REACTIONS OF CHLORINE ATOMS AND CHLORINATED ALKYL RADICALS

by

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INTRODUCTION

A considerable amount of work has been done on the study of free radical reactions since Gomberg, at the turn of this century, isolated the triphenylmethyl radical.

These studies did include chlorine atom reactions and yielded among other information in 1918 the now famous "Nernst chain mechanism" which explained the photochemical production of HCl from molecular chlorine and hydrogen. Up to the last decade studies concerned with the reactivity of Cl atoms followed the path cleared by Nernst and dealt mainly with the photolysis of molecular chlorine in the presence of various substrates. These investigations yielded considerable information regarding chain reactions in general and regarding Cl atom induced chains in particular. It is, however, extremely difficult to obtain accurate and detailed information from investigations in which long chains are produced. It is, after all, difficult to stop such reactions at a stage where little conversion has taken place and, furthermore, the effect of trace amounts of impurities is magnified in long chain systems where the reactants are rapidly depleted.

Chain reactions, in systems containing molecular chlorine and organic chemicals, are caused by the fact that the C-Cl bond is much stronger than the Cl-Cl bond.

Thus, a R radical, produced by the reaction $Cl + RH \longrightarrow R + HCl$, will react with molecular chlorine according to the reaction $R + Cl_2 \longrightarrow RCl + Cl$, starting a chain reaction by regeneration of the Cl atom.

It should be possible to avoid chain reactions by using sources of Cl atoms other than molecular chlorine. In this study Cl atoms were produced by photolysis of CCl_4, $CHCl_3$ and CH_2Cl_2. In particular a detailed study of the photolysis, at room temperature, of CCl_4 in the presence of C_2H_5Cl has been made. The absence of chain reactions has been confirmed and a considerable amount of information has been gained not only regarding the reactivity of Cl atoms but also regarding the reactivity of chlorine substituted methyl and ethyl radicals.

HISTORICAL

This study deals with free radical reactions and it seems, therefore, appropriate to review briefly the history and significance of free radical reactions. The term "radical" or "free radical" is used when referring to a natural atom or group of atoms containing an unpaired electron.

The first free radical, recognized as such, was synthesized by Gomberg in 1900 (1). In attempting to prepare hexaphenylethane, he treated triphenylmethyl chloride with silver in benzene solution and free triphenylmethyl radicals were produced.

In 1929, Paneth and Hofeditz (2) demonstrated the existence of free alkyl radicals. They used a modified method by which hydrogen atoms had been previously studied (3). A stream of inert gas saturated with tetramethyllead vapor was allowed to flow through a glass tube. The tube was heated to a sufficient temperature to cause the decomposition of the tetramethyllead which was visible by the deposit of a lead mirror on the wall of the tube. The gaseous products from the decomposition were passed further down the tube to a previousely deposited metallic mirror which was observed to gradually disappear. The products formed from the reaction of the radicals with the mirrors were identified as metallic alkyls.

During the early years of 1930 Rice and his co-workers (4) showed how the results obtained in the study of the thermal decompositions of CH_3CHO and other hydrocarbons could be explained in terms of chain mechanisms involving free radicals.

The investigation of the additions of hydrogen bromide to allyl bromide by Kharasch, Engelmann and Mayo in 1937 (5) have proved the "anti-Markownikow" reaction also involving radicals. They explained the formation of 1,3-dibromopropane in terms of the scheme:

$$Br + CH_2{=}CHCH_2Br \longrightarrow BrCH_2CHCH_2Br$$

$$BrCH_2CHCH_2Br + HBr \longrightarrow BrCH_2CH_2CH_2Br$$

As a direct result of the quantum theory, and in particular the photochemical laws, radiant energy (photolysis or radiolysis) became a popular method of initiating free radical reactions. Stark in 1908 and Einstein in 1912 (6) applied the concept of the quantum of energy to photochemical reactions of molecules. They stated that a quantum of radiation, absorbed by a molecule, activates this molecule into an excited state. This excited molecule may then decompose to give two free radicals.

Once a molecule has become photoactivated or excited by the absorption of a photon it can lose the energy in several ways. In addition to decomposition

into free radicals it may decompose via a molecular elimination such as (7)

$$CH_3CH_2CH_3^* \longrightarrow CH_3CH{=}CH_2 + H_2$$

or it can lose some of its excess energy by a collisional deactivation

$$CH_3CH_2CH_3^* + M \longrightarrow CH_3CH_2CH_3 + M$$

where M may be some third body species present in the system or the unactivated molecule itself. The excited molecule may also lose its energy by emission of radiation in the form of fluorescence or phosphorescence.

Besides direct excitation by light, photosensitized reactions for producing free radicals are generally used. A molecules M absorbs a photon of energy and then transfers all or part of this energy to a molecule A:B by collision. If the energy transferred is large enough the excited molecule, $A{:}B^*$, may decompose to give the radicals A and B . The first evidence for chemical quenching of photo-excited metal atoms was that of Cario and Franck (8) in 1922. They illuminated a gaseous mixture of hydrogen and mercury with 2537 A resonance radiation and detected "active hydrogen" capable of reducing metallic oxides. The formation of hydrogen atoms was subsequently verified by thermal conductivity measurements. The results of Cario and Franck are explained by the processes

$$Hg(^1S_o) + h\nu(2537A) \longrightarrow Hg(^3P_1)$$

$$Hg(^3P_1) + H_2 \longrightarrow Hg(^1S_o) + 2H(^2S_{\frac{1}{2}})$$

It is well known today (9) that the energy transfer from the excited mercury to the substrate molecule takes place through the formation of Hg-substrate complex intermediate.

The study of free radicals and their reactions has increased considerably since the end of the Second World War. The tremendous improvement of analytical instrumentation has made the kinetic studies on free radical reactions, expecially in gas phase, not only more convenient but also more precise and meaningful. Much has been done with techniques such as: flash photolysis, where radicals in large concentrations are produced; mass spectrometry for the detection and mass determination of radicals as well as the products formed by radicals; gas chromatography, a most valuable tool for the detection and identification of trace amounts of products; electron spin resonance for the detection and identification of radicals trapped in solid or viscous media or in their natural state.

FREE RADICAL REACTIONS

The kinetic studies on free radical reactions have

been formulated largely in terms of the collision theory (10). The specific rate constant, k, for the free radical reaction, obeys the familiar Arrhenius relation: $k=Ae^{-E^*/RT}$. In the collision theory the pre-exponenial factor, A, is factored into a steric factor, P, and the collision frequency, Z, The Arrhenius relation then becomes: $k=PZe^{-E^*/RT}$. The value of Z for bimolecular collisions is usually in the range from 10^{-10} to 10^{-9} molecules $^{-1}$cc.sec.$^{-1}$ or 10^{14} to 10^{15} mole $^{-1}$cc.sec.$^{-1}$. In the collision theory, the frequency factor, Z, gives the number of collisions occurring per sec. in one cc. at a temperature T, between two spherical particles. The steric factor P was introduced to account for the fact that the number of effective collisions (e.g. collision resulting in a reaction) is always smaller than calculated from considerations based upon the activation energy E and the actual collision number Z. The steric factor P varies from about 0.1 to about 10^{-4} depending upon the type of reaction taking place.

The presence of unpaired electrons in free radicals is of the same overriding importance in determining their chemical as well as their physical properties. All radical reactions occur in such a way as to reduce the instability associated with the unpaired electrons. Free radicals may undergo serveral different types of reactions. The most important are: recombination and dis-

proportionation, abstraction, addition to an unsaturated compound, and decomposition reactions.

Recombination and disproportionation: Both recombination and disproportionation reactions involve two free radicals. In a recombination reaction two radicals combine to form a stable compound. This reaction may be considered as the reverse of the decomposition of a normal molecule. The disproportionation reaction, on the other hand, is a reaction between two free radicals to form two stable compounds having a different degree of saturation. When two ethyl radicals react they may either combine to form butane or disproportionate to form an equimolar mixture of ethane and ethylene.

$$CH_3CH_2 + CH_3CH_2 \longrightarrow CH_3CH_2CH_2CH_3 \qquad \text{(recomb.)}$$

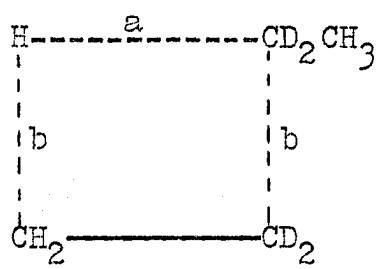
$$CH_3CH_2 + CH_3CH_2 \longrightarrow CH_3CH_3 + CH_2{=}CH_2 \qquad \text{(disp.)}$$

The activation energies of disproportionation reactions are generally slightly larger than those for combination reactions which usually have zero activation energies in the gas phase. The differences are 0.8, 0.9 and 0.5 kcal. for ethyl, s-propyl and s-butyl respectively (11). The possibility of a disproportionation reactions must be considered whenever a recombination reaction occurs.

The disproportionation of ethyl radicals could take place in two ways. The radicals might meet head to head and form an excited butane molecule, which could decompose into ethylene and ethane. Alternatively the two radicals could meet head to tail where one radical could abstract a hydrogen atom from the other. This point has been clarified by Wijnen and Steacie (12) in the study of the photolysis of $(CH_3CD_2)_2CO$. The two CH_3CD_2 radicals disproportionate to CH_2CD_2 and CH_3CD_2H. From the experimental fact of isotopic distribution, they were able to postulate the structure of the activated complex as such

$$CH_3CD_2\text{----}H\text{-----}CH_2CD_2$$

with a head to tail configuration. Kerr and Trotman-Dickenson (13) as well as Bradley (14) suggested a common intermediate complex for the disproportionation and recombination reaction. They suggested that dimer complex might be formed as indicated in the figure below.



If bond "a" breaks the reaction is one of the recombination but if the bonds "b" break the reaction would be disproportionation.

We speak of dimerization in the case of two identical free radicals combining to form stable compound, while in the case of two different radicals we speak of crosscombinations. The relationship between the rate constants of dimerization and crosscombination reactions may be made clear by the following reactions:

$$A + A \xrightarrow{k_1} A_2$$

$$B + B \xrightarrow{k_2} B_2$$

$$A + B \xrightarrow{k_3} AB$$

From these reactions we obtain $R_{AB}/(R_{A_2}^{\frac{1}{2}} R_{B_2}^{\frac{1}{2}}) = k_3/k_1^{\frac{1}{2}}k_2^{\frac{1}{2}}$ where R_x denotes the rate of production of compound x. Accepting that no disproportionation reactions occur between these radicals it can be shown from simple collision theory consideration that the ratio $k_3/k_1^{\frac{1}{2}}k_2^{\frac{1}{2}}$ should be approximately equal to two. It can be seen from Table 1 that almost all values for alkyl radicals are about equal to two.

Table 1. Cross-recombinations of alkyl radicals

Radicals	$k_3/k_1^{\frac{1}{2}}k_2^{\frac{1}{2}}$	Reference
Methyl + Methyl-d_3	1.9	15
Methyl + Ethyl	1.9, 2.0	16, 17
Methyl-d_3 + Ethyl	1.8	18
Methyl + Acetyl	2.0, 2.2	19, 20
Ethyl + Isopropyl	2.0, 2.1	21, 22
Chloroethyl + Trichloromethyl	2.5	23, 24
Isopropyl + n-Butyl	2.2	25

In regard to unsubstituted alkyl radicals, it appears that secondary radicals are relatively more likely to disproportionate than primary radicals. The reason may be that the combination of secondary radicals is retarded by steric effects, or that the primary radicals have fewer hydrogen atoms suitably placed for removal by disproportionation. A list of values obtained for k_d/k_c is given in Table 2, where k_d and k_c are the rate constants for disproportionation and combination reactions respectively.

Table 2. Disproportionation of alkyl radicals

Radicals	k_d/k_c	Reference
Ethyl + Ethyl	0.14	26, 27, 28, 29, 30, 32
Isopropyl + Isopropyl	0.64	21, 31, 33, 34
t-Butyl + t-Butyl	4.6, 2.2	31, 35, 36
Ethyl + Chloroethyl	0.22	24
Chloroethyl + Chloroethyl	0.05	23, 24
Methyl + Acetyl	0.05	15
Ethyl + Trichloromethyl	0.22	24
Chloroethyl + Trichloromethyl	0.12	23, 24
Iodine Atom + Ethyl	0.33	37

Abstraction: Abstraction reactions, also called transfer reaction, may be represented by the equation

$$A + RH \longrightarrow R + HA$$

where A is an atom or a radical and RH is a substrate. In most instances the species abstracted is a hydrogen atom. However other atomic species, such as halogen atoms, may be abstracted although these reactions are usually slower than H atom abstraction reactions.

It is reasonable to expect that the energy required for the rupture of a strong bond is likely to be higher than that for the rupture of a weak bond. But the whole picture obtained from free radical studies seems to quite a bit more complicated. It is well known that the chlorine atom attacks the hydrocarbon molecule only to break a carbon-hydrogen bond rather than a carbon-carbon bond even though the latter bond is weak (The bond dissociation energies for C-H and C-C are about 100 to 83 kcal per mole respectively). This is probably due in part to the possibility of forming the hydrogen-chlorine bond (stronger than carbon-chlorine) and in part to the fact that the carbon atoms are shielded, being surrounded entirely by hydrogen atoms. There is also a great deal of evidence to indicate that activation energies rather than steric effects appear to be the controlling factor in the rate at which the abstraction reactions occur. It is therefore postulated that a transition state of the form

A-------H-------R

exists. The energy or part of the energy that is required to break the R-H bond is supplied by the formation of the A-H bond. A chlorine atom, one of the most reactive radicals, requires less than 1 kcal. activation energy to react with carbon-hydrogen bonds as strong as those in

ethane (38).

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

The transition state for the above reaction will probably involve a very unequal bonding between the atoms undergoing change (39),

$$Cl\text{----------}H\text{---}CH_2CH_3$$

the bond order for C-H and Cl-H are about 0.9 and 0.1 respectively, while the reaction of methyl radical with ethane is a very symmetrical reaction since the bond broken is very like the bond formed. The reaction

$$CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5$$

will, therefore, probably involve equal bonding between the hydrogens and the two carbon atoms at the seat of reaction in the transition state.

$$H_3C\text{-------}H\text{-------}CH_2CH_3$$

In this case the bond orders for both C-H bonds are about 0.5. It might, therefore, be expected that the activation energy for H-atom abstraction from ethane by methyl radicals should be higher than the one for chlorine atoms. This is in agreement with experimental obseractions.

The greater reactivity of tertiary than of secondary and of secondary than primary hydrogen atoms is

general observed in radical abstraction reactions. This effect has been shown by Trotman-Dickson and Steacie (40) in the study of methyl radicals with alkanes. These gradations in reactivity may reflect changes in the strengths of the bonds. The stabilizability of activated complex in transition state due to resonance may also play an important role in determining the activation energies of the reactions.

Johnston and Parr (41) have applied the simple valence bond theory to derive the minimum potential energy of the complex through considerations of the bonding and anti-bonding contributions at the reaction site in the transition state. They were able to estime the activation energy for H-abstraction reactions. Good agreement is obtained between experimental and "theoretical" energies of activation in the case of alkyl radicals.

The important feature of abstraction reactions is their ability to form new radicals. Thus we can use this reaction to produce radicals which can not be produced by a direct photochemical process either because the compound from which these radicals are desired does not absorb light in a convenient wavelength region or because the compound decomposes yielding other radicals than those desired.

Addition: The addition of a radical to an unsaturated compound.

$$R + C{=}C \longrightarrow R{-}C{-}C$$

The reverse of this reaction is the decomposition of a large radical into a smaller radical and an unsaturated compound. The radical formed by this type of addition may possess an excess amount of energy due to the difference between the energy liberated in the R-C bond formation and the energy required to break the ethylenic pi-bond. Such radicals are usually referred to as "hot" radicals and are susceptible to decomposition if some of the excess energy is not removed. However, once deactivation of the excited radical has taken place, it may undergo the normal radical reactions. This includes further addition to the unsatured molecule to start a polymerization process. Indeed most of the early research on addition reactions was concerned with polymerization studies. There are three main steps in free radical polymerization mechanisms; the initiation step producing a free radical, the propagation or chaincarrying step in which the radical reacts with the monomer to produce a polymeric radical which in its turn can add to the monomer, and the termination step in which the radicals are destroyed. Termination may occur by the pairing of two radicals or by a disproportionation reaction between

two radicals.

The activation energy for addition reactions differs from one system to another. Smitz and coworkers (42) observed that the activation energy required for Cl atom addition to ethylene is zero, while methyl radical addition to ethylene requires an activation energy of as much as 7 kcal. (43)

Decomposition: This type of reaction may be represented by the equation.

$$R\text{-}C\text{-}C \longrightarrow R\cdot + C{=}C$$

Certain unstable radicals such as the CH_3CO radical, formed by the photochemical decomposition of acetone, undergo decomposition to yield a methyl radical and carbon monoxide.

In the study of H atom addition to propylene, Falconer, Rabinovitch and Cvetanovic (44) recognized that "hot" propyl radicals would readily undergo decomposition into methyl radicals and ethylene.

$$H + CH_3CH{=}CH_2 \longrightarrow CH_3CH_2CH_3^*$$

$$CH_3CH_2CH_3^* \longrightarrow CH_3 + CH_2{=}CH_2$$

In addition to "hot" radical decomposition, thermal decomposition reactions are observed. The

activation energies required for the thermal decomposition reaction of a free radical depends very much upon the nature of the free radical. Wijnen(45) observed that the activation energy for thermal decomposition of ethoxy radical into CH_2O and methyl radical requires about 13 kcal.

$$C_2H_5O \longrightarrow CH_3 + CH_2O$$

The activation energy for thermal decomposition of t-butoxy radical into CH_3 and CH_3COCH_3 is about 12 kcal.

$$(CH_3)_3CO \longrightarrow CH_3 + CH_3COCH_3$$

reported by several authors.(46, 47, 48, 49)
On the other hand Bywater and Steacie (50) obtained a value of 39.5 kcal/mole for the decomposition of the ethyl radicals into H atoms and ethylene.

Scavenging: This type of reaction is a reaction between a thermal radical and a scavenging molecule. The scavenging reaction needs no or a very low activation energy and it procedes with such efficiency and that it occurs within the first few collisions between the radical and the scavenging molecule.

A molecule such as oxygen, having an unpaired electron, is an excellent free radical scavenger. The reaction of free radicals with oxygen usually leads to

unstable products such as peroxides and hydroperoxides and for this reason other free radical scavengers are often preferred. Iodine and/or hydrogen iodide and free radical scavengers will yield reasonably stable products which can readily be identified by analytical techniques. Free radical scavengers are used to determine whether the reaction products originate from free radical reactions or other reactions.

Diradical Reaction: A diradical is a species with two unpaired electrons. Methylene, CH_2: has two unshared electrons that may be either paired or unpaired; if the electrons are unpaired, it is a diradical.

Diradicals are just as reactive as the ordinary radicals. One of the earliest proofs of the existence of methylene was obtained in 1933 by Norrish and his co-workers, as a result of the investigation of the photochemical decomposition of ketene. (51)

$$CH_2CO \xrightarrow{h\nu} :CH_2 + CO$$

Diradicals may readily take part in addition, abstraction, and insertion reactions as an example of an addition reaction the diradical may add to a double bond to form a cyclopropane derivative;

$$:CH_2 + R\text{-}CH_2\text{=}CH_2 \longrightarrow R\text{-}CH_2\text{-}\overset{\diagup\ CH_2}{CH_2}$$

the abstraction reaction by a diradical is made clear by the following reaction

$$:CH_2 + H_2 \longrightarrow \cdot CH_3 + H$$

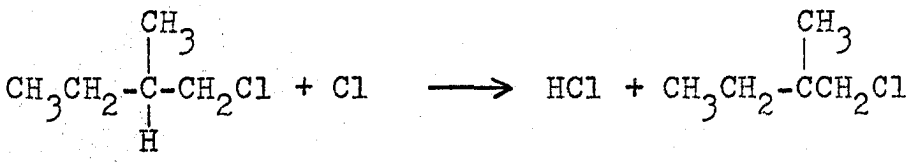
The activation energy for above reaction observed by Steacie is less than 2 kcal. (52)

In the insertion reactions the diradical inserts intself into a normal molecule to form a stable compound such as:

$$:CH_2 + CH_3CH_3 \longrightarrow C_3H_8$$

When methylene reacts with saturated hydrocarbons the insertion occurs mainly into the carbon-hydrogen bond. There is no attack on the carbon-carbon single bonds in these molecules. In the case of alkyl halides the insertion into C-H and into C-Cl bonds has been observed. (53)

Stereochemistry of free radicals Brown, Kharasch and Chao (54) studied the free radical chlorination of optically active 2-methylbutyl chloride and found that the 1,2-dichloro-2-methyl butane formed was racemic. This shows that the intermediate radicals racemized.



Eliel and his coworkers (55) observed that the dimerization of two 2-phenyl-2-butyl radicals produced a mixture of meso- and racemic-3,4-diphenyl-3,4-dimethylhexane. This shows that the free radical reactions can produce different stereochemical isomers.

EXPERIMENTAL

High Vaccum System

All experiments were carried out in a high vacuum system of conventional design (Figure 1). The main purpose of this high vacuum system is to be able to degas all starting materials and thus to provide the opportunity to photolyse compounds in the absence of oxygen. This is extremely important since oxygen is an excellent free radical scavenger. Traces of oxygen might react with free radicals thus producing undeserable side products which would complicate the interpretation of the data immensely.

The high vacuum system consisted of two parts, the high vacuum part in which the experiments were carried out and the low vacuum part which was used to control the mercury levels in the various measuring devices. The high and low vacuum systems were connected by a stopcock thus allowing the evacuation of (and the admission of air in case of a shut-down) in both systems at an equal rate. A diagram of the high vacuum system is whown in Figure 1. The high vacuum side of the system was evacuated by means of a two stage mercury diffusion pump followed by a mechanical vacuum pump. The low vacuum side was evacuated by a mechanical pump only since it was not necessary to maintain as good a vacuum in this part of the system.

The vacuum in the system was measured with a

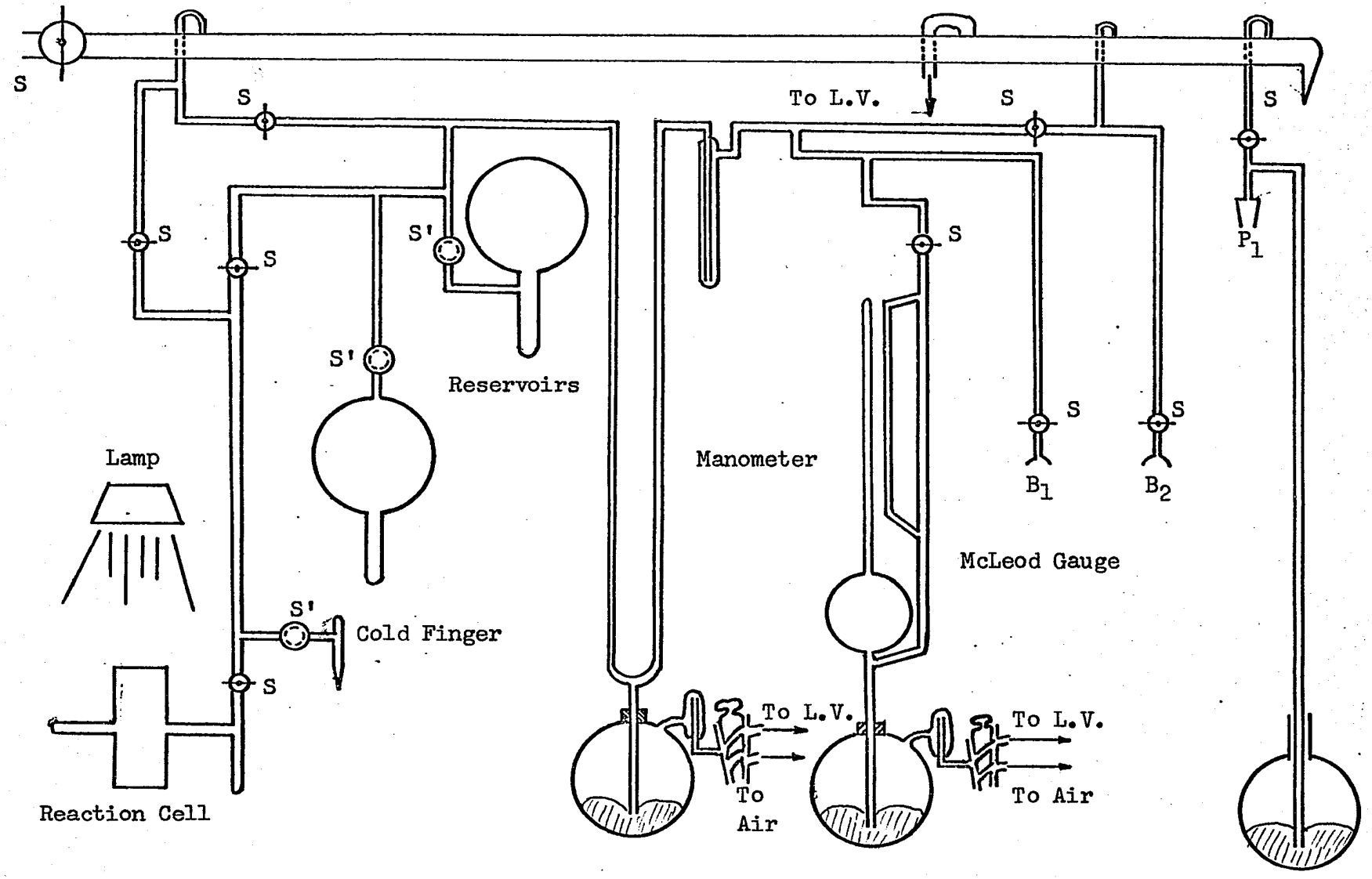


Figure 1. High Vacuum System

Where S=Stopcock, B=Ball-joint, L.V.=Low Vacuum, S'=High vacuum stopcock (telflon)

McLeod Gauge which was capable of measure a minimum pressure of 0.001 micron. All the experiments were carried out at a vacuum of 0.1 micron or better.

Two 1-liter reservoirs were used to store gaseous reactants. The reservoirs were painted with black paint to avoid any possible photochemical decomposition by daylight.

A mercury manometer was used to measure the pressure of the gasous reactants in the reservoirs and to measure the initial presures of the starting materials that were admitted into the quartz reaction cell.

The quartz reaction cell was cylindrical and was about 12 cm. long and 5 cm. in diameter. Its volume was 250 ml. The illumlated volume was 230 ml. The reaction cell was covered with blackened aluminum foil to exclude light except of course for the part which faced the light source.

A narrow and small cold finger, with a volume of about 2ml.,(Figure 2) was attached near the reaction cell direct to the high vacuum system via a teflon high vacuum stopcock. The cold finger was provided with a perforation type rubber stopper which served in two ways. Chemicals could be injected with a Hamilton microliter syringe into the system or withdrawn from it.

After photolysis, the reactants and products were collected at liquid nitrogen temperature in the cold

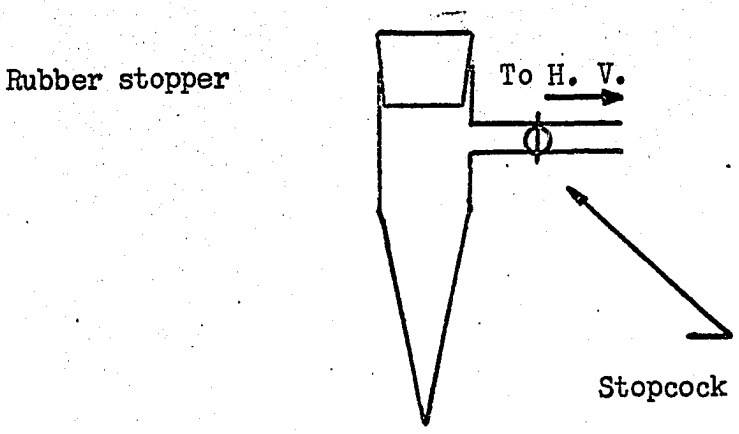


Figure 2. Cold finger

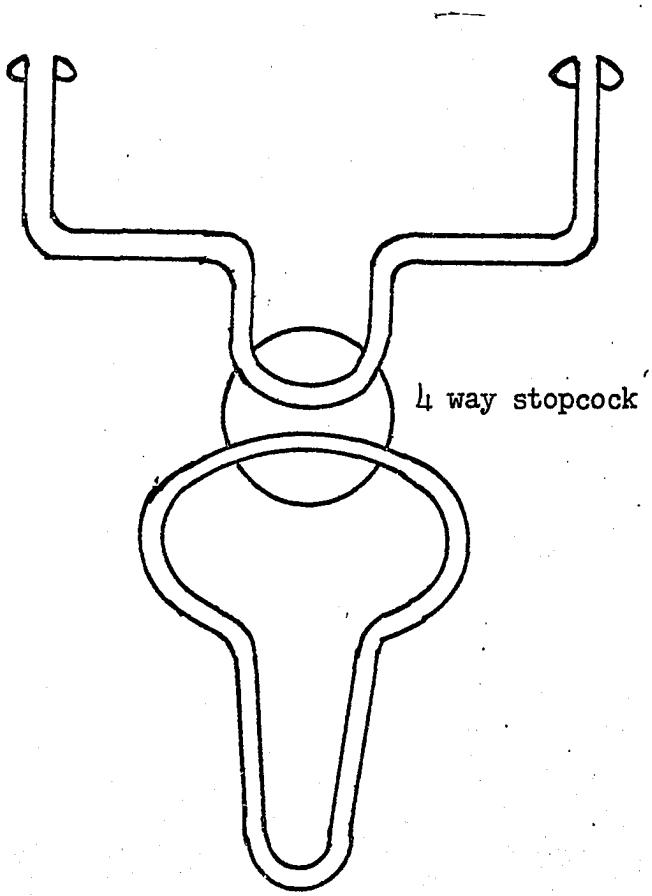


Figure 3. Sample trap

finger or in a U-tube sample trap (Figure 3). The products could then be transferred to the gas chromatographic analysis system by injection or by connecting the sample trap to the gas chromatograph via ball-joints B_3 and B_4 (Figure 4). Both techniques will be described later. The volume of the U-tube was 9.2 ml.

The stopcocks, connected to the reservoirs and the cold finger tube, were teflon high vacuum stopcocks (no grease needed). All other stopcocks on the high vacuum side of the system were pyrex high vacuum stopcocks greased with Ascolube F (fluorocarbon) stopcock grease.

Light Source-----Ultra Violet Light

A Hanovia model 100 SH medium pressure mecury arc was employed as the ultra violet source in all experiments. The mecury arc was collimated by an aluminum shade and reflector. The spectrum of the light source ranges from 2000 A^o through the visible region. Mecury photosensitization can not occur since at these pressure the 2537 A^o resonance line of the arc is reversed. The mercury arc was allowed a warm-up time of at least 15 minutes before exposure in order to permit the lamp to reach its operating temperature and, thus, a uniform intensity and wavelength distribution through out all

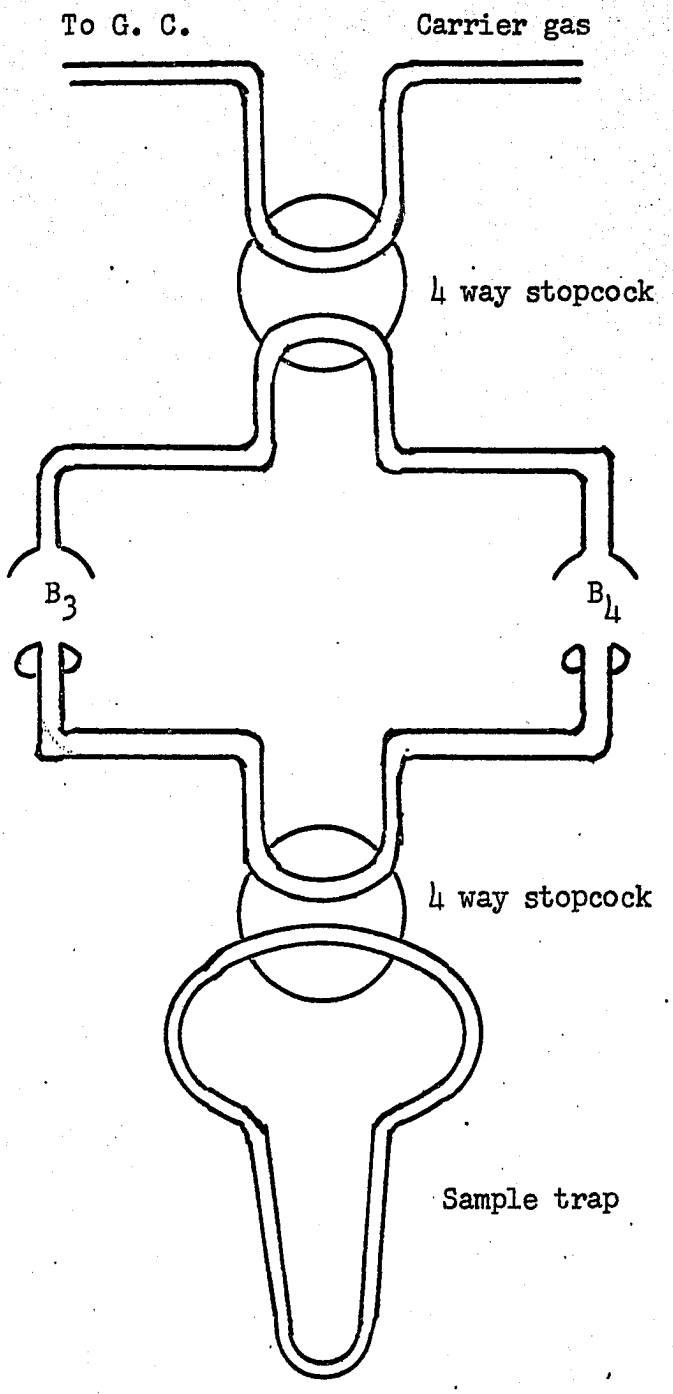


Figure 4. Gas chromatograph attachment

experiments was insured. The distance between mecury arc and the reaction cell was about 10 cm and was kept constant. Appropriate Corning filters were placed between the arc and the reaction cell in order to study the variation of products as a function of the energy of the incident radiation.

Analysis

The photolysis of carbon tetrachloride in the presence of ethyl chloride produced as major reaction products: $CHCl_3$, $CH_3CHClCHClCH_3$ (meso and racemic form), $CH_3CHClCH_2CH_2Cl$, $CH_3CHClCCl_3$, $CH_2ClCH_2CCl_3$ and C_2Cl_6. All the products mentioned above were identified and quantitatively determined using a Burell Kromo-Tog (model KD) gas chromatograph having thermal conductivity detectors. The detector current was 200 milliamperes. A 8-ft. colum packed with silicone grease on 30/60 firebrick was used for the analysis. Trace amounts of $(CH_2CH_2Cl)_2$ were also observed.

To determine the retention times of, and the sensitivity of the detector toward the various products, a known amount of each products was injected directly onto the column by using a Hamilton microliter syrings or a Hamilton gas tight syringe (plungers teflon coated).

The peak area on the gas chromatography chart

was measured with an Ott-planimeter calibrated at 0.084 cm^2. per planimeter unit (P.U.) and related to the actual amount of product injected. In any sensitivity determination, three or more samples were analyzed and the results average. The average deviation in these determinations was 1% or less. The quantitative analysis of the reaction products was always carried out in the presence of a large excess of undecompossed starting material. As will be shown later, the actual conversion of the starting material was usually less than one percent. In order to obtain very precise quantitative data, samples were prepared in which all known products were diluted by the starting material to approach the conditions of the analysis in the photochemical experiments.

The sensitivities of some compounds such as 2,3-dichlorobutane (meso and racemic forms) could not be determined directly since these compounds are not available commercially. In such cases sensitivities for these compounds were calculated. These calculations were based upon (a) their molecular weight and (b) their retention time in the gas chromatographic analysis. It is possible that a systematic error may thus be introduced. This error, if an error at all, must however be very small as shown by similar calculations for compounds with expermentally obtained sensitivites.

It was of course not possible to check the retention time of products not commercially available. Thus, there was some doubt regarding the correct assignment or identification of some products. As will be shown later it is, as a rule, relatively easy to deduce the formulas of some unknown products provided many other products can be determined. Never the less, other checks were carried out to remove any doubt regarding the correct assignment. As an example may be taken $CCl_3CH_2CH_2Cl$ which was not available commercially. However, Roquitte and Wijnen (23) identified this compound by mass spectrometric analysis as a reaction product in the photolysis of CCl_4 in the presence of C_2H_4. Thus $CCl_3CH_2CH_2Cl$ was prepared photochemically by this method and its retention time on the gas chromatography was thus obtained.

Products, produced by the photolysis of chloroform in the presence of ethane and ethylene were CH_2Cl_2, $(CHCl_2)_2$, $CH_2ClCH_2CHCl_2$, $CH_3CH_2CCl_3$, $CH_2ClCH_2CCl_3$ and $CHCl_2CCl_3$. All these products were routinely measured during the analysis.

In the case of the photolysis of CCl_3H in the presence of C_2H_6 an additional product, $CH_3CH_2CH_2CH_3$, was observed. Due to the large excess of undecompossed ethane it was not possible to measure this product routinely. The amount of butane produced was, therefore,

calculated. This calculation was made possible by previous data reported in the literature and the method will be explained later. Spot check were, never the less, carried out and comparisons were made between calculated and experimentally obtained data. The two sets of data were in excellent agreement and did not vary by more than ten percent.

The gas chromatography column used in this study is listed in Table 3. Also shown are the flow rate of the helium carrier gas, the approximate column temperatures and the retention times of the compounds analyzed on the column. It should be made clear that many experiments were necessary before a suitable column and suitable column temperatures were obtained. At least ten experiments were usually necessary before the correct column and operating conditions could be obtained. The operating conditions (flow rate and temperature programming) were always chosen so that maximun separation between the various products would be obtained.

Periodic checks on the sensitivities were made during a series to test possible deteriorations of the thermistors.

Materials

The chemicals used in the various experiments were

Table 3 Gas Chromatography Column

Packing and Length	Flow Rate (ml/min.)	Operating* Temp. (°C)	Compounds and Their Retention Time (min.)	
Silicone	42	50	CH_2Cl_2	3.8
Grease	"	85	$CHCl_3$	5.2
on 30/60	"	135	$CH_3CH_2CHCl_2$	6.6
firebrick	"	165	CCl_4	7.8
8 feet long	"	260	2,3 DCB** (meso)	10.8
	"	275	2,3 DCB (racemic)	11.6
	"	"	1,3 DCB	13.5
	"	"	1,4 DCB	15.6
	"	"	$C_2H_2Cl_4$	16.2
	"	"	$CCl_3CHClCH_3$	21.0
	"	"	$CCl_3CH_2CH_2Cl$	21.8
	"	"	C_2HCl_5	23.2
	"	"	C_2Cl_6	37.5

* The analysis was started at 25°C. After three minutes the temperature programmer was turned on, increasing the temperature at a rate of 30°C/min.. At 275°C the programming would stop, maintaining a temperature of 275°C until the analysis was completed.

** DCB represents dichlorobutane

C_2H_4, C_2H_6, C_2H_5Cl, CCl_4 and $CHCl_3$. All the gaseous materials were obtained in lecture bottles from the Matheson Company, Inc., East Rutherford, New Jersey. A list of the gases, their purities and possible impurities present (56) is shown in Table 4.

All gases were admitted to the high vacuum system by attaching the lecture bottle via pressure tubing to pyrex joint P_1 (Figure 1). The tubing was flushed through the open end mercury reservoir with the gas to be admitted. Thus all air inside the tubing would be replaced by the gas. The gas would then be admitted into the reservoir of the high vacuum system via stopcock S_1 at such a rate that slow bubbling through the mercury reservoir would be maintained. This guaranteed a positive internal pressure and prevented air leaking inward. This technique also served as a precaution to avoid the possibility of an explosion since under these conditions it is impossible to admit more than one atmosphere pressure into the high vacuum system. The gas then was frozen into a reservoir at 80°K and degassed to remove all air.

The carbon tetrachloride and chloroform were obtained in Fisher Certificate Reagent grade from Fisher Scientific Company, Pittsburgh, Pa.. Chloroform was further purified by fractional distillation in order to get rid of the added preservative C_2H_5OH. A Vigreux

Table 4 Purity of Gas Reactants (56)

Gas	Stated Purity	Possible Impurities
C_2H_5Cl	99.7%(min.)	Residue (0.0008%)
C_2H_6	99.0 mole%(min.)	Small amounts of C_2H_4, C_3H_6, and C_3H_8; trace amount of CH_4
C_2H_4	99 mole%	CO_2(30 p.p.m), C_3H_8(5 p.p.m) C_2H_6(50 p.p.m), O_2(10 p.p.m) C_2H_2(10 p.p.m), H_2O(5 p.p.m)

Abbreviations used in above table: min. = minimum; p.p.m = parts per million

Table 5 Purity of Liquid used as Reactants (57)

Liquid	Stated Purity	Possible Impurities
CCl_4	99 mole%	Residue(0.0002%); Sulfur compounds(0.0005%); Chloride (0.0002); Heavy Metals pb (0.0001%)
$CHCl_3$	99 mole%	Residue (0.00005%0; Acetone and Aldehyde(0.005%)

column was used and insulated by wrapping with asbestos paper.

All reactants were degassed three times a 80°K. Samples taken from the reservoirs after degassing showed no impurities when tested on the gas chromatography. The only exception was $CHCl_3$ which still contained a trace amount of alcohol (0.01%). Frequent checks were made on reactant purity through each experiment series.

Experimental Procedure

(A) Photolysis of Ethyl Chloride: The experimental technique used in studying the photolysis of ethyl chloride will be described first since it is less complicated than the technique used in studying the photolysis of mixture. Ethyl chloride was admitted to the reaction cell. The pressure was measured via the manometer. The quartz reaction cell was then closed and exposed to ultra violet radiation. After photolysis, the reactant and products were collected in the evacuated U-tube sample trap at 80°K for five minutes. The sample trap was then degassed at liquid nitrogen temperature for one minute to remove any traces of air that might have leaked in through the ball-joints during the collection process. Then, the sample trap was connected to the gas chromatography via ball-joints B_3 and B_4 as shown in Figure 4.

The bottom portion of the sample trap was immersed into a dewar filled with liquid nitrogen. The air in the top portion of the sample trap was passed through the column by opening the 4-way stopcock. At this stage the detector was in off position in order to minimize detector oxidation and to prolong life of the detector. After all air had passed through the detector, the detector was turned on and allowed a warm up time of at least 10 minutes before the start of the analysis in order to permit the detector to stabilize. The liquid nitrogen was then removed and the sample trap was heated by wires wapped around it with the current through the wires controlled by a variac. As a rule the sample trap was heated to a temperature of about 85°C. The sample trap was heated in order to vaporize as many products as possible. This is necessary to produce sharp, well defined, peaks on the gas chromatograph. Compounds which do not completely vaporize show long trailing peaks on the chromatogram which make the separation and quantitative determination extremely difficult.

In order to have a good separation for the volatile compounds, the column temperature was cooled to 0°C by immersing the column in ice water. After three minutes the cooling container was removed and the column was heated by turning on the temperature programmer, increasing the temperature at a rate of 30°C/min. The

programmer would automatically stop at a previously set temperature (275°C), and maintain this temperature until the analysis was completed.

Some of the photochemical products obtained were high boiling compounds, such as 1,3-dichlorobutane, 1,4-dichlorobutane, and hexachloroethane with boiling points of 132°C, 162°C, and 186°C respectively. These high boiling products evaporated only slowly from the sample trap when the trap was heated to 85°C and appeared therefore on the gas chromatogram in the form of long tailing peaks. It would of course have been possible to heat the sample trap to a higher temperature in order to make certain that all products would be present in the gaseous state before they were swept on to the gas chromatographic column by the helium carrier gas. This was not done in order to avoid possible thermal decomposition reactions of some of the products. A different technique was, therefore, used to analyse these samples by which the samples were injected directly onto the column. This technique will be described in the next section.

(B) Photolysis of Carbon Tetrachloride in the presence of Ethyl Chloride: Known amounts of degassed ethyl chloride were admitted to the reaction cell and frozen into the

cold finger connected to the cell by using liquid nitrogen. The pressure of CCl_4 was then measured in a known volume outside the cell and frozen into the reaction cell on the top of the ethyl chloride. The cold finger was warmed up quickly with boiling water in order to obtain a homogenous distribution of the reactants in the cell. Most of the products formed by the photolysis were nonvolatile compounds and the injection technique was, therefore, used to analyse for the products.

After photolysis, all the reactants and products were frozen into the cold finger storage tube at 80°K. The teflon stopcock, connecting the cold finger to the reaction cell was closed and the liquid nitrogen was removed. The needle of a hypodermic was then inserted through the rubber stopper so that the unreacted ethyl chloride could escape through this needle. This was necessary since too high a pressure might build up in this cold finger storage area. The volume of the cold finger was about 2 ml compared to a volume of 250 ml of the reaction cell. As soon as the products were transformed from the solid into the liquid phase a sample was withdrawn with a hypodermic and injected onto the gas chromatographic column. It was of course impossible to withdraw the total sample. The unreacted CCl_4 was, therefore, used as an internal standard. The amount of CCl_4 in the cell before the photolysis was known by

pressure measurements. Less than 1% of initially present CCl_4 was decomposed during the photolysis, measurement of the CCl_4 peak permitted the determination of the fraction of the original sample injected and through this accurate data regarding the rates of formation of all products were obtained.

(C) Photolysis of Ethane in the Presence of Chloroform: In general the experimental procedure was similar to the one described before except that it was necessary to use both the sample trap and the injection technique to analyses for the reaction products. The injection technique was necessary because of the formation of $C_2H_2Cl_4$ and other high boiling products. The injection technique could, however, not be used for the analysis of butane which was formed as a product. Since the butane would evaporate with the unreacted ethane thus escaping analysis. Duplicate experiments were carried out in which one experiment would be analysed by the injection technique and the other by the sample trap technique. Some products such as CH_2Cl_2, $C_3H_6Cl_2$ and $C_3H_5Cl_3$ could be determined by both techniques. It is extremely gratifying to report that within experimental error ($\pm$ 5%) identical data were obtained for these compounds regardless of which method had been used for analysis.

(D) Irradiation Time Study: A series of experiments was first carried out to study the amount of products as a function of photolysis time while keeping the substrate pressure constant. A plot of these data obtained in the photolysis of carbon tetrachloride in the presence of ethyl chloride at room temperature is shown in Figure 5. This plot is typical of the others obtained in this study. All experiments in this investigation were carried out by using an irradiation time well within the linear region of the time study to insure that the reaction products were not undergoing secondary reactions.

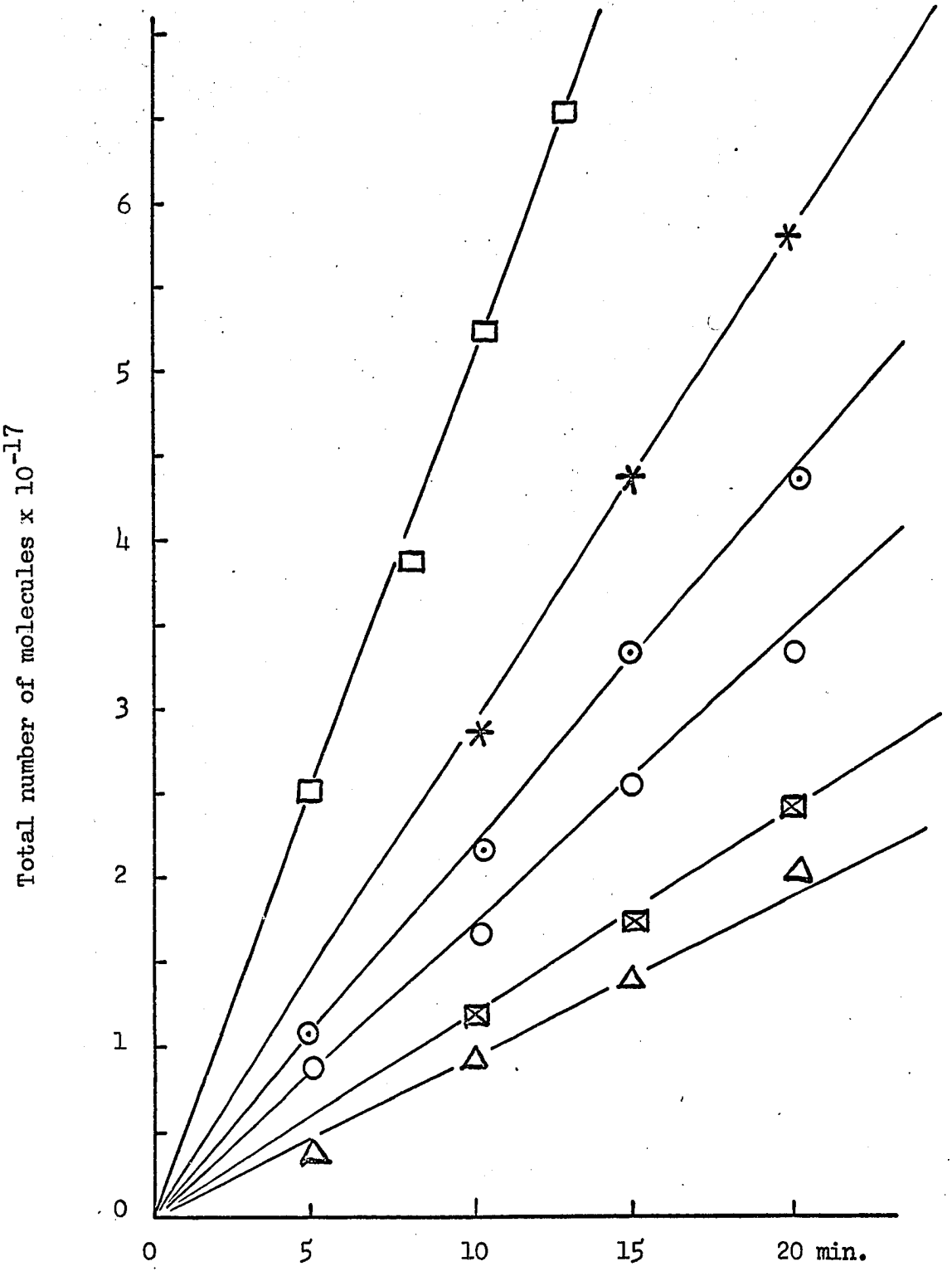


Fig. 5 Time study of the photolysis of CCl_4 in the presence of C_2H_5Cl

RESULTS

(I). Photolysis of Carbon Tetrachloride in the Presence of Ethylchloride.

The photolysis of carbon tetrachloride in the presence of ethyl chloride was carried out at various CCL_4 to C_2H_5Cl ratios. Less than 1% of the carbon tetrachloride initially present was decomposed during the photolysis. The results of these experiments are reported in Table 6.

The first column of Table 6 gives the number of the experiment, the second and the third columns give the initial pressure of CCl_4 and C_2H_5Cl repectively. The initial pressures are expressed in molecules/cc.. The rates of the products formed are given in molecules/(sec.cc.). A corning filter 9-54 was used in experiment run number 4 to omit raditation below 2200°A. All experiments given in Table 6 were carried out at room temperature.

To explain the formation and distribution of the reaction products, the following reaction mechanism is proposed.

$$CCl_4 + h\nu \longrightarrow CCl_3 + Cl \qquad (1)$$

$$CH_3CH_2Cl + Cl \longrightarrow CH_3CHCl + HCl \qquad (2)$$

$$CH_3CH_2Cl + Cl \longrightarrow CH_2CH_2Cl + HCl \qquad (3)$$

Table 6 Photolysis of Carbon Tetrachloride in the presence of Ethyl Chloride

Exp. No.	Init. conc. in molecules/cc.x10^{-17}		Rates of products in molecules/(sec. cc) x 10^{-12}						
	CCl_4	C_2H_5Cl	$CHCl_3$	meso $(CH_3CHCl)_2$	racemic $(CH_3CHCl)_2$	$CH_3CHClC_2H_4Cl$	$CH_3CHClCCl_3$	$CCl_3C_2H_4Cl$	C_2Cl_6
1	20.12	6.83	1.02	0.88	0.82	0.62	3.87	0.75	1.91
2	3.70	3.32	0.52	0.42	0.40	0.32	1.72	0.32	0.87
3	13.65	19.89	0.90	0.79	0.68	0.57	3.78	0.79	1.78
4*	12.81	13.01	0.11	0.07	0.07	0.05	0.34	0.06	0.15
5	4.22	23.74	0.53	0.49	0.44	0.38	2.29	0.40	1.05
6	19.99	6.63	0.95	0.81	0.55	0.54	3.31	0.68	1.64
7	14.01	13.30	1.13	0.90	0.91	0.60	3.85	0.77	1.95
8	6.35	30.40	0.61	0.55	0.50	0.36	2.23	0.39	1.11
9	13.59	6.57	0.94	0.84	0.70	0.58	3.60	0.72	1.85
10	13.65	8.94	0.93	0.83	0.73	0.61	3.42	0.68	1.67
11	12.51	13.16	1.17	0.78	0.80	0.62	3.81	0.80	1.84
12	13.39	13.68	1.17	0.80	0.78	0.70	3.84	0.83	2.09

Note: All experiments were carried out at room temperature.

* Experiment No. 4 was carried out with Corning filter 9-54.

$$2CCl_3 \longrightarrow C_2Cl_6 \qquad (4)$$

$$2CH_3CH\text{-}Cl \longrightarrow (CH_3CHCl)_2 \qquad (5)$$

(meso and racemic)

$$2CH_3CHCl \longrightarrow C_2H_5Cl + C_2H_3Cl \qquad (6)$$

$$2CH_2CH_2Cl \longrightarrow (CH_2CH_2Cl)_2 \qquad (7)$$

$$2CH_2CH_2Cl \longrightarrow C_2H_5Cl + C_2H_3Cl \qquad (8)$$

$$2CH_2CH_2Cl \longrightarrow C_2H_4 + C_2H_4Cl_2 \qquad (9)$$

$$CH_3CHCl + CCl_3 \longrightarrow CH_3CHClCCl_3 \qquad (10)$$

$$CH_3CHCl + CCl_3 \longrightarrow CCl_3H + C_2H_3Cl \qquad (11)$$

$$CH_2CH_2Cl + CCl_3 \longrightarrow CCl_3CH_2CH_2Cl \qquad (12)$$

$$CH_2CH_2Cl + CCl_3 \longrightarrow CCl_3H + C_2H_3Cl \qquad (13)$$

$$CH_2CH_2Cl + CH_3CHCl \longrightarrow CH_3CHClCH_2CH_2Cl \qquad (14)$$

$$CH_2CH_2Cl + CH_3CHCl \longrightarrow C_2H_5Cl + C_2H_3Cl \qquad (15)$$

$$CH_2CH_2Cl + CH_3CHCl \longrightarrow C_2H_4Cl_2 + C_2H_4 \qquad (16)$$

The primary step in the photolysis of CCl_4 produces CCl_3 radicals and Cl atoms as shown in reaction 1. This reaction is well established by earlier studies of photolysis and radiolysis of carbon tetrachloride (references 58 to 62). The chlorine atoms, produced by photolysis of CCl_4, may abstract H atoms from either the

CH_3 side of CH_3CH_2Cl to produce primary CH_2CH_2Cl radicals (reaction 3) or from the CH_2Cl side of CH_3CH_2Cl to produce secondary CH_3CHCl radicals (reaction2). Thus, reactions 1, 2 and 3 produce CCl_3, CH_3CHCl and CH_2CH_2Cl radicals. A qualitative proof for the fact that indeed CCl_3 radicals are produced is clearly shown by the products C_2Cl_6, $CCl_3CHClCH_3$, $CCl_3CH_2CH_2Cl$ and CCl_3H since all these products have a CCl_3 radical in common. Similarly the presence of CH_3CHCl and of CH_2CH_2Cl radicals is shown by the formation of $(CH_3CHCl)_2$, $CCl_3CHClCH_3$ and of $CCl_3CH_2CH_2Cl$ and $CH_3CHClCH_2CH_2Cl$. Reactions 4 to 16 discuss the fate of CCl_3, CH_2CH_2Cl and CH_3CHCl radicals produced by reactions 1 to 3.

In particular, the formation of C_2Cl_6 is explained by the recombination of CCl_3 radicals (reaction 4). The formation of the meso and racemic forms of 2,3-dichlorobutane is explained by recombination of two CH_3CHCl radicals (reaction 5), and the production of trace amounts of 1,4-dichlorobutane by recombination of CH_2CH_2Cl radicals (reaction 7). It should be mentioned here that 1,4-dichlorobutane was formed in trace quantities only and for this reason this compound is not reported in Table 6. Later an explaination will be given for the fact that this compound was produced in minute quantities only. Reactions 6, 8, and 9 represent possible disproportionation reactions of CH_3CHCl and

CH_2CH_2Cl radicals. In the presence of a large excess of C_2H_5Cl it was impossible to analyse for small amounts of C_2H_4, C_2H_5Cl and C_2H_3Cl possibly produced by these reactions. These reactions have been included to represent a picture as complete as possible. Furthermore, literature data on some of these reactions will be discussed later.

Elementary kinetics requires that two radicals A and B will not react exclusively to form A_2 and B_2 but will also react by cross combination to form AB. Thus, it is possible to explain the formation of 1,1,1,2-tetrachloropropane by cross combination of CCl_3 and CH_3CHCl radicals (reaction 10); of 1,1,1,3-tetrachloropropane via CCl_3 and CH_2CH_2Cl radicals (reaction 12) and finally the formation of 1,3-dichlorobutane from CH_2CH_2Cl and CH_3CHCl radicals (reaction 14). Reactions 11 and 13 are disproportionation reactions which must be considered to explain the formation of CCl_3H as a reaction product. Reactions 15 and 16 represent possible cross disproportionation reactions of CH_3CHCl and CH_2CH_2Cl radicals.

The above reaction mechanism does not include the photochemical decomposition of ethyl chloride. The reason for this is that the absorption coefficient of C_2H_5Cl is considerably smaller than CCl_4. The UV spectra of carbon tetrachloride and ethyl chloride are shown in Figure 6 (63). These spectra clearly indicate

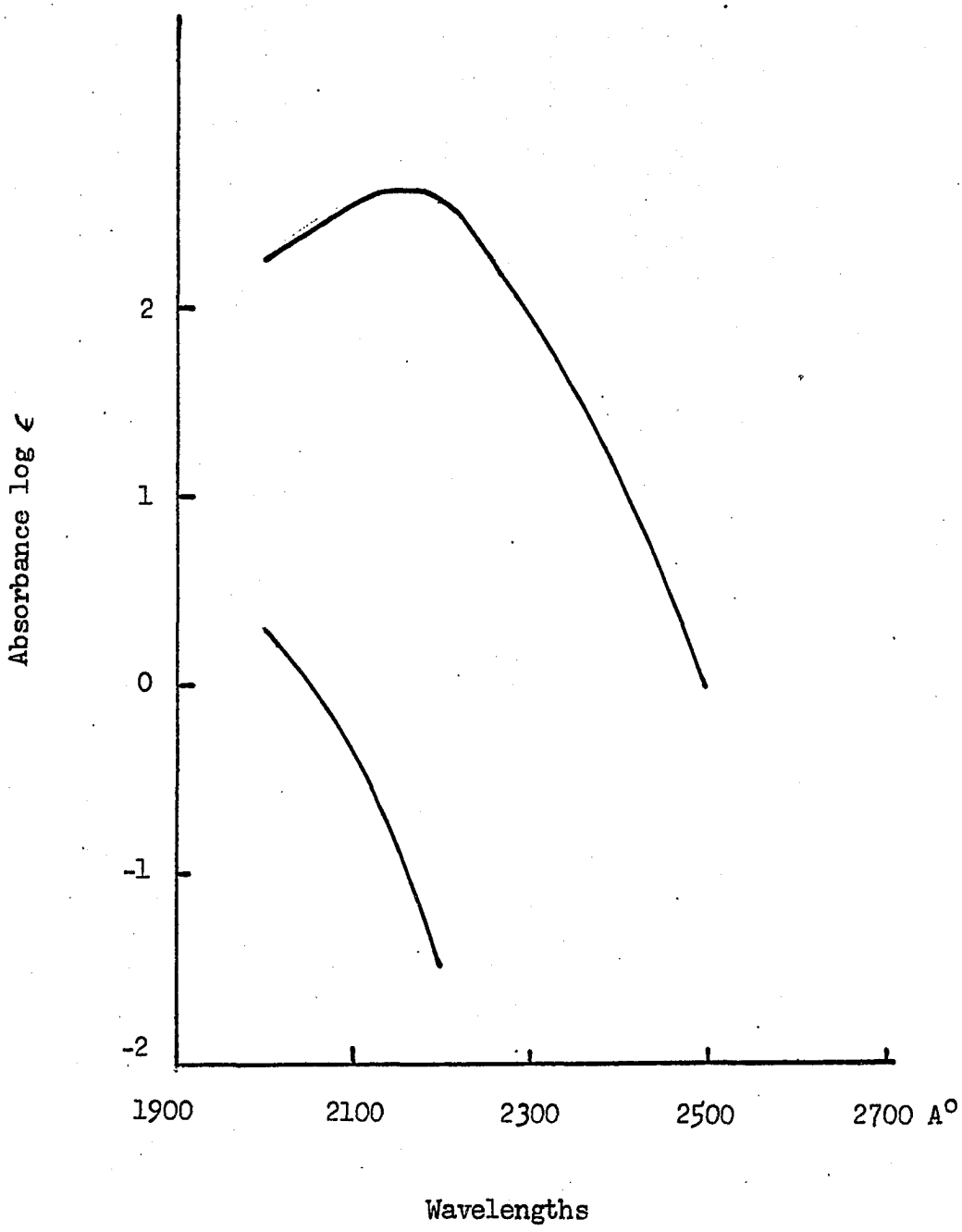


Figure 6. Absorption spectra of CCl_4 and C_2H_5Cl

that most, if not all, of the incident light will be absorbed by CCl_4. The experimental data to confirm this will be discussed later.

It is clear that the reaction mechanism explains in a qualitative way all the reaction products which have observed.

It is now interesting to study data in a quantitative manner. According to the reaction mechanism the following equation can be derived.

$$\frac{R_{CH_3CHClCCl_3}}{R^{\frac{1}{2}}_{C_2Cl_6}\, R^{\frac{1}{2}}_{(CH_3CHCl)_2}} = \frac{k_{10}(CH_3CHCl)\,(CCl_3)}{k_4^{\frac{1}{2}}(CCl_3)\; k_5^{\frac{1}{2}}(CH_3CHCl)}$$

$$= k_{10}/k_4^{\frac{1}{2}}\, k_5^{\frac{1}{2}}$$

The equation indicates that the ratio of $R_{CH_3CHClCCl_3}/\, R^{\frac{1}{2}}_{C_2Cl_6} R^{\frac{1}{2}}_{(CH_3CHCl_3)_2}$ should be constant regardless of the initial pressures of C_2H_5Cl and CCl_4. The data in Table 7 clearly establish that the ratio of $R_{CH_3CHClCCl_3}/\, R^{\frac{1}{2}}_{C_2Cl_6} R^{\frac{1}{2}}_{(CH_3CHCl)_2}$ is constant within experimental error. The particular value obtained for the ratio, reported in Table 7, will be discussed later. From the rates formation of $CH_3CHClCH_2CH_2Cl$, $(CH_3CHCl)_2$, $CH_3CHClCCl_3$, and $CCl_3CH_2CH_2Cl$ the following equation may be obtained.

$$R = \frac{R_{CH_3CHClCH_2CH_2Cl}\ R_{CH_3CHClCCl_3}}{R_{(CH_3CHCl)_2}\ R_{CCl_3CH_2CH_2Cl}}$$

$$= \frac{k_{14}(CH_3CHCl)(CH_2CH_2Cl)\ k_{10}(CH_3CHCl)(CCl_3)}{k_5(CH_3CHCl)_2^2\ k_{12}(CH_2CH_2Cl)(CCl_3)}$$

$$= k_{14}\ k_{10}/k_5k_{12}$$

The experimentally data for the ratio $k_{10}k_{14}/k_5k_{12}$ are given in column 4, Table 7. Again a, within experimental error, constant value was obtained.

According to the reaction mechanism, chloroform is produced exclusively by disproportionation reactions 11 and 13. These reactions are repeated here for clarification together with the corresponding recombination reactions 10 and 13.

$$CH_3CHCl + CCl_3 \longrightarrow CH_3CHClCCl_3 \qquad (10)$$

$$CH_3CHCl + CCl_3 \longrightarrow CCl_3H + C_2H_3Cl \qquad (11)$$

$$CH_2CH_2Cl + CCl_3 \longrightarrow CCl_3CH_2CH_2Cl \qquad (12)$$

$$CH_2CH_2Cl + CCl_3 \longrightarrow CCl_3H + C_2H_3Cl \qquad (13)$$

Thus, $^{R}CHCl_3(total) = {}^{R}CHCl_3(11) + {}^{R}CHCl_3(13)$. Where $^{R}CHCl_3(11)$ denotes the rate of formation of chloroform

Table 7 Ratios of rate constants for the photolysis of CCl_4 in the presence of C_2H_5Cl

Exp. No.	$\frac{R_{CH_3CHClCCl_3}}{\frac{1}{2}R_{CH_3CHClCHClCH_3}\ \frac{1}{2}R_{C_2Cl_6}}$	$\frac{R_{CHCl_3}(11)}{R_{CH_3CHClCCl_3}}$	$\frac{R_{CH_3CHClCCl_3}\ R_{CH_3CHClC_2H_4Cl}}{R_{CCl_3C_2H_4Cl}\ R_{CH_3CHClCHClCH_3}}$	$\frac{R_{\Sigma CH_2CH_2Cl}}{R_{\Sigma CH_3CHCl}}$
1	2.21	0.24	1.9	0.17
2	2.08	0.28	2.1	0.16
3	2.33	0.22	1.9	0.18
4	2.32	0.29	2.0	0.15
5	2.30	0.23	2.1	0.16
6	2.22	0.26	1.9	0.17
7	2.05	0.27	1.7	0.16
8	2.13	0.25	2.0	0.17
9	2.14	0.24	1.9	0.17
10	2.15	0.25	2.0	0.17
11	2.24	0.28	1.9	0.18
12	2.11	0.26	2.0	0.19

Note: R_x = Rate of formation of compound x in molecules/(sec. cc.)$\times 10^{-12}$

from reaction 11 and $^{R}CHCl_3$(13) that from reaction 13. Although it is of course impossible to measure directly which fraction of $CHCl_3$ is produced by reaction 11 or 13 it is, never the less, quite clear that the following relationships must hold if the mechanism is correct:

$$\frac{R_{CHCl_3}(11)}{R_{CCl_3CH_3CH\text{-}Cl}} = \frac{k_{11}(CH_3CHCl)(CCl_3)}{k_{10}(CH_3CHCl)(CCl_3)} = \frac{k_{11}}{k_{10}}$$

By the same token, the rate formation of vinyl chloride or chloroform from reaction 13 over the rate of recombination of CH_2CH_2Cl and CCl_3 radicals in reaction 12 may be given by:

$$\frac{R_{CHCl_3}(13)}{R_{CCl_3CH_2CH_2Cl}} = \frac{k_{13}(CH_2CH_2Cl)(CCl_3)}{k_{12}(CH_2CH_2Cl)(CCl_3)} = \frac{k_{13}}{k_{12}}$$

Roquitte and Wijnen obtained the value of $k_{13}/k_{12}=0.12$(24). Since the rate of production of $CCl_3CH_2CH_2Cl$ is known from experimental results, R_{CHCl_3}(13) can be calculated as indicated in the following equation.

$$R_{CHCl_3}(13) = 0.12\ R_{CCl_3CH_2CH_2Cl}$$

The chloroform produced by reaction 11 can now be obtained:

$$R_{CHCl_3}(11) = R_{CHCl_3}(\text{total}) - R_{CHCl_3}(13)$$

$$= R_{CHCl_3}(\text{total}) - 0.12\, R_{CCl_3CH_2CH_2Cl}$$

Thus, it is possible to obtain k_{11}/k_{10} from the equation given on the previous page. In spite of the rather cumbersome method employed to calculate k_{11}/k_{10} a within experimental error constant value is obtained as shown in column 3 of Table 7.

As stated before, the chlorine atom can abstract a hydrogen atom from either the CH_3 side or the CH_2Cl side of the CH_3CH_2Cl molecule as shown by reactions 2 and 3.

$$CH_3CH_2Cl + Cl \longrightarrow CH_3CHCl + HCl \qquad (2)$$

$$CH_3CH_2Cl + Cl \longrightarrow CH_2CH_2Cl + HCl \qquad (3)$$

From these reactions it is clear that:

$$\frac{R_{CH_3CHCl}}{R_{CH_2CH_2Cl}} = \frac{k_2(CH_3CH_2Cl)(Cl)}{k_3(CH\ CH\ Cl)(Cl)} = \frac{k_2}{k_3}$$

In the above expression R_{CH_3CHCl} indicates the rate of production of CH_3CHCl radicals and is given by

$$R_{CH_3CHCl} = 2\, R_{CH_3CHClClCHCH_3}\ (\text{meso + racemic forms}) + R_{CH_3CHClCH_2CH_2Cl} + R_{CH_3CHClCCl_3} + 0.25\, R_{CH_3CHClCCl_3}$$

Where 0.25 $R_{CH_3CHClCCl_3}$ is to account for CCl_3H produced by reaction 11. The term of 2 $R_{CH_3CHClClCHCl_3}$ indicates that two CH_3CHCl radicals are used up to produce one molecule of 2,3-dichlorobutane. The rate of CH_2CH_2Cl radicals production is given by

$$R_{CH_2CH_2Cl} = R_{CH_3CHClCH_2CH_2Cl} + R_{CH_2CH_2ClCCl_3} + 0.12 \; R_{CH_2CH_2ClCCl_3}$$

Where 0.12 $R_{CH_2CH_2ClCCl_3}$ accounts for the CH_2CH_2Cl radicals reacting with CCl_3 radicals to form $CHCl_3$ and C_2H_3Cl (reaction 13). Not included in the above calculations are the CH_2CH_2Cl radicals reacting to form 1,4-dichlorobutane. As pointed out earlier 1,4-dichlorobutane is produced in trace amounts only. Neglecting to account for $R_{(CH_2CH_2Cl)_2}$ should therefore not upset the material balance calculations for $R_{CH_2CH_2Cl}$ radicals to any appreciable extent. The observed value of $R_{CH_2CH_2Cl}/R_{CH_3CHCl}$ is equal to 0.17 ± 0.02 and is reported in Table 7. This value and its meaning will be discussed in detail later.

Since trichloromethane radicals and chlorine atoms are both produced in the primary step, it is clear that R_{CCl_3}/R_{Cl} should be equal to unity. If Cl atom react exclusively with C_2H_5Cl to form either CH_2CH_2Cl or CH_3CHCl radicals than the rate of production of Cl atoms is of course equal to the rate production of the sum of

CH_3CHCl and CH_2CH_2Cl radicals. Thus,

$$R_{Cl} = R_{CH_2CH_2Cl} + R_{CH_3CHCl}$$
$$= 2\, R_{CH_3CHClClCHCH_3} \text{ (meso + racemic forms)} +$$
$$R_{CH_3CHClCH_2CH_2Cl} + R_{CH_3CHClCCl_3} + 0.25$$
$$R_{CH_3CHClCCl_3} + R_{CH_2CH_2ClCCl_3} +$$
$$0.12\, R_{CH_2CH_2ClCCl_3} + R_{CH_3CHClCH_2CH_2Cl}$$

The rate of CCl_3 radicals production is given by

$$R_{CCl_3} = R_{CH_3CHClCCl_3} + 0.25\, R_{CH_3CHClCCl_3} +$$
$$R_{CCl_3CH_2CH_2Cl} + 0.12\, R_{CCl_3CH_2CH_2Cl} +$$
$$2\, R_{C_2Cl_6}$$

where $2\, R_{C_2Cl_6}$ accounts for the fact that one molecule of C_2Cl_6 requires two CCl_3 radicals.

Although the results of this material balance calculations have not been reported in Table 7, calculations have been carried out for every experiment. These calculations yield $R_{CCl_3}/R_{Cl} = 1.07 \pm 0.05$. This excellent result is an other proof of the correctness of the proposed reaction mechanism.

(II). Photolysis of other Chlorinated Systems

Some experiments on the photolysis of related compounds were carried out in order to provide additional evidence and support for the reactions and quantitative data obtained in the study of the photolysis of carbon tetrachloride in the presence of ethyl chloride. Additional systems, which have been investigated are:

A. Photolysis of Methylene Chloride in the presence of Ethyl Chloride

B. Photolysis of Ethyl Chloride at room temperature

C. Photolysis of Chloroform in the presence of Ethylene

D. Photolysis of Chloroform in the presence of Ethane

A. Photolysis of Methylene Chloride in the presence of Ethyl Chloride

It is well known (64) that the primary step in the photolysis of methylene chloride is given by:

$$CH_2Cl_2 + h\nu \longrightarrow CH_2Cl + Cl \qquad (17)$$

This step is, of course, completely analogous to the

observed C-Cl rupture in the photolysis of CCl_4.

In the previous section it has been suggested that Cl atoms produced by the photolysis of CCl_4 abstract H atoms from C_2H_5Cl to produce CH_2CH_2Cl and CH_3CHCl radicals. These two radicals were considered to be responsible for the observed formation of meso- and racemic-2,3-dichlorobutane and of 1,3-dichlorobutane. It is obvious that, if these assumption is correct, these products must also be formed by the photolysis of CH_2Cl_2 in the presence of ethyl chloride.

It is also clear that the over-all reaction mechanism of the photolysis of CH_2Cl_2 in the presence of C_2H_5Cl must be considerably more complicated than was the case with CCl_4 and C_2H_5Cl. In the case of CH_2Cl_2, the Cl atoms produced in the primary step may abstract not only H atoms from C_2H_5Cl but also from CH_2Cl_2. Thus recombination and disproportionation reaction between CH_3CHCl, CH_2CH_2Cl, CH_2Cl and $CHCl_2$ radicals will take place. Only one single experiment was carried out on the photolysis of CH_2Cl_2 in the presence of C_2H_5Cl not with the purpose of investigating this relatively complex system but rather with the aim to obtain additional evidence for the reactions leading to 2,3- and 1,3-dichlorobutane.

It was extremely gratifying to observe that these products were indeed produced. Even more significant was the fact that the ratio $R_{\text{meso-2,3-dichlorobutane}}$ over

$R_{\text{racemic-2,3-dichlorobutane}}$ was equal to unity in excellent agreement with the ratios reported in the previous section.

B. Photolysis of Ethyl Chloride at room temperature

The single experiment on the photolysis of CH_2Cl_2 in the presence of C_2H_5Cl confirmed the reaction mechanism proposed to explain the products observed in the photolysis of CCl_4 in the presence of C_2H_5Cl. Never the less, some doubt remained. In systems where quite a few products are formed there is always the possibility that some products might have coincided in the gas chromatographic analysis thus producing erroneous results for the calculated rate constants. Although this possibility seemed extremely remote since different gas chromatographic columns had yielded identical results some experimnets were carried out on the direct photolysis of ethyl chloride. The reaction products of this photolysis were: butane, 1-chlorobutane, 2-chlorobutane, meso 2,3-dichlorobutane, racemic 2,3-dichlorobutane and 1,3-dichlorobutane. The photolysis was carried out at room temperature and the rates of formation of all products except butane are reported in Table 8. It was extremely difficult to separate butane from the large excess of undecomposed C_2H_5Cl and butane was, therefore, not

Table 8 Photolysis of Ethyl Chloride at room temperature

Exp. No.	Init. conc. in molec./cc X 10^{-17}	Relative rates of reaction products						
	C_2H_5Cl	2-C_4H_9Cl	n-C_4H_9Cl	meso 2,3-DCB	racemic 2,3-DCB	meso/rac.	$\frac{2\text{-}C_4H_9Cl \quad 1,3\text{-DCB}}{n\text{-}C_4H_9Cl \quad 2,3\text{-DCB}}$	1,3-DCB
1	6.75	98	16	140	128	1.09	1.65	72
2	6.28	100	10	97	95	1.02	2.16	42
3	5.40	200	28	168	152	1.10	--	--
4	5.11	100	16	68	64	1.06	2.27	48
5	10.05	188	20	80	76	1.05	2.16	36
6	3.85	124	16	52	48	1.08	2.02	26
7	8.50	240	24	138	130	1.06	2.38	64

Note: DCB = Dichlorobutane

routinely measured. The formation of butane was, however, confirmed by a special analysis in which the gas chromatographic columns were cooled to -78°C to obtain a separation between C_4H_{10} and C_2H_5Cl. As mentioned earlier two techniques were generally used to analyse for the products on the gas chromatograph. In the "sample trap" technique all products and excess starting material would be frozen into a sample trap which would then be transferred to the gas chromatograph. The sample trap would be heated and the content would be swept in to the columns by the carrier gas. Unfortunately in this particular case the relatively high boiling dichlorobutanes did not evaporate immediately and appeared therefore on the gas chromatogram as long tailing peaks which made it extremely difficult to obtain quantitative measurements. The injection technique was, therefore, used. In this technique the products and excess starting material are frozen into a small cold finger. The material is then allowed to liquefy and part of it is withdrawn by a hypodermic inserted through a puncture type stopper. In this case, however, even this technique was difficult since C_2H_5Cl boils at 12.2°C. The syringe was therefore cooled by placing it on top of some dry ice before the products and excess C_2H_5Cl were withdrawn. In spite of these precautions there is no guarantee that some C_2H_5Cl may have evaporated from the syringe before injection in the gas chromato-

graphic column. The products given in Table 8 are therefore not reported in absolute rates but in relative rates. An example may be used to clarify this. It was not possible to determine how much meso-and racemic-2.2-dichlorobutane were formed in experiments 1 (Table 8) but it was possible to determine that the ratio $R_{meso\text{-}2,3\text{-}DCB}/R_{racemic\text{-}2,3\text{-}DCB}$ was equal to 1.09.

To explain the formation and relative distribution of the reaction products observed in the photolysis of C_2H_5Cl the following mechanism is proposed.

$$C_2H_5Cl + h\nu \longrightarrow C_2H_5 + Cl \quad (18)$$

$$CH_3CH_2Cl + Cl \longrightarrow CH_3CHCl + HCl \quad (19)$$

$$CH_3CH_2Cl + Cl \longrightarrow CH_2CH_2Cl + HCl \quad (20)$$

$$2C_2H_5 \longrightarrow C_2H_6 + C_2H_4 \quad (21)$$

$$C_2H_5 + CH_3CHCl \longrightarrow CH_3CH_2CHClCH_3 \quad (22)$$

$$C_2H_5 + CH_2CH_2Cl \longrightarrow CH_3CH_2CH_2CH_2Cl \quad (23)$$

$$2CH_3CHCl \longrightarrow CH_3CHClCHClCH_3 \text{ (meso and racemic)} \quad (24)$$

$$CH_3CHCl + CH_2CH_2Cl \longrightarrow CH_3CHClCH_2CH_2Cl \quad (25)$$

In order to keep the mechanism simple, possible disproportionation reactions between ethyl and C_2H_4Cl radicals have not been included. Products formed by disproportionation are all low boilers (such as C_2H_6, C_2H_4

C_2H_3Cl) and can not interfere with the analysis for the heavier products which are important for comparison with the previous by reported data.

The weak link in the C_2H_5Cl molecule is the C-Cl bond and primary step 16 needs almost no further explanation. The formation of ethyl radicals is clearly shown by the production of butane, 1,-and 2-chlorobutane; compounds which contain at least one ethyl radical.

The chlorine atom abstraction reactions and the subsequent reactions of CH_3CHCl and CH_2CH_2Cl radicals are completely analogous to those observed in the photolysis of CCl_4 in the presence of C_2H_5Cl.

The ratio $R_{\text{meso 2,3 DCB}}/R_{\text{racemic 2,3 DCB}} = 1.05 \pm 0.05$ in excellent agreement with the date from the previous section, where DCB represent dichlorobutane.

Some additional and new information may be gained from these data. From the reaction mechanism the following equation may be derived:

$$\frac{R_{2\text{-}C_4H_9Cl}\ R_{1,3\text{-DCB}}}{R_{1\text{-}C_4H_9Cl}\ R_{2,3\text{-DCB}}} =$$

$$\frac{k_{22}(C_2H_5)(CH_3CHCl)\ k_{25}(CH_3CHCl)(CH_2CH_2Cl)}{k_{23}(C_2H_5)(CH_2CH_2Cl)\ k_{24}(CH_3CHCl)(CH_3CHCl)} =$$

$$\frac{k_{22}k_{25}}{k_{23}k_{24}}$$

Data for $k_{22}k_{25}/k_{23}k_{24}$ are given in the last column of Table 8 and indicate that this ratio is equal to 2.1 ± 0.2.

C. Photolysis of Chloroform in the presence of Ethylene

A considerable amount of information has been gained in the previous section regarding combination and cross combination reactions of CH_3CHCl, CH_2CH_2Cl and various chlorinated methyl radicals. It seemed interesting to expand this knowledge by studying yet another system: the photolysis of chloroform in the presence of ethylene. From the information gained in the previous sections it was expected that the following reactions would occur:

$$CHCl_3 + h\nu \longrightarrow CHCl_2 + Cl \qquad (26)$$

$$C_2H_4 + Cl \longrightarrow C_2H_4Cl \qquad (27)$$

$$CHCl_3 + Cl \longrightarrow CCl_3 + HCl \qquad (28)$$

$$2\ CHCl_2 \longrightarrow C_2H_2Cl_4 \qquad (29)$$

$$2\ C_2H_4Cl \longrightarrow (C_2H_4Cl)_2 \qquad (30)$$

$$2\ C_2H_4Cl \longrightarrow C_2H_5Cl + C_2H_3Cl \qquad (31)$$

$$CHCl_2 + C_2H_4Cl \longrightarrow CHCl_2C_2H_4Cl \qquad (32)$$

$$CHCl_2 + C_2H_4Cl \longrightarrow CH_2Cl_2 + C_2H_3Cl \qquad (33)$$

$$CCl_3 + C_2H_4Cl \longrightarrow CCl_3CH_2CH_2Cl \qquad (34)$$

$$CCl_3 + C_2H_4Cl \longrightarrow HCCl_3 + C_2H_3Cl \qquad (35)$$

$$CCl_3 + CHCl_2 \longrightarrow C_2HCl_5 \qquad (36)$$

$$2\ CCl_3 \longrightarrow C_2Cl_6 \qquad (37)$$

Again C-Cl rupture is proposed as primary step in the photolysis of $CHCl_3$ (65) thus producing Cl atoms and $CHCl_2$ radicals. The chlorine atoms produced in the primary step may add to C_2H_4 to form CH_2CH_2Cl radicals (reaction 27) or they abstract a hydrogen atom from chloroform to form HCl and CCl_3 radicals (reaction 28). The addition of Cl atoms to C_2H_4 to produce C_2H_4Cl radicals is well extablished from photochlorination studies of ethylene. Stewart and Weidenbaum (66) suggested an activation energy of less than 1.4 kcal/mole for this reaction. Schmitz, Schumacher, and Jager (67) concluded that the activation energy for this reaction is approximately zero. It is interesting to point out that the C_2H_4Cl radicals produced in this system are exclusively CH_2CH_2Cl radicals and that thus mexo-and racemic-2,3-dichlorobutane will not be present as reaction products. This is confirmed by the data given in Table 9. This Table gives the rate of production of all compounds observed in the photolysis of $CHCl_3$ in the

Table 9 Photolysis of Chloroform in the presence of Ethylene

Exp. No.	Init. conc. in molec./cc X 10^{-17}		Rates of products in molecules/(sec. cc.) X 10^{-12}				
	$CHCl_3$	C_2H_4	CH_2Cl_2	1,3-$C_3H_5Cl_3$	$(CHCl_2)_2$ + $(C_2H_4Cl)_2$	1,1,1,3-$C_3H_4Cl_4$	C_2HCl_5
1	13.39	6.76	0.11	1.64	1.56	0.26	0.33
2	6.53	13.52	0.06	0.90	0.88	0.10	0.13
3	15.44	14.63	0.11	1.51	1.43	0.23	0.31
4	14.50	14.70	0.11	1.35	1.28	0.20	0.32
5	26.07	3.38	0.11	1.44	1.37	0.30	0.49
6	39.49	6.66	0.10	1.33	1.32	0.32	0.64
7*	39.32	4.84	--	0.01	0.01	0.01	0.02
8	39.29	3.12	0.09	1.36	1.33	0.36	0.53

* Experiment No. 7 was carried out with Corning filter 9-54.

presence of C_2H_4. All experiments were carried out at room temperature and the ratio of the starting materials $CHCl_3$ and C_2H_4 was varied by a factor of 13. In experiment number 7 a Corning filter 9-54 was used to omit radiation below 2200 A^o. The products reported in Table 9 are a direct result of disproportionation, recombination and cross-combination reactions of the three radicals (CH_2Cl, CCl_3 and CH_2CH_2Cl) produced by reactions 26, 27 and 28.

Unfortunately it was not possible to separate by gas chromatographic analysis 1,1,2,2-tetrachloroethane from 1,4-dichlorobutane and the sum of these products are reported in column 6 of Table 9. Thus, it was impossible to obtain a simple relationship for the recombination and cross-combination reactions of $CHCl_2$ and C_2H_4Cl radicals.

$$2\ CHCl_2 \longrightarrow CHCl_2CHCl_2 \qquad (29)$$

$$2\ C_2H_4Cl \longrightarrow ClC_2H_4C_2H_4Cl \qquad (30)$$

$$CHCl_2 + C_2H_4Cl \longrightarrow CHCl_2C_2H_4Cl \qquad (32)$$

In order to obtain, never the less, some quantitative information from the data reported in Table 9, the following derivations were made. According to the reaction mechanism given earlier the rates of $R_{CCl_3CH_2CH_2Cl}$ and $R_{C_2HCl_5}$ are related by the following

expression.

$$\frac{R_{CCl_3CH_2CH_2Cl}}{R_{C_2H_5Cl}} = \frac{k_{34}}{k_{36}} \frac{(CCl_3)(C_2H_4Cl)}{(CCl_3)(CHCl_2)} =$$

$$\frac{k_{34}}{k_{36}} \frac{(C_2H_4Cl)}{(CHCl_2)} \qquad (I)$$

The rate of $R_{CH_2ClCH_2CH_2Cl}$ is given by

$$R_{CHCl_2CH_2CH_2Cl} = k_{32}(CHCl_2)(C_2H_4Cl) \qquad (II)$$

Thus the concentration of $(CHCl_2)$ radicals may be expressed by:

$$(CH_2Cl) = R_{CH_2ClCH_2CH_2Cl} / k_{32}(C_2H_4Cl)$$

substitution this value into equation I yields

$$\frac{R_{CCl_3CH_2CH_2Cl}}{R_{C_2H_5Cl}} = \frac{k_{34}\ k_{32}\ (C_2H_4Cl)^2}{K_{36}\ R_{ClCH_2CH_2CH_2Cl}}$$

or

$$(C_2H_4Cl)^2 = \frac{k_{36}}{k_{34}k_{32}} \frac{R_{ClC_2H_4CHCl_2}\ R_{CCl_3C_2H_4Cl}}{R_{C_2HCl_5}}$$

As stated earlier it was not possible to measure the rates of production individually for 1,1,2,2-tetrachloroethane and 1,4-dichlorobutane but it was possible to measure the sum of these rates. Indicating the sum of these rates by R_{comb} the following equations may be given

$$R_{comb} = R_{C_2H_2Cl_4} + R_{(C_2H_4Cl)_2}$$

$$= k_{29}(CHCl_2)^2 + k_{30}(C_2H_4Cl)^2$$

Substitution of the values derived for $(CHCl_2)^2$ and $(C_2H_4Cl)^2$ yields

$$R_{comb} = \frac{k_{29}\ k_{34}}{k_{36}\ k_{32}} \frac{R_{ClC_2H_4CH_2Cl}\ R_{C_2HCl_5}}{R_{CCl_3C_2H_4Cl}} +$$

$$\frac{k_{30}k_{36}}{k_{34}k_{32}} \frac{R_{ClC_2H_4CH_2Cl}\ R_{CCl_3C_2H_4Cl}}{R_{C_2H_5Cl}}$$

This equation may be simplified to:

$$\frac{R_{comb}\ R_{C_2HCl_5}}{R_{CCl_3C_2H_4Cl}\ R_{C_2H_4ClCHCl_2}} =$$

$$\frac{k_{30}k_{36}}{k_{34}k_{32}} + \frac{k_{29}k_{34}}{k_{36}k_{32}} \frac{(R_{C_2HCl_5})^2}{(R_{CCl_3C_2H_4Cl})^2} \qquad \text{(III)}$$

or to:

$$\frac{R_{comb}\ R_{CCl_3C_2H_4Cl}}{R_{C_2H_4ClCHCl_2}\ R_{C_2HCl_5}} =$$

$$\frac{k_{29}k_{34}}{k_{36}k_{32}} + \frac{k_{30}k_{36}}{k_{34}k_{32}} \frac{(CCl_3C_2H_4Cl)^2}{(C_2HCl_5)^2} \qquad \text{(IV)}$$

The plot of the rate functions III and IV are given in Fibures 7 and 8 respectively. These plot yield $k_{29}k_{34}/k_{36}k_{32}$ equal to 0.32 and $k_{30}k_{36}/k_{34}k_{32}$ equal to 0.71. Thus, it is possible to obtain the ratio $k_{32}/k_{29}^{\frac{1}{2}}k_{30}^{\frac{1}{2}} = 2.09$.

Finally it is possible to compare the following disproportionation and recombination reactions.

$$CHCl_2 + C_2H_4Cl \longrightarrow ClCH_2CH_2CHCl_2 \qquad (32)$$

$$CHCl_2 + C_2H_4Cl \longrightarrow CH_2Cl_2 + C_2H_3Cl \qquad (33)$$

Although the data have not been tabulated in Table 9 the results yield $k_{33}/k_{32} = 0.08 \pm 0.01$. No previous values have been reported in the literature for this ratio of rate constants.

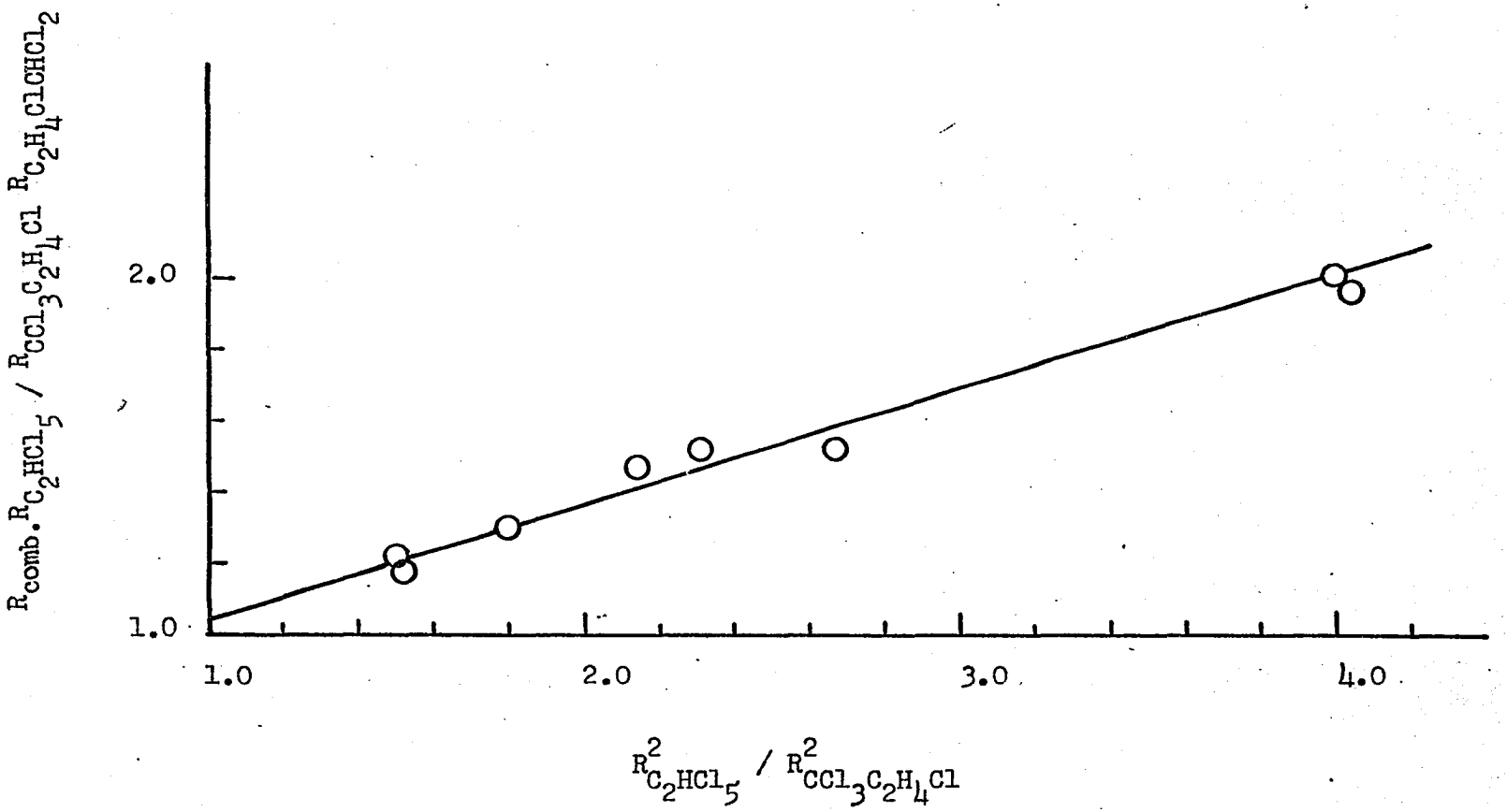


Figure 7. Photolysis of Chloroform in the Presence of Ethylene

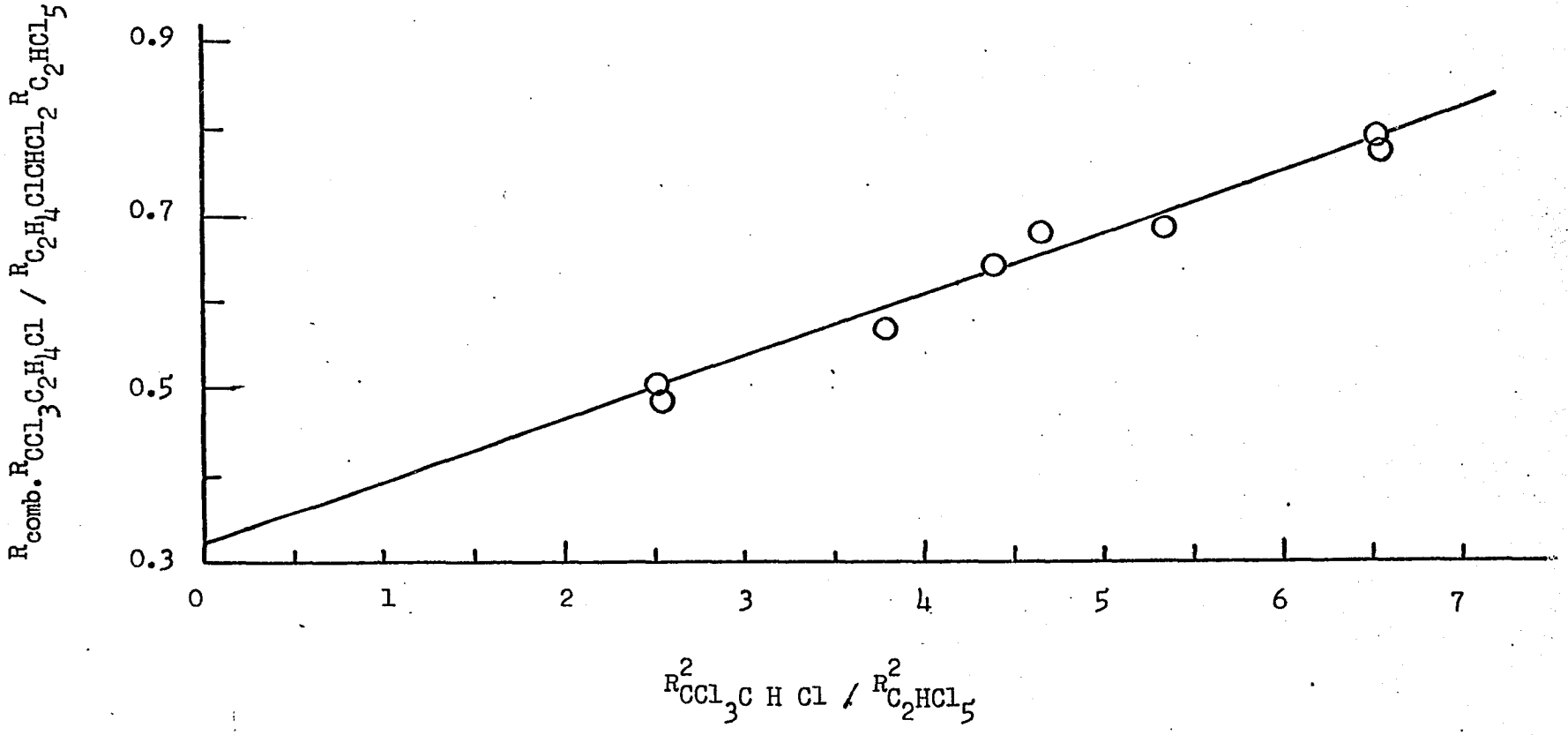


Figure 8. Photolysis of Chloroform in the Presence of Ethylene

D. Photolysis of Chloroform in the presence of Ethane

So far this study has dealt mainly with the reactions of Cl atoms with C_2H_5Cl and C_2H_4 and with the recombination and cross-combination reactions of CH_3CHCl and CH_2CH_2Cl radicals among themselves and with various chlorinated methyl radicals (CCl_3, $CHCl_2$ and CH_2Cl).

It seemed of interest to expand this study to include Cl atom reactions with ethane. Since the photolysis of CCl_4 in the presence of ethane has been studied previously (24), chloroform was choosen as the Cl atom donor. It was hoped that the results of this study could be compared and correlated not only to the data reported earlier in this thesis but also to the previously reported data on the photolysis of CCl_4 in the presence of C_2H_6.

Chlorine atoms produced by the photolysis of chloroform in the presence of ethane may abstract hydrogen atoms not only from ethane but also from chloroform itself. Data regarding these competing reactions should yield information regarding the relative strength of the C-H bond in ethane and chloroform.

The results of a series of experiments in which chloroform was photolyzed in the presence of ethane are reported in Table 10. The ratio of $CHCl_3$ to CH_3CH_3 was varied by a factor of 3. Less than 1% of the chloroform initially present was decomposed during the photolysis.

Table 10 Photolysis of Chloroform in the presence of Ethane

Exp. No.	Init. conc. in molecules/cc.X10^{-17}		Rates of products in molecules/(sec. cc.)X10^{-12}						
	C_2H_6	$CHCl_3$	CH_2Cl_2	$C_2H_5CHCl_2$	$C_2H_5CCl_3$	$(CHCl_2)_2$	C_2HCl_5	C_2Cl_6	C_4H_{10}
1	6.95	13.91	0.08	0.97	0.33	0.68	0.47	0.07	0.35
2	13.51	14.36	0.08	1.14	0.38	0.83	0.53	0.08	0.40
3	7.54	19.90	0.10	1.18	0.53	0.94	0.69	0.11	0.37
4	13.32	20.03	0.09	1.40	0.64	1.07	0.83	0.12	0.46
5	8.26	13.26	0.10	0.99	0.38	0.82	0.52	0.08	0.30
6	8.16	13.03	0.07	0.93	0.35	0.70	0.54	0.09	0.31
7	3.80	3.81	0.03	0.48	0.11	0.32	0.13	0.01	0.18
8	17.36	17.80	0.05	0.99	0.43	0.79	0.59	0.10	0.31

Note: All experiments were carried out at room temperature.

The following reactions are suggest to explain the formation and distribution of the reaction products.

$$CHCl_3 + h\nu \longrightarrow CHCl_2 + Cl \quad (38)$$

$$C_2H_6 + Cl \longrightarrow C_2H_5 + HCl \quad (39)$$

$$CHCl_3 + Cl \longrightarrow CCl_3 + HCl \quad (40)$$

$$2\ CHCl_2 \longrightarrow (CHCl_2)_2 \quad (41)$$

$$2\ C_2H_5 \longrightarrow C_4H_{10} \quad (42)$$

$$2\ C_2H_5 \longrightarrow C_2H_6 + C_2H_4 \quad (43)$$

$$2\ CCl_3 \longrightarrow C_2Cl_6 \quad (44)$$

$$CCl_3 + CHCl_2 \longrightarrow C_2HCl_5 \quad (45)$$

$$CCl_3 + C_2H_5 \longrightarrow C_2H_5CCl_3 \quad (46)$$

$$CCl_3 + C_2H_5 \longrightarrow C_2H_4 + CHCl_3 \quad (47)$$

$$CHCl_2 + C_2H_5 \longrightarrow C_2H_5CHCl_2 \quad (48)$$

$$CHCl_2 + C_2H_5 \longrightarrow CH_2Cl_2 + C_2H_4 \quad (49)$$

As shown in reaction 38, the primary step in the photolysis of CCl_3H produces $CHCl_2$ radical and chlorine atom. The chlorine atoms can abstract hydrogen atoms from both ethane and chloroform as indicated in reactions 39 and 40. The recombination reactions between two identical radicals such as $CHCl_2$, C_2H_5 and CCl_3 are

indicated by reactions 41, 42 and 44 respectively. The formation of the products such as C_2HCl_5, $C_2H_5CCl_3$, $C_2H_5CHCl_2$, and CH_2Cl_2 is explained by cross-combination and cross-disproportation as proposed in reactions 45, 46, 48 and 49 respectively. All the observed reaction products are clearly accounted for the above proposed reaction mechanism.

From the reaction mechanism the following equations may be derived.

$$\frac{R_{C_2H_5CCl_3}\ R_{(CHCl_2)_2}}{R_{C_2H_5CHCl_2}\ R_{CHCl_2CCl_3}} = \frac{k_{32}(C_2H_5)(CCl_3)\ k_{27}(CHCl_2)^2}{k_{34}(C_2H_5)(CHCl_2)\ k_{30}(CCl_2)^2}$$

$$= k_{27}k_{32}/k_{31}k_{34}$$

$$\frac{R_{C_2H_5CCl_3}\ R_{C_2HCl_5}}{R_{C_2H_5CHCl_2}\ R_{C_2Cl_6}} = \frac{k_{32}(C_2H_5)(CCl_3)\ k_{31}(CCl_3)(CHCl_2)}{k_{34}(C_2H_5)(CHCl_2)\ k_{30}(CCl_3)^2}$$

$$= k_{31}k_{32}/k_{30}k_{34}$$

These equations indicate that the ratios

$$\frac{R_{C_2H_5CCl_3}\ R_{(CHCl_2)}}{R_{C_2H_5CHCl_2}\ R_{C_2HCl_5}} \text{ and } \frac{R_{C_2H_5CCl_3}\ R_{C_2HCl_5}}{R_{C_2H_5CHCl_2}\ R_{C_2Cl_6}} \text{ should}$$

be constant at a given temperature. This is confirmed by the data which yield $k_{41}k_{46}/k_{45}k_{48} = 0.5 \pm 0.05$ and $k_{45}k_{46}/k_{44}k_{48} = 2.5 \pm 0.3$

From the rates of production of $(CHCl_2)_2$, C_2Cl_6 and C_2HCl_5, the following cross-combination relationship may be obtained. This relationship ought to be constant, independent of the concentration of the reactants, chloroform and ethane, and independent of the total pressure in the initial state.

$$\frac{R_{CHCl_2CCl_3}}{R^{\frac{1}{2}}_{(CHCl_2)_2}\ R^{\frac{1}{2}}_{C_2Cl_6}} = \frac{k_{45}(CHCl_2)_2(CCl_3)}{k^{\frac{1}{2}}_{41}(CHCl_2)\ k^{\frac{1}{2}}_{44}(CCl_3)} = k_{45}/k^{\frac{1}{2}}_{41}k^{\frac{1}{2}}_{44}$$

The results show that within experimental error this ratio is constant and establishes that $k_{45}/k^{\frac{1}{2}}_{41}k^{\frac{1}{2}}_{44}$ is equal to 2.2 ± 0.1.

It is interesting to carry out a material balance calculation in order to see whether, within experimental error, all products are accounted for. If all the chlorine atoms produced by primary step 38 react with ethane or chloroform, the ratio $R_{CHCl_2}/R_{CCl_3} + R_{C_2H_5}$ should be equal to unity. In the above expression R_{CHCl_2}, R_{CCl_3}, and $R_{C_2H_5}$ denote the rates of production of $CHCl_2$, CCl_3 and C_2H_5 radicals respectively. These rates have been calculated according to

$$R_{CHCl_2} = R_{CH_2Cl_2} + R_{C_2H_5CHCl_2} + R_{C_2HCl_5} + 2\,R_{(CHCl_2)_2} \qquad (V)$$

$$R_{CCl_3} = R_{C_2HCl_5} + 2\,R_{C_2Cl_6} + 1.22\,R_{C_2H_5CCl_3} \qquad (VI)$$

and

$$R_{C_2H_5} = R_{CH_2Cl_2} + R_{C_2H_5CHCl_2} + 1.22\,R_{C_2H_5CCl_3} + 2.28\,R_{C_4H_{10}} \qquad (VII)$$

Collisions between C_2H_5 and CCl_3 radicals may lead to $CCl_3C_2H_5$ or to C_2H_4 and CCl_3H as indicated by reactions 46 and 47.

$$C_2H_5 + CCl_3 \longrightarrow C_2H_5CCl_3 \qquad (46)$$

$$C_2H_5 + CCl_3 \longrightarrow C_2H_4 + CHCl_3 \qquad (47)$$

It was impossible to analyse for trace amounts of C_2H_4 produced in the presence of a large excess of C_2H_6. Neither is it, of course, possible to determine the amount of $CHCl_3$ produced by reaction 47 since chloroform is a starting material. Previous investigation (24) have however reported $k_{47}/k_{46} = 0.22$. Thus, it is possible to calculate the amount of C_2H_5 and CCl_3 radicals which have reacted according to reaction 47 from the amount of $C_2H_5CCl_3$ produced in reaction 46. Hence R_{CCl_3} and $R_{C_2H_5}$

(equations VI and VII) contain the term 1.22 $R_{C_2H_5CCl_3}$ where 1.0 $R_{C_2H_5CCl_3}$ accounts for reaction 46 and 0.22 $R_{C_2H_5CCl_3}$ for reaction 47.

Similarly it has been reported that the value $k_{43}/k_{42} = 0.14$ (26-30). Where k_{29} and k_{28} are the rate constants of reactions 42 and 43 respectively.

$$2\ C_2H_5 \longrightarrow C_4H_{10} \qquad (42)$$

$$2\ C_2H_5 \longrightarrow C_2H_6 + C_2H_4 \qquad (43)$$

Since two ethyl radical disappear in each reaction the total amount of ethyl radicals involved in these reactions is therefore given by 2.28 $R_{C_4H_{10}}$ as indicated in equation VII.

The results of this material balance calculations are given in column 4 Table 11. Considering the complexity of these calculations the data are in good agreement with the theoretical value of unity expected for this ratio.

Information on the reactivity difference between reactions 25 and 26 may be obtained in the following manner.

$$C_2H_6 + Cl \longrightarrow C_2H_5 + HCl \qquad (39)$$

$$CHCl_3 + Cl \longrightarrow CCl_3 + HCl \qquad (40)$$

According to these reactions

Table 11 Ratios of rate constants for the photolysis of Chloroform in the presence of Ethane

Exp. No.	$\frac{R_{C_2H_5CHCl_2} R_{C_2HCl_5}}{R_{C_2H_5CCl_3} R_{(CHCl_2)_2}}$	$\frac{R_{C_2H_5CCl_3} R_{C_2HCl_5}}{R_{C_2H_5CHCl_2} R_{C_2Cl_6}}$	$\frac{R_{CHCl_2}}{R_{(C_2H_5 + CCl_3)}}$	$\frac{R_{C_2HCl_5}}{R^{\frac{1}{2}}_{C_2Cl_6} R^{\frac{1}{2}}_{(CHCl_2)_2}}$	$P_{C_2H_6} \times R_{CCl_3} / P_{CHCl_3} \times R_{C_2H_5}$
1.	2.0	2.3	0.88	2.12	0.23
2	1.9	2.3	0.92	2.07	0.41
3	1.7	2.8	0.89	2.17	0.24
4	1.7	3.0	0.87	2.30	0.37
5	1.7	2.6	0.98	2.10	0.32
6	2.0	2.2	0.90	2.09	0.34
7	1.8	2.4	0.96	2.12	0.26
8	1.8	2.5	0.90	2.11	0.56

Note: R_x = Rate of formation of compound x in molecules/(sec. cc.)$\times 10^{-12}$.

P_x = Initial concentration of reactant x in molecules/cc$\times 10^{-17}$.

R_{CCl_3} = Rate formation of radicals CCl_3.

$$R_{CCl_3}P_{C_2H_6}/R_{C_2H_5}P_{CHCl_3} = k_{40}/k_{39}$$

In the above equation R_{CCl_3} again denotes the rate of production of CCl_3 radicals, $R_{C_2H_5}$ the rate of production of ethyl radicals; $P_{C_2H_6}$ denotes the initial pressure of ethane, P_{CHCl_3} the initial pressure of chloroform. The data obtained for k_{40}/k_{39} are given in the last column of Table 11 and, omitting the result of experiment number 8, indicate that $k_{40}/k_{39} = 0.3 \pm 0.1$.

Finally it is possible to obtain data regarding the disproportionation over recombination reactions between $CHCl_2$ and C_2H_5 radicals.

$$CHCl_2 + C_2H_5 \longrightarrow C_2H_5CHCl_2 \qquad (48)$$

$$CHCl_2 + C_2H_5 \longrightarrow CH_2Cl_2 + C_2H_4 \qquad (49)$$

Although the results of the individual experiments are not tabulated in Table 11, the results clearly indicate that $k_{49}/k_{48} = 0.08 \pm 0.02$.

The data obtained for the various rate constants will be discussed in the next chapter.

DISCUSSION

The reactions which have been given in the previous section to explain the observed results may be classified in three parts: primary reactions, chlorine atom abstraction reactions and finally recombination and disproportionation reactions. It seems logical to discuss the obtained results in this order.

(I). Primary Reactions.

Primary reactions are reactions which are a direct result of the absorption of a quantum of light by a molecule. Since the main study dealt with the photolysis of carbon tetrachloride in the presence of ethyl chloride it is important to consider in detail the possible primary reactions.

In order to explain the observed results it was suggested that the absorption of a quantum of light by CCl_4 caused this molecule to decompose into a CCl_3 radical and a Cl atom as indicated by reaction 1.

$$CCl_4 + h\nu \longrightarrow CCl_3 + Cl \qquad (1)$$

This step has been previously suggested by Pfordte (58) and has recently been discussed in detail by Roquitte and Wijnen (23) who studied the photolysis of CCl_4 in the

presence of ethylene. It has also been suggested by Abramson, Buckhold and Firestone (62) as well as by several other authors (59-61) that CCl_4 decomposes into Cl atoms and CCl_3 radicals as a result of the gamma-ray irradiation of carbon tetrachloride. Curme and Rollefson (68) have proposed the same primary process in order to explain the data obtained in the quenching of the fluorescence of bata-naphthylamine by CCl_4.

Simons and Yarwood (69) have shown that vibrationally excited CCl_3 radicals are produced in the flash photolysis of CCl_3Br and that these vibrationally excited radicals may decompose into CCl radicals and molecular chlorine. However, this step is not important in the present investigation as explained by Roquitte and Wijnen (23). The absorption maximum of carbon tetrachloride is at about 2200 A^o (63, 70), and the energy absorbed by the CCl_4 molecule in the primary step will thus be about 120 kcal/mole. The carbon-chlorine bond in CCl_4 is given as 68 kcal/mole (71). This leaves only a maximum of 52 kcal per mole of excess energy to be concentrated in the CCl_3 radical. The decomposition of a CCl_3 radical into CCl and Cl_2 requires about 80 kcal/mole, as calculated by Simons and Yarwood (69), and, thus, it is clear that this step cannot be important to any appreciable extent. Further more, at the relatively high pressures of the present investigation, collisional deactivation of excited radicals

would occur rapidly and would increase with increasing pressures. The fact that the data do not show any pressure dependence confirms that excited radicals did not play a role in the formation of the observed products.

In the photolysis of mixtures of CCl_4 and C_2H_5Cl one other possible primary process must be considered-the decomposition of C_2H_5Cl itself.

$$C_2H_5Cl + h\nu \longrightarrow C_2H_5 + Cl \qquad (18)$$

That this step may, indeed, occur is clearly indicated by the reaction products obtained in the direct photolysis of C_2H_5Cl itself (see previous chapter, section II part B). The carbon-chlorine bond rupture in C_2H_5Cl is obviously completely analogous to the primary step in the photolysis of CCl_4. Reaction 18 has also been suggested by Schindler (72) to explain data obtained by the gamma-ray radiolysis of C_2H_5Cl.

Thus, in principle, two primary processes must be considered-reactions 1 and 18 if a mixture of CCl_4 and C_2H_5Cl is photolysed. Never-the-less, the results obtained in the previous section indicate clearly that the products originate exclusively from primary step 1 and not from reaction 18. The following experimental facts are given to support this statement:

(a). If direct photochemical decomposition of ethyl chloride had occurred, the ethyl radicals produced in this

step would have reacted by recombination among themselves to form butane or by recombining with other radicals present in the system (such as CCl_3, CH_2CH_2Cl etc.) to produce $C_2H_5CCl_3$, $C_2H_5CH_2CH_2Cl$ etc. None of these products were observed.

(b). The material balance calculation for this investigation did yield $R_{CCl_3}/R_{Cl} = 1.07 \pm 0.05$. This value was calculated under the assumption that all radicals were initiated exclusively by step 1- the photolysis of carbon tetrachloride.

$$CCl_4 + h\nu \longrightarrow CCl_3 + Cl \qquad (1)$$

It is easy to see that under this condition R_{CCl_3}/R_{Cl} must be equal to unity as indeed, within experimental error, observed. If, on the other hand, also reaction 18 occurs

$$C_2H_5Cl + h\nu \longrightarrow C_2H_5 + Cl \qquad (18)$$

then the ratio R_{CCl_3}/R_{Cl} must be smaller than unity since now Cl atoms are also produced by reaction 18. Furthermore, this ratio must decrease with increasing C_2H_5Cl pressure if reaction 18 plays an important role in the overall reaction mechanism. The fact that the ratio R_{CCl_3}/R_{Cl} is completely independent of the initial pressures of CCl_4 and C_2H_5Cl clearly shows that these two molecules do not compete in absorbing light within

the concentration range of this investigation. This observation is in complete agreement with information obtained from the absorption spectra of carbon tetrachloride and ethyl chloride. Data by Treiber, Berndt and Toplak (63), given in figure 6, confirm that the absorption coefficient of CCl_4 is considerably larger than that of C_2H_5Cl thus confirming that the reaction products should originate mainly, if not exclusively, from reaction 1, the absorption of light by CCl_4.

(II). Chlorine atom abstraction reactions

Chlorine atoms, produced by the primary step of the photolysis of CCl_4, may abstract hydrogen atoms from either the CH_3 side or the CH_2Cl side of ethyl chloride to produce primary or secondary C_2H_4Cl radicals as given by reactions 2 and 3.

$$Cl + CH_3CH_2Cl \longrightarrow CH_3CHCl + HCl \qquad (2)$$

$$Cl + CH_3CH_2Cl \longrightarrow CH_2CH_2Cl + HCl \qquad (3)$$

The following two abstraction reactions were not included in the general mechanism given on page 42.

$$Cl + CCl_4 \longrightarrow CCl_3 + Cl_2 \qquad (50)$$

$$Cl + CH_3CH_2Cl \longrightarrow C_2H_5 + Cl_2 \qquad (51)$$

The C-Cl bond in CCl_4 is 68 kcal/mole (71) and the Cl-Cl bond in Cl_2 is 57 kcal/mole (78). Thus, reaction 50 will have an activation energy of at least 11 kcal/mole. The same reasoning leads to a minimum activation energy of 23 kcal/mole for reaction 51 since the C-Cl bond in C_2H_5Cl is approximately 80 kcal/mole (74). Reactions 2 and 3, on the other hand, will have activation energies not exceeding 1 kcal/mole. Reaction 3 may be compared to the following reactions:

$$Cl + CH_3CH_3 \longrightarrow C_2H_5 + HCl \qquad (39)$$

$$Cl + CH_3CH_2CH_3 \longrightarrow CH_2CH_2CH_3 + HCl \qquad (52)$$

In reaction 52 the Cl atom in C_2H_5Cl has been replaced by a methyl radical. If it is accepted that ethylchloride may be considered as propane than the activation energy of reaction 3 should be 1 kcal/mole-the value reported for reactions 52 by Knox and Nelson (75). Alternately it may be stated that the abstraction of an H atom from the methyl group in CH_3CH_2Cl will not be more difficult than the abstraction of an H atom from C_2H_6 and in that case an activation energy of unity is also expected since both Knox and Nelson (75) and also Goldfinger and co-workers (76) report an activation energy of 1 kcal/mole for reaction 39. Furthermore, experiments carried out in this laboratory by Kelly, Yu and Wijnen (77) indicate that the C-H bonds in carbons neighbouring to carbons containing a

Cl atom are weakened considerably. Thus, it is expected that the C-H bond in the methyl group of C_2H_5Cl may be less than the value of 1 kcal/mole reported for ethane. Since the experimental results prove that $E_2 < E_3$ it is completely justifiable to assume that reactions 50 and 51 (having activation energies exceeding 11 kcal/mole) will not play a significant role in the overall reaction mechanism.

As pointed out in the previous chapter the rate of production of CH_3CHCl radicals by reaction 2 and of CH_2CH_2Cl radicals by reaction 3 was measured and yielded

$$R_{\Sigma CH_2CH_2Cl}/R_{\Sigma CH_3CHCl} = 0.17 \pm 0.02$$

$$Cl + CH_3CH_2Cl \longrightarrow CH_3CHCl + HCl \qquad (2)$$

$$Cl + CH_3CH_2Cl \longrightarrow CH_2CH_2Cl + HCl \qquad (3)$$

From reactions 2 and 3 the relationship of

$$\frac{R_{\Sigma CH_2CH_2Cl}}{R_{\Sigma CH_3CHCl}} = \frac{k_3(C_2H_5Cl)(Cl)}{k_2(C_2H_5Cl)(Cl)} = 0.17 \pm 0.02$$

This equation may be modified to:

$$\frac{R_{\Sigma CH_2CH_2Cl}}{R_{\Sigma CH_3CHCl}} = \frac{3\,k_3}{2\,k_2} = 0.17 \pm 0.02$$

Since C_2H_5Cl provides three hydrogen atoms for abstraction by reaction 3 and only two hydrogen atoms for abstraction by reaction 2. Thus a value of $k_3/k_2 = 0.11 \pm 0.01$ is obtained. It should be pointed out that no previous quantitative data are available regarding reactions 3 and 2. Most recently Kelly and Wijnen (73) have studied the chlorination of C_2H_5Cl by photodecomposition of ICl in daylight. They obtained a value $k_3/k_2 = 0.14 \pm 0.02$. Considering the fact that these data have been obtained from completely different systems the agreement is excellent. The data establish without any doubt that reaction 2 proceeds much more rapidly than reaction 3 and that thus the C-H bond in the CH_2Cl group of C_2H_5Cl is much weaker than the C-H bond in the CH_3 group of C_2H_5Cl.

To explain this difference in reactivity of the C-H bonds in C_2H_5Cl the following points may be considered. First it is appropriate once more to consider C_2H_5Cl as a substituted propane, where the methyl group has been replaced by a Cl atom. Reactions 2 and 3 are then analogous to reactions 53 and 52:

$$Cl + CH_3CH_2CH_3 \longrightarrow CH_3\dot{C}HCH_3 + HCl \qquad (53)$$

$$Cl + CH_3CH_2CH_3 \longrightarrow \dot{C}H_2CH_2CH_3 + HCl \qquad (52)$$

Data by Knox and Nelson (75) yield $k_{52}/k_{53} = 0.47$, data by Kelly and Wijnen (84) give a value of $k_{52}/k_{53} = 0.44$. In both cases the individual rate constants are calculated

per available hydrogen atom as was done in calculating k_3/k_2. The fact that k_3/k_2 is much smaller than k_{52}/k_{53} indicates that the comparison between propane and ethyl chloride is not too valid.

A much better explanation for the observed difference in k_3 and k_2 is provided by the electron withdrawing power of the highly electronegative Cl atom. The electrons are drawn toward the Cl atom thus weakening the C-H bonds. This explanation is in complete agreement with other observations regarding the C-H bond strengths in substituted methanes. As an example may be given the activation energies of 18.3, 14.5 and 9.3 kcal/mole for the H atom abstraction reaction by bromine atoms from CH_4, CH_3Cl and $CHCl_3$ respectively (79). Finally it should be mentioned that the data regarding k_3 and k_2 are also in qualitative agreement with estimates by Semenov (80) regarding the C-H bond strengths in C_2H_5Cl. From thermochemical data Semenov estimates that the C-H bond on the CH_2Cl side is approximately 4 kcal/mole weaker than the C-H bond in the methyl group of C_2H_5Cl. Thus reaction 2 should proceed much faster than reaction 3 as indeed observed.

One other set of data was obtained regarding H atom abstraction reactions by Cl atoms. By photolysis of $CHCl_3$ in the presence of ethane information regarding the following reactions was obtained:

$$Cl + C_2H_6 \longrightarrow C_2H_5 + HCl \qquad (39)$$

$$Cl + CHCl_3 \longrightarrow CCl_3 + HCl \qquad (40)$$

The data yielded $R_{CCl_3}/R_{C_2H_5} = 0.3 \pm 0.1$. Taking into account that ethane has six hydrogen atoms and chloroform only one hydrogen atom available for abstraction the relative ratio of rate constants per available hydrogen atom $k_{40}/k_{39} = 1.8 \pm 0.6$. It must be admitted that these data are not as accurate as might have been hoped for. However, in general, data throughout the literature regarding Cl atoms show considerable scatter. As an example may be given the H atom abstraction reaction from CH_3Cl by Cl atoms

$$Cl + CH_3Cl \longrightarrow CH_2Cl + HCl \qquad (54)$$

Knox reports $k_{54} = 2.6 \times 10^{13} e^{-3070/RT}$ (81), while Pritchard, Pyke and Trotman-Dickenson report $k_{54} = 5 \times 10^{13} e^{-3400/RT}$ cm^3/mole sec. Nevertheless, the value $k_{40}/k_{39} = 1.8 \pm 0.6$ proves conclusively that the H atom abstraction from $CHCl_3$ proceeds faster than the H atom abstraction from C_2H_6 by Cl atoms. Some data are available in the literature regarding Cl atom abstractions and in Table 12 a summary is given of data relating directly to the present investigation. The data in Table 12 yield $k_{40}/k_{39} = 1 \times 10^{-3}$; this investigation indicates $k_{40}/k_{39} = 1.8 \pm 0.6$. It is not possible to offer an

explanation for this enormous discrepancy. It is, however, possible to take a closer look at these abstraction reactions. In the reaction

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

the same H-Cl bond is formed regardless of the nature of RH. It is, thus, to be expected that the activation

Table 12. Literature data regarding H atom abstraction reactions by Cl atoms.

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

RH	$10^{-10}k(298^{\circ}K)$ per available H atom	$E_{activ.}$ cal/mole	Reference
CH_4	0.94	3850	75
$CHCl_3$	2.5	3350	81
C_2H_6	2500	1040	75

Note: k = rate constant in $cm^3/(sec. mole)$.

energy of the abstraction reaction would depend to a large extent on the strength of the C-H bond in the RH molecule. The C-H bond in CH_4 is 102 kcal/mole (83)

in C_2H_6 98 kcal/mole (85) and in $CHCl_3$ about 90 kcal/mole (83). These data are not consistent with the activation energies and reaction rates reported in Table 12. These bond strengths data suggest that H atom abstraction by Cl atoms might be easier from $CHCl_3$ than from C_2H_6 as indeed suggested by the experimental value k_{40}/k_{39} obtained in this research. In addition it may be pointed out that Kelly and Wijnen (86) also disagree with the data reported in Table 12. Since they obtained a value $k_{C_2H_6}/k_{CH_4} = 53$ rather than 2500 as indicated in Table 12. In conclusion it may be stated that the data from this research raise serious doubt regarding the accuracy of some data in the literature for Cl atom abstraction reactions.

(III). Recombination and Disproportionation Reactions

A considerable amount of information has been gained in the present study regarding recombination and disproportionation reactions of CCl_3, CH_3CHCl, CH_2CH_2Cl, $CHCl_2$ and C_2H_5 radicals.

A. Cross Combination Reactions

Regarding cross combination reactions, the following data have been obtained.

$$2\ CCl_3 \longrightarrow C_2Cl_6 \qquad (4)$$

$$2\ CH_3CHCl \longrightarrow (CH_3CHCl)_2 \qquad (5)$$

$$CCl_3 + CH_3CHCl \longrightarrow CH_3CHClCCl_3 \qquad (10)$$

$$k_{10}/k_4^{\frac{1}{2}}k_5^{\frac{1}{2}} = 2.2 \pm 0.1$$

$$2\ CHCl_2 \longrightarrow (CHCl_2)_2 \qquad (29)$$

$$2\ CH_2CH_2Cl \longrightarrow (CH_2CH_2Cl)_2 \qquad (30)$$

$$CHCl_2 + CH_2CH_2Cl \longrightarrow CHCl_2CH_2CH_2Cl \qquad (32)$$

$$k_{32}/k_{29}^{\frac{1}{2}}k_{30}^{\frac{1}{2}} = 2.0 \pm 0.1$$

$$2\ CHCl_2 \longrightarrow (CHCl_2)_2 \qquad (29)$$

$$2\ CCl_3 \longrightarrow C_2Cl_6 \qquad (4)$$

$$CHCl_2 + CCl_3 \longrightarrow CCl_3CHCl_2 \qquad (45)$$

$$k_{45}/k_{29}^{\frac{1}{2}}k_4^{\frac{1}{2}} = 2.2 \pm 0.1$$

None of the above data have previously been reported in the literature. Thus, it is not possible to make a direct comparison. These values, however, are in excellent agreement with similar ratios of rate constants observed for alkyl radicals by various authors as given in Table 1 (17-25). Little information regarding chlorinated alkyl radicals has been reported in the literature; Schindler (72) obtained the cross combination relationship for the following system:

$$2\ C_2H_5 \longrightarrow C_4H_{10} \qquad (42)$$

$$2\ C_2H_4Cl \longrightarrow (C_2H_4Cl)_2 \qquad (30)$$

$$C_2H_5 + C_2H_4Cl \longrightarrow C_4H_9Cl \qquad (50)$$

and observed: $k_{50}/k_{42}^{\frac{1}{2}}k_{31}^{\frac{1}{2}} = 1.92 \pm 0.2$

Wijnen (24) studied the combination and cross-combination reactions of ethyl and trichloromethyl radicals:

$$2\ C_2H_5 \longrightarrow C_4H_{10} \qquad (42)$$

$$2\ CCl_3 \longrightarrow C_2Cl_6 \qquad (4)$$

$$CCl_3 + C_2H_5 \longrightarrow C_2H_5CCl_3 \qquad (46)$$

and obtained: $k_{46}/k_{42}^{\frac{1}{2}}k_4^{\frac{1}{2}} = 2.0 \pm 0.15$

All these values are in good agreement with each other as expected through the simple collision theory consideration. From the data obtained for the ratios of cross-combination over combination reactions it is clear that these values are all approximately equal to two-regardless of the nature of the participating radicals. This is to be expected from considerations of the collision theory if no disproportionation reactions occur or if disproportionation reactions are negligible compared to combination reactions.

Since disproportionation reactions between $CHCl_2$ and CCl_3 radicals are extremely unlikely it is interesting to calculate the theoretical value of $k_{45}/k_4^{\frac{1}{2}}k_{29}^{\frac{1}{2}}$ and to

compare this value to the experimental value of 2.2 ± 0.1 obtained in this investigation.

According to the collision theory the rate constant is given by $k = PZ\exp(-E/RT)$ where P is a steric factor, Z is the collision number per unit concentration and E is the activation energy of the particular reaction. The collision number between indentical radicals is given by $Z_{AA} = \sigma_A^2(4\pi kT/M_A)^{\frac{1}{2}}$ and between unlike radicals by

$$Z_{AB} = \sigma_{AB}^2(8\pi kT/u)^{\frac{1}{2}} \quad (87)$$

Thus:

$$k_{45}/k_4^{\frac{1}{2}}k_{29}^{\frac{1}{2}} = \frac{P_{AB}\sigma_{AB}^2(8\ kT/u)^{\frac{1}{2}}}{P_{AA}^{\frac{1}{2}}P_{BB}^{\frac{1}{2}}\sigma_A\sigma_B(4\pi kT/M_A)^{\frac{1}{4}}(4\pi kT/M_B)^{\frac{1}{4}}}\ \exp(E_A+E_B-E_{AB}/RT) \quad \text{(VIII)}$$

In the above expression: k_{45}, k_4 and k_{29} are the rate constants of reactions 45, 4 and 29 repectively, k is the Boltzman constant, u is the reduced mass $= M_AM_B/(M_A+M_B)$, where M_A is the mass of a $CHCl_2$ radical M_B the mass of a CCl_3 radical, σ_A, σ_B and σ_{AB} are collision diameters.

No accurate data are available for the collision diameters of free radicals. It is seems, however, reasonable to assume that the collision diameter of the $CHCl_2$ radical will not differ to any appreciable extent from the diameter of CH_2Cl_2 and a value of 4.76 A^o, reported by Lambert and Salter (88) as the collision diameter of

CH_2Cl_2, has been used for σ_{CHCl_2}. Similarly σ_{CCl_3} has been accepted to be equal to 5.43 A^o reported as the collision diameter of $CHCl_3$ by Sette, Busala and Hubbard (89). The collision diameter σ_{AB} for a reaction between unlike radicals has been calculated from $\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B)$.

It is generally accepted that recombination reactions between free radicals in the gas phase have zero activation energies thus equation VIII simplifies to:

$$k_{45}/k_4^{\frac{1}{2}}k_{29}^{\frac{1}{2}} = \frac{P_{AB}\sigma_{AB}^{\frac{1}{2}}(8\pi kT/u)^{\frac{1}{2}}}{P_{AA}^{\frac{1}{2}}P_{BB}^{\frac{1}{2}}\sigma_A\sigma_B(4\pi kT/u)^{\frac{1}{2}}(4\pi kT/M_B)^{\frac{1}{2}}}$$

If it is further accepted that the ratio $P_{AB}/P_{AA}^{\frac{1}{2}}P_{BB}^{\frac{1}{2}}$ is equal to unity a value of 2.04 may be calculated from equation VIII for $k_{45}/k_4^{\frac{1}{2}}k_{29}^{\frac{1}{2}}$. This value is in excellent agreement with the experimental observed value of 2.2 ± 0.1.

Other ratio of rate constants for recombination and cross-combination reactions obtained in this study are:

$$2\ CH_3CHCl \longrightarrow (CH_3CHCl)_2 \qquad (5)$$

$$CH_3CHCl + CCl_3 \longrightarrow CH_3CHClCCl_3 \qquad (10)$$

$$CH_2CH_2Cl + CCl_3 \longrightarrow CCl_3CH_2CH_2Cl \qquad (12)$$

$$CH_3CHCl + CH_2CH_2Cl \longrightarrow CH_3CHClCH_2CH_2Cl \qquad (14)$$

$$k_{10}k_{14}/k_5k_{12} = 2.0 \pm 0.1$$

$$C_2H_5 + CH_3CHCl \longrightarrow 2\text{-}C_4H_9Cl \quad (22)$$

$$C_2H_5 + CH_2CH_2Cl \longrightarrow 1\text{-}C_4H_9Cl \quad (23)$$

$$2\ CH_3CHCl \longrightarrow (CH_3CHCl) \quad (5)$$

$$CH_3CHCl + CH_2CH_2Cl \longrightarrow CH_3CHClCH_2CH_2Cl \quad (14)$$

$$k_{22}k_{14}/k_{23}k_5 = 2.1 \pm 0.2$$

$$2\ CHCl_2 \longrightarrow (CHCl_2)_2 \quad (29)$$

$$CHCl_2 + CCl_3 \longrightarrow C_2HCl_5 \quad (45)$$

$$C_2H_5 + CCl_3 \longrightarrow C_2H_5CCl_3 \quad (46)$$

$$CHCl_2 + C_2H_5 \longrightarrow C_2H_5CHCl_3 \quad (48)$$

$$k_{45}k_{48}/k_{29}k_{46} = 1.82 \pm 0.2$$

$$2\ CCl_3 \longrightarrow C_2Cl_6 \quad (4)$$

$$CHCl_2 + CCl_3 \longrightarrow C_2HCl_5 \quad (45)$$

$$C_2H_5 + CCl_3 \longrightarrow C_2H_5CCl_3 \quad (46)$$

$$CHCl_2 + C_2H_5 \longrightarrow C_2H_5CHCl_2 \quad (48)$$

$$k_{45}k_{46}/k_4k_{48} = 2.5 \pm 0.3$$

In looking over these data, the ratio's of rate constants of these reactions again seem to have an approximate value of two.

In a rather rough manner this may be explained by the following considerations. If, as stated before, the activation energies of recombination reactions are zero and if the ratio of steric factors of these reactions is

approximately equal to unity then the ratio of rate constants is determined by the collision numbers. accepting for simplicity's sake that the radicals are present in unit concentrations and applying these considerations to the following set of equations.

$$2\ CH_3CHCl \longrightarrow (CH_3CHCl_2)_2 \qquad (5)$$

$$CH_3CHCl + CCl_3 \longrightarrow CH_3CHClCCl_3 \qquad (10)$$

$$CH_2CH_2Cl + CCl_3 \longrightarrow CCl_3CH_2CH_2Cl \qquad (12)$$

$$CH_3CHCl + CH_2CH_2Cl \longrightarrow CH_3CHClCH_2CH_2Cl \qquad (14)$$

It is clear that one molecule of $CH_3CHClCCl_3$, of $CCl_3CH_2CH_2Cl$ or of $CH_3CHClCH_2CH_2Cl$ may be formed by reactions 10, 12 or 14 but that only one half of one molecule can be formed via reaction 5. Thus the ratio of rate constants $k_{10}k_{14}/k_5k_{12}$ should be approximately equal to 1 x 1/1 x $\frac{1}{2}$ = 2 as indeed observed. Deviations from this extremely crude calculated value of two may of course be caused by the fact that the steric factors do not cancel each other out as assumed and by the fact that in some cases disproportionation reactions between two radicals occur which should be taken in to account since these reactions result from the same collision between two radicals as that one leading to recombination products.

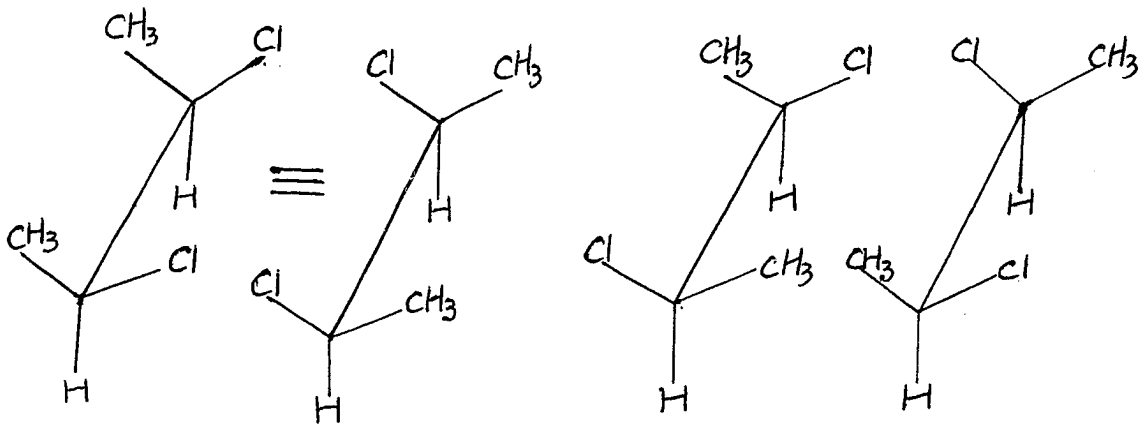
Finally it is of interest to study in somewhat great detail the recombination of two CH_3CHCl radicals

since this reaction produces different stereochemical isomers.

$$2\ CH_3CHCl \longrightarrow (CH_3CHCl)_2 \qquad (4)$$

meso and racemic

The configuration of the meso and racemic isomers of 2,3-dichlorobutane can be clearly represented by the following structures.



meso form racemic (dl pair)

(I) (II) (III) (IV)

Stractures I and II are identical and superimposable. The two structures are superimposable because one half of the molecule is the mirror image of the other half. Thus the meso is optical inactive even though the structure contains two asymmetric carbon atoms. Structures III and IV represent the racemic mixture of dl pair of the 2,3-dichlorobutane. A great deal of evidence in the literature indicates that racemization readily takes

place via free radical intermediates:

Gruver and Calvert (90) studied the photolysis of active 2-methylbutanal in the presence of I_2 and found that one of the reaction products was optically inactive (racemic) 2-butyl-iodide.

$$C_2H_5\underset{\underset{CH_3}{|}}{C}HCHO + h\nu \longrightarrow C_2H_5\underset{\underset{CH_3}{|}}{C}H + CHO \qquad (55)$$

$$C_2H_5\underset{\underset{CH_3}{|}}{C}H + I_2 \longrightarrow C_2H_5\underset{\underset{CH_3}{|}}{C}HI \qquad (56)$$

Brown and coworkers (54) indicated that the chlorination at the tertiary carbon of 2-methyl-1-chlorobutane gave rise to racemic 1,2-dichloro-2-methylbutane. This reaction presumably proceeds via the tertiary radical as shown in reaction 57.

$$C_2H_5\underset{\underset{CH_3}{|}}{C}HCH_2Cl + Cl \longrightarrow C_2H_5\underset{\underset{CH_3}{|}}{C}CH_2Cl + HCl \qquad (57)$$

Eliel, Wilken, Fang, and Wilen (55) observed that the dimerization of 2-phenyl-2-butyl radical produced a mixture of meso- and racemic-3,4-diphenyl-3,4-dimethylhexane as represented in reaction 58.

$$2\ C_2H_5\underset{\underset{C_6H_5}{|}}{C}CH_3 \longrightarrow (C_2H_5C(C_6H_5)CH_3)_2 \qquad (58)$$
meso and racemic

The dimerization of two CH CHCl radicals to form 2,3-dichlorobutane may be illulstracted by Figure 9.

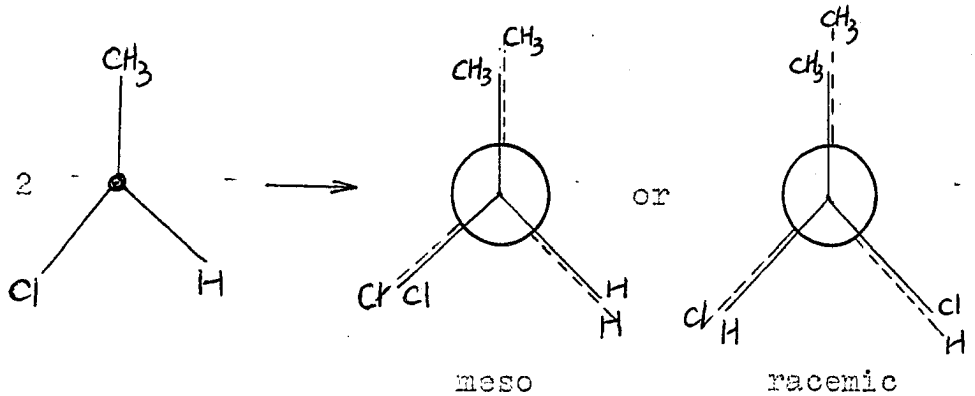


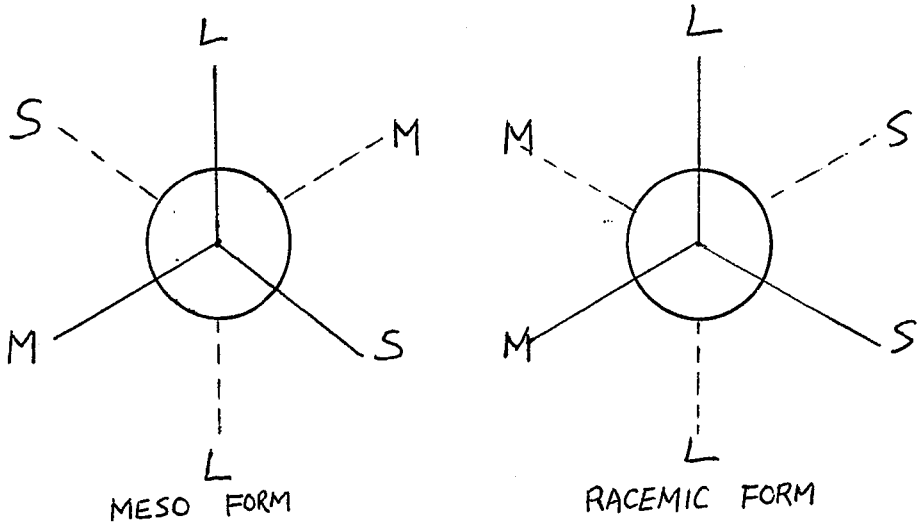
Figure 9. Dimerization of two CH_3CHCl radicals

The two CH_3CHCl radicals may collide with each other front to front or back to back to give the meso form or they may collide front to back or back to front to give the racemic mixture. The formation of meso- and racemic-2,3-dichlorobutane in this investigation is therefore not surprising but rather to be expected. Meso- and racemic-2,3-dichlorobutane have also been observed as reaction products in the gamma-ray radiolysis of ethyl chloride by Schindler (72).

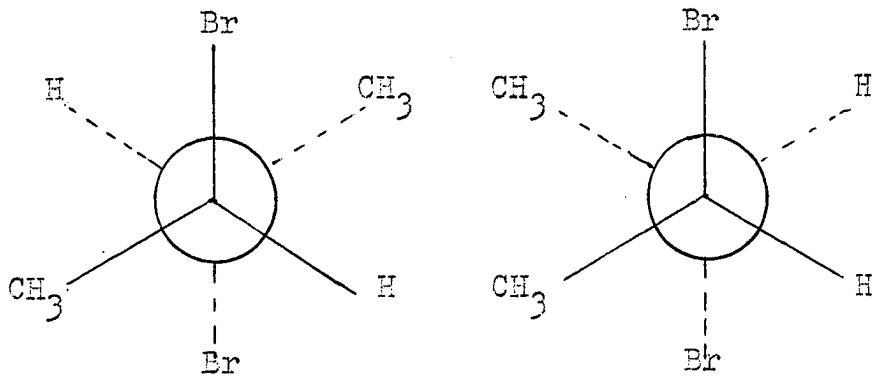
It is interesting to study the rate of meso over racemic isomers in order to gain some insight in free radical stereochemistry. The theorethical value of $k_{meso}/k_{racemic}$ should be equal to unity if there are no steric effects and if there is no difference in the stability of these two forms. The ratio R_{meso} $(CH_3CHCl)_2$ over $R_{racemic}$ $(CH_3CHCl)_2$ obtained in this study is equal to 1.08 ± 0.08. Although this value includes a remote possibility that this ratio may be equal to unity, the

data tend to favor a ratio larger than unity and may indicate that the meso form of 2,3-dichlorobutane is more stable than the racemic form. This has, as a matter of fact, been observed for 2,3-dibromobutanes and dibromostilbenes. The preferred configurations of these two compounds have been determined by electron diffraction (91) and X-ray diffraction (92) techniques.

These studies indicate that the most stable conformations of the meso and racemic isomers may be represented by the following general diagram.



L denotes the largest substituent in the two isomers, M the medium-size substituent, and S the small substituent. In the meso case of 2,3-dibromobutanes, the large size bromine atoms and methyl groups are anti to each other to minimize steric and dipole-dipole interactions, while in the racemic form methyl groups are forced to be gauche as may be seen in Figure 10.



meso form racemic form

Figure 10.-The most stable conformations of 2,3-dichlorobutane isomers.

Thus it is understood that the meso isomer is more stable than the racemic form as was indeed observed by Buckles (93). Since chlorine atoms are smaller than bromine atoms the effect is not expected to be as large for 2,3-dichlorobutane as for 2,3-dibromobutane but an identical trend might be expected and this is, without any doubt, confirmed by the data obtained in this investigation.

B. Disproportionation Reactions

Regarding rate constants for disproportionation over recombination reactions, the following data have been obtained.

$$CH_3CHCl + CCl_3 \longrightarrow CH_3CHClCCl_3 \qquad (10)$$

$$CH_3CHCl + CCl_3 \longrightarrow CCl_3H + C_2H_3Cl \qquad (11)$$

The data obtained in this investigation indicate $k_{11}/k_{10} = 0.25 \pm 0.03$. No ther data are available in the literature for this ratio. Previously, data have been reported for the reactions

$$C_2H_5 + CCl_3 \longrightarrow CCl_3C_2H_5 \qquad (46)$$
$$C_2H_5 + CCl_3 \longrightarrow CCl_3H + C_2H_4 \qquad (47)$$

and a value $k_{47}/k_{46} = 0.22 \pm 0.03$ was obtained.

Reactions 11 and 47 are very much alike since in both cases the CCl_3 radical reacts to abstract a hydrogen atom from the CH_3 groups of the CH_3CHCl respect CH_3CH_2 radical. Thus the data for k_{11}/k_{10} and k_{47}/k_{46} are in excellent agreement.

It is also interesting to compare these data to those reported in the literature for the reactions

$$C_2H_5 + CH_3 \longrightarrow C_3H_8 \qquad (59)$$
$$C_2H_5 + CH_3 \longrightarrow CH_4 + C_2H_4 \qquad (60)$$

In this case $k_{60}/k_{59} = 0.05 \pm 0.01$ (94, 95). Thus a trichloro methyl radical reacts quite different from a non-substituted methyl radical. No data have, so far, been reported in the literature regarding disproportionation reactions involving $CHCl_2$ radicals. Two ratios of rate constants have been obtained in this study for

reactions in which $CHCl_2$ radicals take part these reactions are:

$$CH_2CH_2Cl + CHCl_2 \longrightarrow CH_2CH_2ClCHCl_2 \qquad (32)$$

$$CH_2CH_2Cl + CHCl_2 \longrightarrow CH_2Cl_2 + C_2H_3Cl \qquad (33)$$

$$k_{33}/k_{32} = 0.08 \pm 0.01$$

$$C_2H_5 + CHCl_2 \longrightarrow C_2H_5CHCl_2 \qquad (48)$$

$$C_2H_5 + CHCl_2 \longrightarrow CH_2Cl_2 + C_2H_4 \qquad (49)$$

$$k_{49}/k_{48} = 0.08 \pm 0.02$$

It is interesting to compare k_{49}/k_{48} with k_{47}/k_{46} and k_{60}/k_{59}. Such a comparison would tend to indicate that a $CHCl_2$ radical reacts much more like a CH_3 radical than like a CCl_3 radical since the observed value $k_{49}/k_{48} = 0.08$ is much closer to 0.05 (as observed with CH_3 radicals) than to 0.22 (as observed with CCl_3 radicals).

In concluding this section regarding disproportionation and recombination reactions it is important to point out that the mechanism of disproportionation and recombination reactions is still not fully understood (96-98). This lack in understanding of this mechanism is in part due to a lack of data necessary to test any theory. This lack of data was particularly noteworthy for reactions involving substituted alkyl radicals. It is hoped that the data reported in this section may ultimately

contribute to an understanding of the disproportionation and recombination reaction mechanism.

SUMMARY AND CONCLUSION

The study, reported in this thesis, deals with the reactions of Cl atoms produced by photolysis of halogenated methanes and with disproportionation and recombination reactions of Cl substituted methyl and ethyl radicals.

The photolysis of CCl_4 in the presence of C_2H_5Cl has been investigated in detail. Chlorine atoms, produced by photolysis of CCl_4, react with C_2H_5Cl according to reactions 2 and 3.

$$Cl + CH_3CH_2Cl \longrightarrow CH_3CHCl + HCl \qquad (2)$$

$$Cl + CH_3CH_2Cl \longrightarrow CH_2CH_2Cl + HCl \qquad (3)$$

The ratio k_3/k_2, per available hydrogen atom, was determined to be equal to 0.11 ± 0.01, proving that the C-H bond in the CH_3 group of C_2H_5Cl is much stronger than the C-H bond in the CH_2Cl group of C_2H_5Cl.

Disproportionation and recombination reactions of CCl_3 radicals, produced by photolysis of CCl_4, and of CH_3CHCl and CH_2CH_2Cl radicals, produced by reactions 2 and 3, have been investigated.

It is particular noteworthy to mention that quantitative have been obtained for the recombination of CH_3CHCl radicals producing in part the meso form and in part the racemic form of 2,3-dichlorobutane. The data indicate that the production of the meso form is slightly

favored over the production of the racemic form.

In regard to disproportionation and recombination reactions may be mentioned the data obtained for reactions 10 and 11.

$$CCl_3 + CH_3CHCl \longrightarrow CCl_3H + CH_2CHCl \qquad (10)$$

$$CCl_3 + CH\ CHCl \longrightarrow CH_3C(CCl_3)HCl \qquad (11)$$

The data yield $k_{11}/k_{10} = 0.25 \pm 0.03$ confirming that CCl_3 radicals are much more reactive toward disproportionation reactions than unsubstituted methyl radicals.

Additional studies to confirm and extend the above data were carried out by photolysing $CHCl_3$ in the presence of C_2H_4, $CHCl_3$ in the presence of ethane, and CH_2Cl_2 in the presence of C_2H_5Cl.

In general it may be stated that this thesis provides considerable information regarding the reactions of Cl substituted methyl and ethyl radicals. It is particularly in this area that, thus far, few quantitative data have been reported in the literature.

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