) or yields will drop due to the loss of secondary electrons. In series II and III of the hydrocarbon/carbon tetrachloride irradiations the film thickness is about 3 mm and the flux on successive elemental cylindrical film areas is not very divergent. When a vessel with a liquid annulus of perhaps 3 cm thickness is used (Series I), it must be remembered that the flux of radiation from the central rod source will fall off by the combined influences of two effects. Firstly, the flux from the source will fall off inversely as the square of the distance (approximately) and secondly, there is a loss of radiation by interaction with the medium. Realising this, the explanation for the much higher G values for HCl production in Series I may be forthcoming. The dose rate as experimentally determined is really a mean of widely differing dose rates at various points in the solution, and these reactions may have a much higher G value at low dose rates. Alternatively the loss of secondary electrons in Series II and III may have been appreciable, but this seems a less likely explanation.

The energy loss when gamma radiation traverses one

centimetre of water is only about 6% and correspondingly more in the same thickness of material of higher electron density and in order to utilise the energy source to the utmost, thick layers of liquid should be used. Thus the two factors are incompatible. Either an experiment is designed to yield a large amount of product for investigation of its chemical nature, in which case a large vessel is used to obtain the maximum product in the shortest time, regardless of the large variations in flux and dose rate: or, the experiment is intended to furnish G values for comparisons with other work done in other laboratories, when the thin vessel should be used.

Surveying the work of this thesis, the question is not important in the polymerisation of the chloroethylenes, but it does arise in the carbon tetrachloride work. The results in Series II and III are comparable, because although the dose rates in III were about double those of Series II, a change of this order is not likely to be critical. (See Schultes work quoted earlier for a comparable range). In Series I, the liquids were subjected to an exceedingly variable dose rate so that the G values are not comparable to the other CCl_4 systems, and whether different systems in Series I can be safely compared with one another is to be queried. It would be interesting to see whether the same ratios of products were obtained if a constant radiation flux were used.

Most of our knowledge of radicals is derived from studies of simple reactions occurring in the gas phase. This is

natural because reactions in the gas phase can be related to the frequency of collision of the reacting particle and the physical concepts involved are well understood. The behaviour of these same radicals in a liquid is certain to be very different. Not only will new factors be introduced but the existing factors will alter in relative importance. Exciting molecules will be de-energised much more rapidly. If a medium is polar, the normal mode of reaction may be completely altered due to redistribution of charge within the fragment. Differing rates of diffusion may result in two reactions having very different rates in a liquid medium although the rates in the gas phase are similar.

The further complexity introduced by the simultaneous production of ions, radicals and excited molecules makes radiolysis studies much more ambiguous and the danger of extrapolating information obtained in the gas phase cannot be overemphasised. The last novel feature to be mentioned here is the distinction between apparent radical yield (assuming the products measured to be derived from radicals) and the true radical yield as measured when a radical trap is present. This feature is well demonstrated by the carbon tetrachloride and carbon tetrachloride solution experiments where the hydrocarbon is acting to a great extent as a radical trap. In an ionisation track, the fragments A and B of a molecule AB will, in general, react by one of three processes; diffusion into the vicinal medium where reaction to form AA, AB and BB may occur (this has already been discussed); attack

of a stable molecule (as in the polymerisations); and immediate recombination with its fellow fragment. This last effect, the Franck-Rabinowitsch cage effect ⁹⁸, results when the fragments have insufficient kinetic energy to penetrate the surrounding "cage" of stable molecules and hence are forced to recombine. The addition of solutes would be expected to reduce this effect when sufficiently high concentrations were reached for solute molecules to form part of the cage, and higher yields of product would result. The importance of this effect is probably not very great and would probably not be readily observed.

To summarise, the work presented in this thesis is incomplete (as any such work must needs be) but an approach has been made and the advantages, limitations and possibilities of the methods used have been discussed. The use of radiation as an energy source promises to be of great application and even more important, it sets many new physical problems concerning the fundamental properties of matter, the satisfactory elucidation of which will contribute much to our understanding of natural processes and the ultimate nature of energy.

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