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THE PRIMARY PROCESSES IN THE PHOTOLYSIS OF CHLORINATED ETHANES

BY

THOMAS S. YUAN

A dissertation submitted to the Graduate
Faculty in Chemistry in partial fulfillment of the
requirements for the degree of Doctor of Philosophy.
The City University of New York.

1978

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

Aug 29 1978
Date

Chairman of Examining Committee

13 September 78
Date

David C. Locke
executive Officer

Supervisory Committee

The City University of New York

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MATERIALS

1,1,1 - trichloroethane ---- was obtained from the Aldrich Chemical Company, New Jersey. It was purified by successive distillations, using a column packing with glass helices. The only impurity in the sample used was 1,1 - dichloroethylene which comprised less than 0.1 % of the sample.

1,1,2,2 - tetrachloroethane ---- also was obtained from the Aldrich Chemical Company. It was purified by gas chromatograpy to better than 99.98 % purity.

Iodine ---- was a " Baker Analyzed Reagent " of about 99.99 % purity.

Octafluorocyclobutane ---- was supplied by the Matheson Company, Inc. East Rutherford, New Jersey. Its purity was better than 99.99 %. The major impurity was air which was removed by degassing after the OFCB had been admitted to the vacuum system.

INTRODUCTION

Chlorinated hydrocarbons became interesting research topics for scientist recently, since Rowland and Molina (1) presented the theory of ozone destruction by chlorofluroethane gas which was widely used as propellants by the aerosol-dispenser industry.

It was found that such compounds decompose to atomic chlorine and other products after absorbing U.V. light, and the chlorine atom then acts as a catalyst to deplete the upper atomsphere's protective layer of ozone. The resultant depletion of the ozone would allow more ultraviolet light to reach the earth which would result in a sharp rise in human skin cancer and worldwide damage to crops. (2)

In our research which deals with free-radical reactions of chloro-hydrocarbons, two of the C_2 chlorohydrocarbons - 1,1,1 - trichloroethane and 1,1,2,2 - tetrachloroethane - were chosen as models. One of them is symmetric and the other is unsymmetric.

The term " radical " or " free radical " is used when referring to any electrically neutral species having an odd number of electrons.

Many chemical bonds are made up of two electrons, and bonds therefore can break in two different ways. In the first, both electrons in the bond remain attached to one of the fragments;

$$A\overset{\curvearrowright}{\text{———}}B \longrightarrow A^{+} + :B^{-}$$

This process is called heterolysis, and the charged fragments are, of course, called ions. In the second way of bond-breaking, the two electrons in the bond divide symmetrically;

$$A\overset{\curvearrowleft\curvearrowright}{\text{———}}B \longrightarrow A\bullet + \bullet B$$

This process is called homolysis, and the fragments are radicals.

The first radical was isolated by Gomberg (3) in 1900. In attempting to prepare hexaphenylethane, by treating triphenylmethyl chloride with silver in benzene solution, triphenylmethyl radical was produced.

Although radical-forming processes are quite simple, kinetic studies of free radical reactions did not become widespread until 1929 when Paneth and coworker (4) showed that free alkyl radicals could exist in the gas phase. They observed that passing a mixture consisting of inert gas saturated with tetramethyllead vapor through a glass tube heated at sufficiently high temperatures resulted in the decomposition of tetramethyllead, depositing a lead mirror on the wall of the tube. The gaseous products from the decomposition were passed further down the tube to a previously deposited lead or zinc mirror at temperature of 100°C. This mirror was observed to disappear gradually.

In order to get homogeous bond scission energy must be supplied to the reaction system. The energy may come in different forms; electrical, thermal, radiolytic or photolytic. Radiant energy has become a frequent method of initiating free radical reactions.

The quantum theory states that by absorbing a photon of light, a molecule will be activated to a excited state. This excited molecule may then decompose to give two free radicals. In addition to decomposition into free radicals, it may decompose via molecular elimination such as the following reaction (5);

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

or it may lose its excess energy through collisional deactivation with an inert molecule;

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

where M may be some other species present in the system or even an unactivated $CH_3CH_2CH_3$.

Radical reactions may involve chains; an initiation step forms radicals, propagation steps occur in which new radicals are formed, and finally termination reactions destroy the radicals and end the chain. An example of a chain process is the light initiated chlorination of a hydrocarbon (6), RH;

$$Cl_2 \longrightarrow 2\ Cl\cdot \qquad \text{(Initiation)}$$

$$Cl\cdot + RH \longrightarrow R\cdot + HCl \qquad \text{(Propagation)}$$

$$R\cdot + Cl_2 \longrightarrow RCl + Cl\cdot \qquad \text{(Propagation)}$$

$$2\ Cl\cdot \longrightarrow Cl_2 \qquad \text{(Termination)}$$

$$2\ R\cdot \longrightarrow R\text{-}R \qquad \text{(Termination)}$$

$$R\cdot + Cl\cdot \longrightarrow R\text{-}Cl \qquad \text{(Termination)}$$

The propagation steps in the chain reactions are of great interest, since they are very often the key to understanding the nature of the products which are formed.

There are four main types of reaction which occur as part of the propagation.

(1) Abstraction; abstraction reactions are also referred to as atom transfer reaction. This type of reaction may be represented by the equation;

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

where A is an atom or a radical and RH is a substrate. In most cases the hydrogen atom is abstracted. However other atomic species, in particular halogen atom, have been shown to be abstracted. A few examples are;

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

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

$$R\cdot + CH_3I \longrightarrow RI + CH_3\cdot$$

(2) Addition; This includes the addition of radicals to ordinary olefins. For example;

$$RCH{=}CH_2 + Cl\cdot \longrightarrow R\dot{C}HCH_2Cl$$

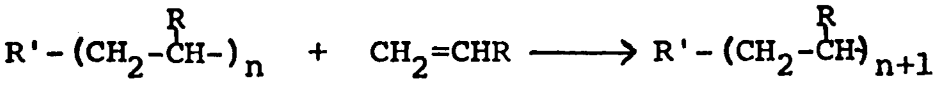
$$RCH{=}CH_2 + CH_3\cdot \longrightarrow R\dot{C}HCH_2CH_3$$

Addition occurs so as to form more stable radicals, in the above example, a secondary radical is formed in preference to a primary radical. The radical formed by this type of reaction 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 ethylentic π bond.

Such radicals are usually referred to as hot radicals and may undergo decomposition reactions if the excess energy is not removed.

However, once deactivation of the excited radical has taken place, it may undergo the normal radicals reaction. This includes further addition to the unsaturated molecules to start a polymerization process. As an example, a polymeric radical containing n units adds one more unit of the olefin to form the n + 1 radical. This can be symbolized as shown below;

$R\cdot (CH$



$$R'-(CH_2-\overset{R}{C}H-)_n + CH_2=CHR \longrightarrow R'-(CH_2-\overset{R}{C}H)_{n+1}$$

Indeed most of the early research on addition reactions was concerned with polymerization studies.

(3) Fragmentation or decomposition reactions.

Occasionally one of the radicals in the chain undergoes fragmentation. The most common fragmentation reaction is β - scission, in which a pair of electrons β to the odd electron divide and a radical fragment is ejected, this may be represented by;

This reaction is just the reverse of an addition reaction.

Certain unstable radicals such as the $CH_3\dot{C}O$ 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, Rabinovitch and coworkers (7,8) found that hot propyl radicals decompose into methyl radicals and ethylene.

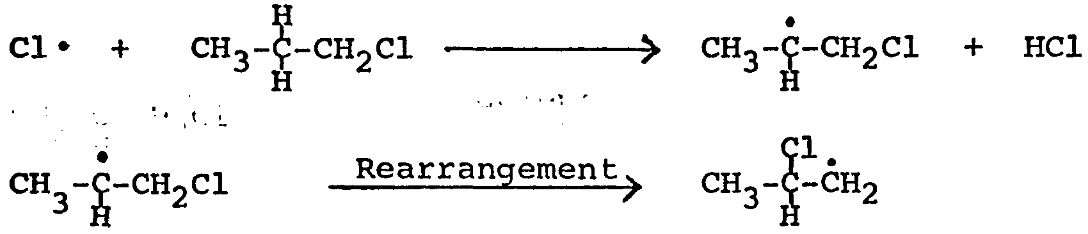
$$H\bullet + CH_3CH=CH_2 \longrightarrow CH_3CH_2CH_2\bullet\ *$$
$$CH_3CH_2CH_2\bullet\ * \longrightarrow CH_3\bullet + CH_2=CH_2$$

In addition to " hot " radical decomposition thermal decomposition reaction are also observed. As an example Wijnen (9) reports that the activation energy for the thermal decomposition of ethoxy radicals into CH_2O and methyl radicals is about 13 Kcal/mole.

$$C_2H_5O\bullet \longrightarrow CH_3\bullet \quad + CH_2O$$

The activation energy required for decomposition of t-butoxyl radical into $CH_3\bullet$ and CH_3COCH_3 is about 12 Kcal/mole. (10,11,12,13)

(4) Rearrangement; Radical rearrangements are not common. Nevertheless the rearrangement reaction is occasionally observed for some radical species. For example, a halogen atom may move as in the reaction of 1-chloropropane with chlorine atoms to form HCl:



$$Cl\bullet \quad + \quad CH_3-\overset{H}{\underset{H}{C}}-CH_2Cl \longrightarrow CH_3-\overset{\bullet}{\underset{H}{C}}-CH_2Cl \quad + \quad HCl$$

$$CH_3-\overset{\bullet}{\underset{H}{C}}-CH_2Cl \xrightarrow{\text{Rearrangement}} CH_3-\overset{Cl}{\underset{H}{C}}-\overset{\bullet}{C}H_2$$

There are two main types of reactions which terminate free radical chains. This type of reaction involves two free-radicals.

(1) Recombination; Two radicals combine to form a stable compound. This can be represented by,

$$R'CH_2\cdot + R''CH_2\cdot \longrightarrow R'CH_2CH_2R''$$

$$Cl\cdot + Cl\cdot \longrightarrow Cl_2$$

This reaction may be considered as the reverse of the decomposition of a molecule.

(2) Disproportionation; This type of reaction involves two free radicals reacting to form two stable compounds with d different degree of saturation. This can be represented by the equation,

$$R'CH_2CH_2\cdot + R''CH_2CH_2\cdot \longrightarrow R'CH_2CH_3 + R''CH{=}CH_2 \quad (a)$$

$$\text{or} \longrightarrow R'CH{=}CH_2 + R''CH_2CH_3 \quad (b)$$

In many instances R' and R" are the same so that disproportionation reaction (a) and (b) are identical.

The activation energy for disproportionation reactions and recombination reactions are usually about zero Kcal in the gas phase.

Other important reactions are scavenging reactions. These reactions need zero or very low activation energies, and, proceed with very high efficiency occuring 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 peroxides and/or hydroperoxides. (14)

Iodine and hydrogen iodide have often been used as scavengers and have the advantage that they yield relative stable products which can readily be identified by analytical techniques.

Over the past few years a considerable amount of research concerning the decomposition of vibrationally excited halogenated ethanes and ethylenes has been carried out by Setser (16,17,18) and Pritchard(19, 20). One of the primary steps in the decomposition of vibrational excited halogenated ethane either by recombining two radicals or direct photolysis of this ethane leads to dehydrohalogenation. The dehydrohalogenation of haloethanes generally occurs via a four center transition state (α , β elimination) in both thermal and chemical activated system. However, some of the recent experiments on the vibrationally hot molecules of CF_2HCD_3* (19) indicate that also a three center transition elimination (α , α elimination) may occur.

The photolysis of 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane chosen for this study are interesting due to the fact that one of the compounds is totally unsymmetric and the other is totally symmetric. It's very easy to verify the transition state of three center or four center dehydrohalogenation reaction by dealing with these two particular compounds.

In order to obtain information regarding the mode of decomposition of these two chloroethanes, extensive investigations were carried out in which the compounds were irradiated with light of different wave lengths, in the presence of free radical scavgengers and occasionally in the presence of inert deactivators.

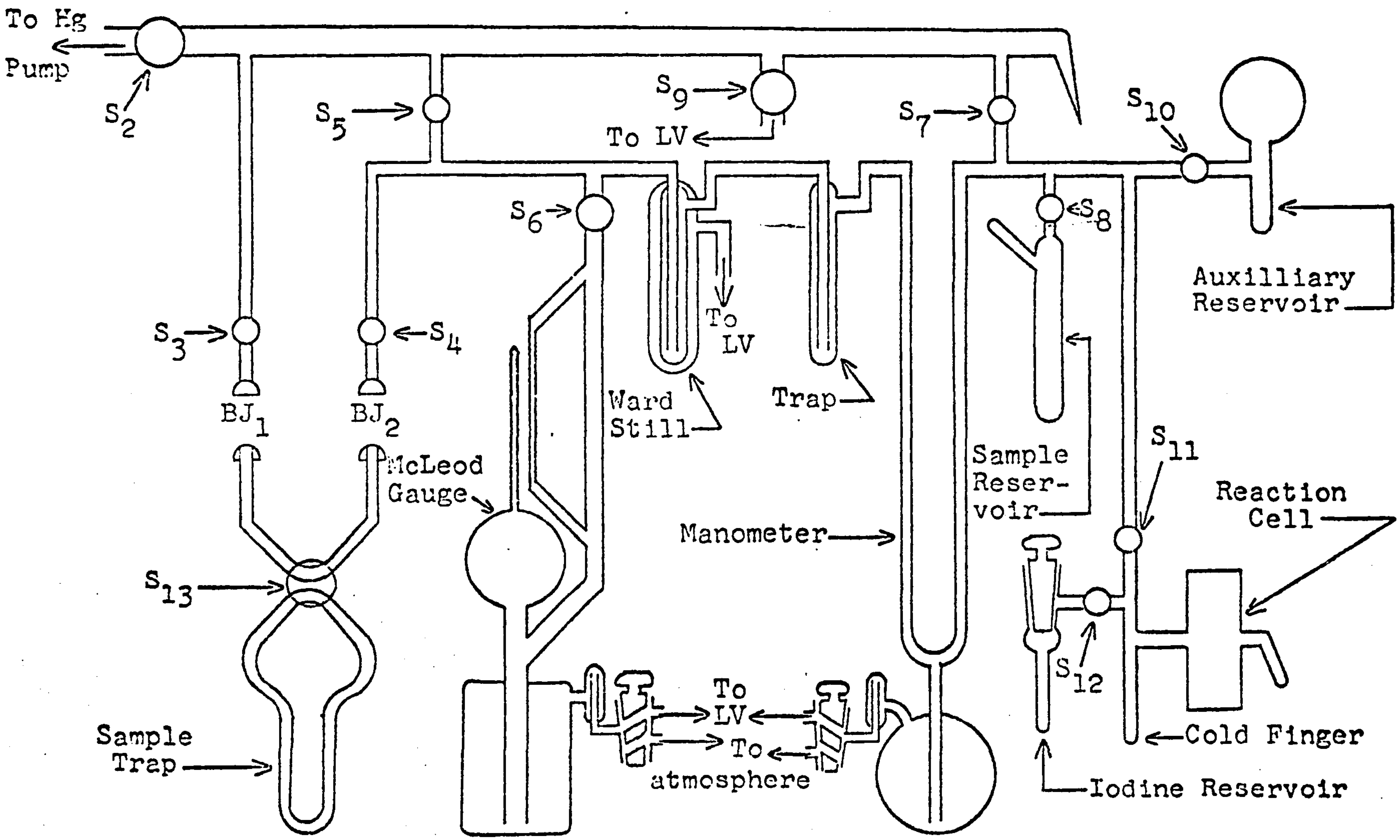
EXPERIMENTAL

HIGH VACUUM SYSTEM

The photolysis of 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane was studied in a high vacuum system. The main purpose of this high vacuum system is to keep the reactions as simple as possible by carrying out all experiments in the absence of air. This is extremely important since it is well known that oxygen is an excellent scavenger for free radicals. Traces of oxygen might react with free radicals, thus producing undesirable 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. These high and low vacuum parts were connected by a stopcock thus allowing the evacuation or the admission of air, in case of shut-down, to both parts at an equal rate. A diagram of the high vacuum system is shown in Figure 1. The high vacuum part of the system was evacuated by means of a two stage mercury diffusion pump followed by a mechnical vacuum pump.

Figure 1. The High Vacuum System



LV = Low Vacuum; S_x = Stopcock; BJ_x = Ball Joint.

The low vacuum part was evacuated by oil pump only since it is not necessary to maintain a vacuum of less than 1 or 2 mm Hg.

The vacuum in the system was measured with a Mcleod Gauge which was calibrated to minimum pressure of 0.001 micron. A vacuum of 0.1 micron or less was achived before an experiment was carried out.

A mercury manometer was used to measure the pressure of the reactants which were admitted into the reaction cell.

The quartz window reaction cell was cylindrical and was about 12 cm long 5 cm in diameter. Its volume was 250 ml A small iodine reservoir in the shape of a cold finger was attached directly to the quartz reaction cell via a high vacuum stopcock. A narrow and small cold finger with a volume about 2 ml was attached near the reaction cell directly 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. Auxilliary reservoirs with a volume of 1 liter were filled by admitting the gaseous compounds such as octaflurocyclobutane through one of the ball joint outlets.

After being introduced into the high vacuum system, the various compounds were then degassed thoroughly. This consisted of freezing the compound with liquid nitrogen and pumping on the reservoir with high vacuum. The processes were repeated at least three times.

LIGHT SOURCE ----- ULTRA VIOLET LIGHT

A Hanovia model 16A13 medium pressure mercury arc was employed as the ultraviolet source in all experiments. The mercury arc was collimated by an aluminum shade reflector. The spectrum of the light source ranges from 2000 Å through the visible region (8000 Å). Mercury photosensitization can not occur since at this pressure the 2537 Å resonance line of the arc is reversed. The mercury arc was allowed a warm up time of at least fifteen minutes before each exposure in order to permit the lamp to reach its operating temperature and, thus, a uniform intensity and wavelength distribution through out all experiments was insured.

The distance between mercury arc and reaction cell was about 12 cm and was kept constant.

In order to study the dependence of various products upon the wavelength of the incident light, an appropriate corning filter was placed between the arc and reaction cell. The transmittance spectra of these filters are shown in figure 2.

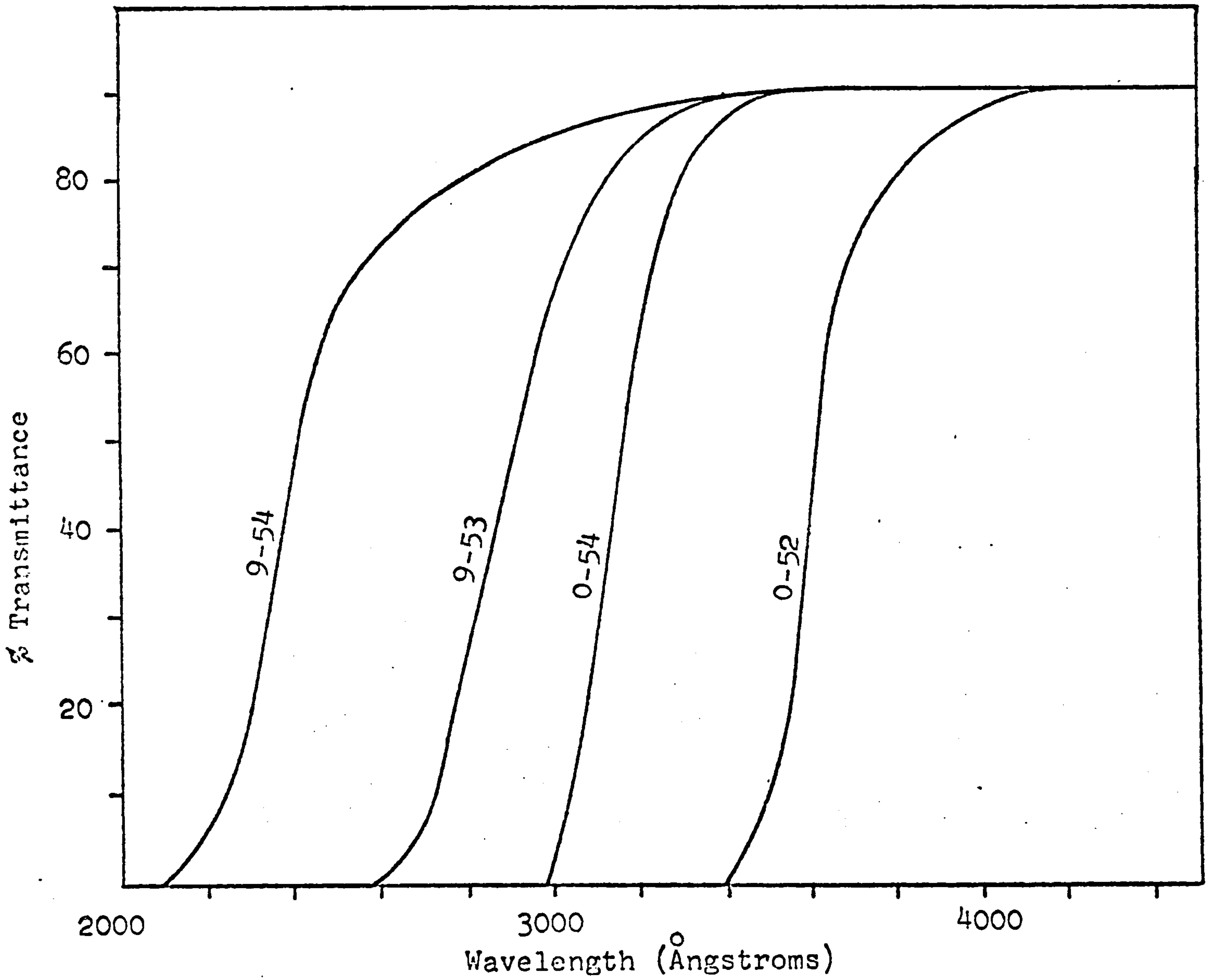
EXPERIMENTAL PROCEDURE

(a) Photolysis of 1,1,1-trichloroethane

The experimental technique used in studying the photolysis of 1,1,1-trichloroethane will be described first since it is less complicated than the technique used in studying the photolysis of 1,1,2,2-tetrachloroethane.

A typical experiment was started; when the vacuum as measured on the Mcleod gauge was adequate. The 1,1,1-trichloroethane in the sample reservoir was allowed to warm up. The mercury in the manometer was raised and the right side of the high vacuum system was isolated from the high vacuum manifold by closing stopcock 7. The 1,1,1-trichloroethane was allowed to expand into the tubing extending from the manometer to stopcocks 10 and 11. Stopcock 11 then was opened allowing the

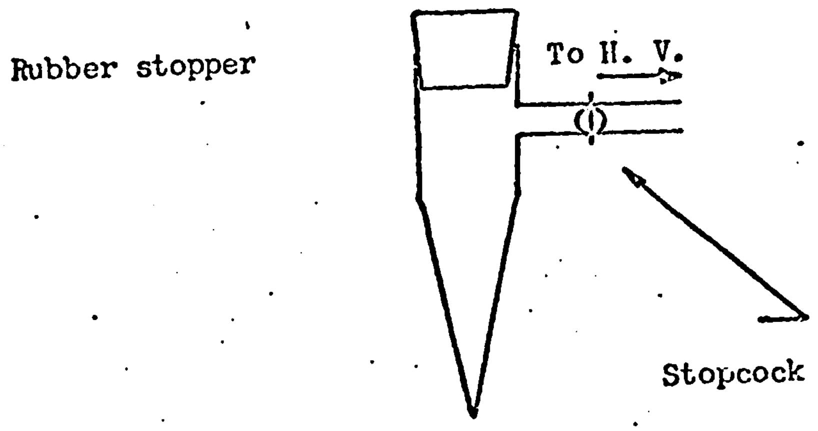
Figure 2. Transmittance Spectra of Selected Corning Filters



1,1,1-trichloroethane to expand into the reaction cell. When the desired pressure was reached, the sample reservoir stopcock 8 was closed. The pressure was read on the manometer. Then the reaction cell stopcock 11 was closed and stopcock 7 was opened to pump away the 1,1,1-trichloroethane remaining in the tubing. The cold finger of the reaction cell was immersed into liquid nitrogen to freeze the 1,1,1-trichloroethane. Stopcock 8 was opened for degassing of possible traces of air which might be present. Then stopcock 8 was closed and stopcock 7 connected to the I_2 reservoir was opened and iodine was condensed into the reaction cell. After one minute the iodine stopcock 7 was closed and stopcock 8 connecting to the reaction cell was opened again for a degassing of three minute duration. After that stopcock 8 was closed and the liquid nitrogen removed from the cold finger and the mixture of 1,1,1-trichloroethane and iodine was ready for photolysis. The Hanovia lamp was allowed to warm up for at least fifteen minutes before the start of the photolysis. While the sample was being prepared and the lamp was warming up, a blackened asbestos plate was inserted between the light source and the reaction cell to prevent the ultraviolet light from entering the cell. As the plate was removed and the ultraviolet light entered the cell, a stop watch was activated manually. To halt the photolysis, either the light was shut off or the blackened plate was replaced.

If another compound, a deactivator, was to be added to the cell, the tubing was evacuated. The deactivator in its auxilliary reservoir was condensed with liquid nitrogen and then degassed. The coolant was removed allowing the deactivator to expand into the tubing. When the pressure in the tubing exceeded the pressure in the cell, stopcock 11 could be opened to admit the deactivator to the cell. When the total pressure wanted in the cell was reached, the auxilliary stopcock 10 was closed and the cell stopcock 11 left open until the pressure was read. Stopcock 11 was closed. Again the deactivator and reactant were ready for photolysis.

To collect the sample, a sample trap also shown in figure 3 was connected to the ball joint outlets below stopcocks 3 and 4. The ball joints were greased with each use and attached with the aid of clamps. While the experiment was in prograss, but after the tubing had been evacuated, the sample trap was attached to the outlets. The sample trap stopcock 13 was open. With both high vacuum manifold stopcocks, 5 and 7, closed stopcock 3 was opened. This evacuated the sample trap without letting



Cold finger

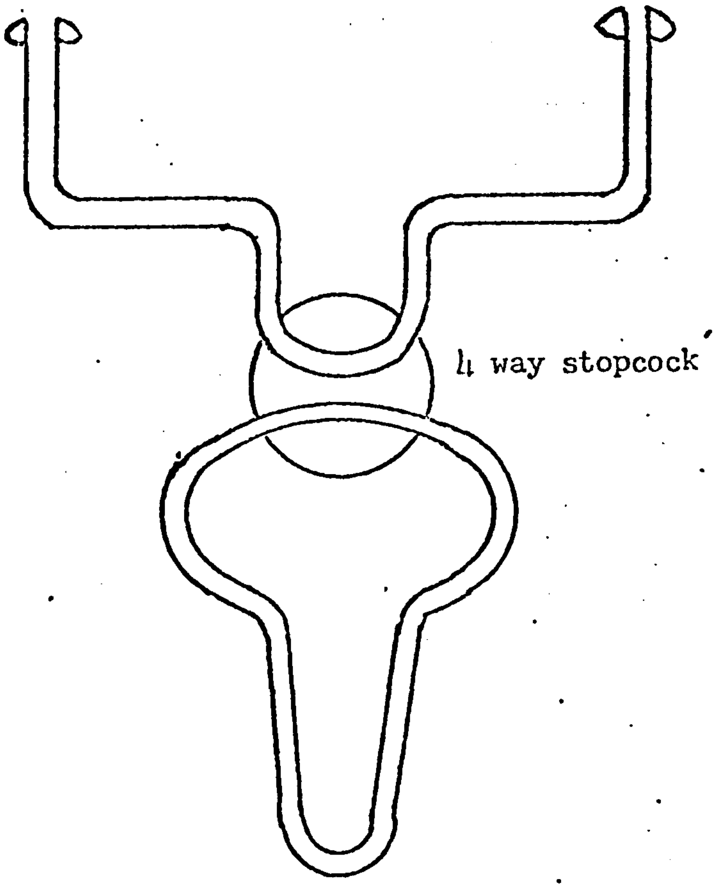


Figure 3. Sample trap

any of the air into the high vacuum system.

After the photolysis, stopcock 11 was opened and stopcock 3 was closed. The reactants and products were collected in the evacuated U-shape sample tube at liquid nitrogen temperature for five minutes. The sample trap was degassed at liquid nitrogen temperature for two minutes to remove any traces of air that might have leaked in through the balljoint during the collecting process.

The sample trap was taken to a gas chromatograph which had been adapted to allow the insertion of the sample trap into the flow line of the carrier gas via ball joint 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 the " off " position in order to minimize de detector oxidation and to prolong the life of the detector. After all the air had passed through the detector, the detector was turned on and allowed a warm up time of at least ten minutes before the start of the analysis, in order to permit the detector to stabilize. The liquid nitrogen was then

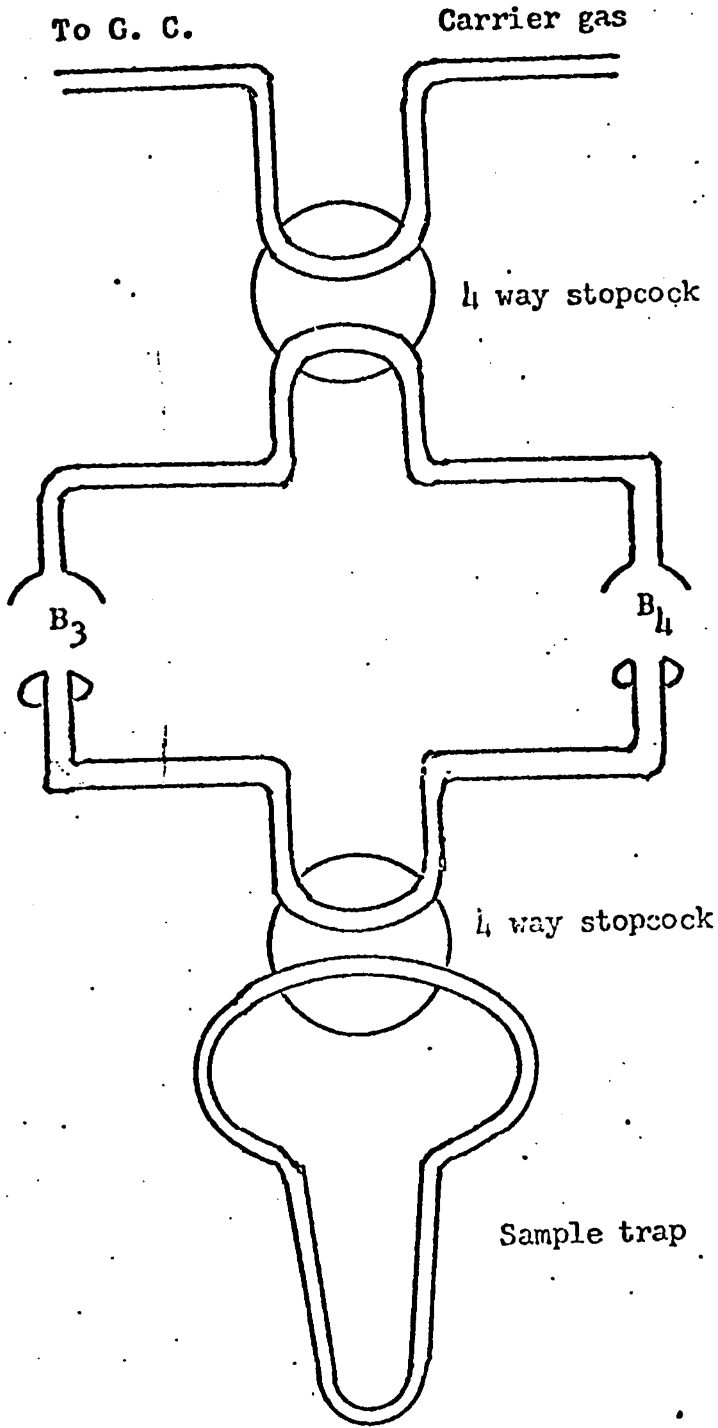


Figure 4. Gas chromatograph attachment

removed and the sample trap was heated by wire wrapped 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 80°C. The sample trap was heated in order to vaporize as many products as fast as possible. This is necessary to produce sharp, well defined peaks. Compounds which do not completely vaporize show long trailing peaks which make separation and quantitative analysis extremely difficulty.

In order to have a good separation for the volatile compounds the column temperature was cooled to - 40°C by immersing the column in dry ice and acetone mixture. After a few minutes the cooling container was removed and the column was heated by turning on the temperature programmer increasing the temperature at a rate 10°C per minute. 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-iodo-1,1-dichloroethane, 1-iodo-1,2,2-trichloroethane. These high boiling products evaporated only slowly from the sample trap when the temperature was heated to 80°C and appeared therefore on the gas chromatograph 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 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 gas chromatograph's column. This technique will be described later.

(b) Photolysis of 1,1,2,2-tetrachloroethane

In general the experimental procedure was similiar to the one just described. The vapor pressure of 1,1,2,2-tetrachloroethane is 0.5 cm mercury height at room temperature. This pressure was kept constant for all the experiments. After the 1,1,2,2-tetrachloroethane was admitted to the reaction cell and frozen by liquid nitrogen for two minutes and degassed for three minutes and the cold finger was warmed up quickly with boiling water in order to obtain a homogeneous distribution of the reactants in the cell. Some of the iodo-compounds formed by the photolysis were nonvolatile compounds and injection technique was therefore used to analyze for the products.

After the photolysis, excess reactants and products were frozen into the cold finger storage tube connected to the cell at liquid nitrogen temperature. 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. As soon as the products were transformed from the solid into the liquid phase, the sample was withdrawn with a hypodermic and directly injected onto the gas chromatographic column. It was of course impossible to withdraw the total sample. The unreacted 1,1,2,2-tetrachloroethane was, therefore, used as an internal standard. The amount of 1,1,2,2-tetrachloroethane in the cell before the photolysis was known by pressure measurements. Less than one per cent of initially present 1,1,2,2-tetrachloroethane was decomposed during the photolysis, measurement of the 1,1,2,2-tetrachloroethane 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.

When octafluorocyclobutane (OFCB) was used as a deactivator the procedure for collection of the sample had to be modified. If the OFCB would have been frozen out in the sample trap together with the products and undecomposed tetrachloroethane, the sample trap certainly would have exploded upon heating. It was therefore necessary to pump the deactivator away before collecting the sample in the sample trap. The sample was, therefore condensed into a Ward Still. By applying about 5 volts to the heating wires of the still, the temperature was elevated to a point where the vapor pressure of OFCB was sufficiently high for it to be pumped away, the manometer mer mercury was raised and stopcock 4 closed. The observation of a pressure on the manometer would indicate that not all the deactivator had been pumped off. When all the OFCB finally had evaporated, the liquid nitrogen was removed from the Ward Still. Stopcock 13 and 4 were closed and the variac raised to 20 volts. Any increase in pressure was indicated by the manometer. When, after a considerable period of time, the pressure no longer increased, it was accepted that all the sample had evaporated. The sample trap was immersed in liquid nitrogen. Stopcock 12 and 4 were opened. The variac was shut off. Then the normal sample collection procedures were followed.

IDENTIFICATION AND ANALYSIS OF PRODUCTS

All the photolyzed products were identified and quantitatively determined by using a Burell Kromo-Tog (Model KD) gas chromatograph having thermal conductivity detectors. The detector current was 200 milliampheres. A 8 foot column packed with silicone grease on 30/60 carbowax was used for the analysis.

The major products produced by photolysis of 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane in the presence of iodine as scavenger were; 1,1-dichloroethylene, cis and trans-1,2-dichloroethylene, trichloroethylene, tetrachloroethylene, 1-iodo-1,1-dichloroethane and 1-iodo-1,2,2-trichloroethane. To determine the retention time of, and the sensitivity of the detector toward the various products, a known amount of each products were injected directly onto the column by using a Hamilton microliter syringe or a Hamilton gas tight syringe (plungers teflon coated).

The peak area on the gas chromatograph chart was measured with an Ott-planimeter. In any sensitivity determination, three or more samples were analyzed and the results averaged.

The average deviation in these determinations was one per cent or less. The quantitative analysis of the reaction products was always carried out in the presence of a large excess of undecomposed starting material. As will be shown later, the actual conversion of the starting material was usually less than one per cent. 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 condition of the analysis in the photochemical experiments.

The sensitivities of the chromatograph to the various compounds were reported in molecules per planimeter unit. For an experimental chromatogram, the peak was integrated in the same manner, using the same Ott planimeter. The rate of production of the compound then was determined by multiplying the area of the compound in planimeter units by the sensitivity of that compound and dividing this number by the illuminated volume of the reaction cell and by the exposure time. The rates are, therefore, reported in molecules per milliliter per second.

The determination of sensitivities were performed for 1,1-dichloroethylene, trans-1,2 dichloroethylene, cis-1,2 dichloroethylene, 1,1,2-trichloroethylene, tetrachloroethylene, 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane. All of which were available for quantitative analysis. The sensitivities of 1-iodo-1,1-dichloroethane and 1-iodo-1,2,2-trichloroethane could not be determined directly, since these compounds are not available commercially. In this case sensitivities for these compounds were estimated. By comparing the sensitivity of compounds of similiar molecular weight and retention time, an estimate could be made. Such estimates are not liable to be wrong by more than 10 %.

It should be mentioned that at least ten experiments were usually necessary before a suitable column and suitable column temperatures were obtained. The operating conditions (flow rate and temperature programming) were always chosen so that maximum separation between the various products would be achieved.

RESULTS AND INTERPRETATION

I. PHOTOLYSIS OF 1,1,1-TRICHLOROETHANE

A. Introduction :

1,1,1-trichloroethane has been photolyzed in the presence of I_2 and of HI as free radical scavengers. In the presence of I_2, two reaction products were observed, CH_2CCl_2 and CH_3CCl_2I; in the presence of HI, the observed products were CH_2CCl_2 and CH_3CCl_2H.

The fact that the production of CH_2CCl_2 is independent of the nature of the free radical scavenger, present during the photolysis, and indeed, independ of the presence or absence of free radical scavengers at all indicates that this compound is produced by a non-free radical step, most likely by a molecular elimination of HCl,

$$CH_3CCl_3 + h\nu \longrightarrow CH_2CCl_2 + HCl$$

The formation of CH_3CCl_2I in the presence of I_2 and

CH_3CCl_2H in the presence of HI proves that the precursor to this compound must be the $CH_3CCl_2\cdot$ radical.

These preliminary data indicate the presence of two primary reactions,

$$CH_3CCl_3 + h\nu \longrightarrow CH_2CCl_2 + HCl$$

$$\longrightarrow CH_3CCl_2\cdot + Cl\cdot$$

B. Time Study :

In order to obtain information regarding the nature of the excited states leading to the above products, experiments were carried out at different wave lengths. These experiments were performed in the nature of time studies in order to make certain that the obtained data are not the results of secondary reactions.

Three studies were carried out,

(a) Photolysis in the absence of a filter, using the direct light of the Hanovia-medium pressure arc, the light absorbed by CH_3CCl_3 ranged, therefore, from 2000 Å to 4000 Å.

(b) Photolysis in which corning filter 9-54 (transmitting above 2200 Å) was inserted between reaction cell and arc.

(c) Photolysis in which corning filter 0-52 (transmitting above 3400 Å) was used.

All experiments were [illegible] in the [illegible] at a constant

All experiments were carried out in the presence of I_2, and at a constant starting pressure of 20 torr of CH_3CCl_3.

The data are given in table I.

The results of these experiments are plotted in figures 5, 6 and 7 for the total amount of products as a function of photolysis time. These figures clearly indicate that the results are linear throughout the exposure time; the rates of production are constant. All other experiments in this investigation were carried out by using an irradiation time well within the linear region of this time study to insure that reaction products were not the results of secondary reactions. The data establish quite clearly that the ratio $R_{CH_2CCl_2}$ / $R_{CH_3CCl_2I}$ is wavelength dependent and give the following results ;

range of light absorbed	ratio of $R_{CH_2CCl_2}/ R_{CH_3CCl_2I}$
2000 Å to 4000 Å	0.3
2200 Å to 4000 Å	2.4
3400 Å to 4000 Å	5.5

The relative importance of CH_3CCl_2I increases immensely with shorter wavelengths. Thus, it is clear that we are dealing with at least two different excited states of the

TABLE I

Time Study of CH_3CCl_3 with I_2

Run No.	$P_{CH_3CCl_3}$ (torr)	Exposure Time (second)	Corning Filter	$R_{CH_2CCl_2}$ (10^{12} molecule / cc sec.)	$R_{CH_3Cl_3I}$
A-10	20	40	None	2.77	7.51
A-12	20	40	None	2.27	/
A-13	20	45	None	1.82	7.56
A-15	20	70	None	2.68	6.84
A-14	20	90	None	2.40	7.80
B-2	20	120	9-54	0.85	0.32
B-3	20	360	9-54	0.82	0.23
B-1	20	600	9-54	0.87	0.38
B-4	20	900	9-54	0.63	0.33
C-33	20	300	0-52	0.28	0.04
C-30	20	600	0-52	0.38	/
C-31	20	1200	0-52	0.29	0.05
C-34	20	1500	0-52	0.52	0.09

Figure 5. Production of CH_2CCl_2 and CH_3CCl_2I as a function of Time in the Photolysis of CH_3CCl_3 at λ > 2000 Å.

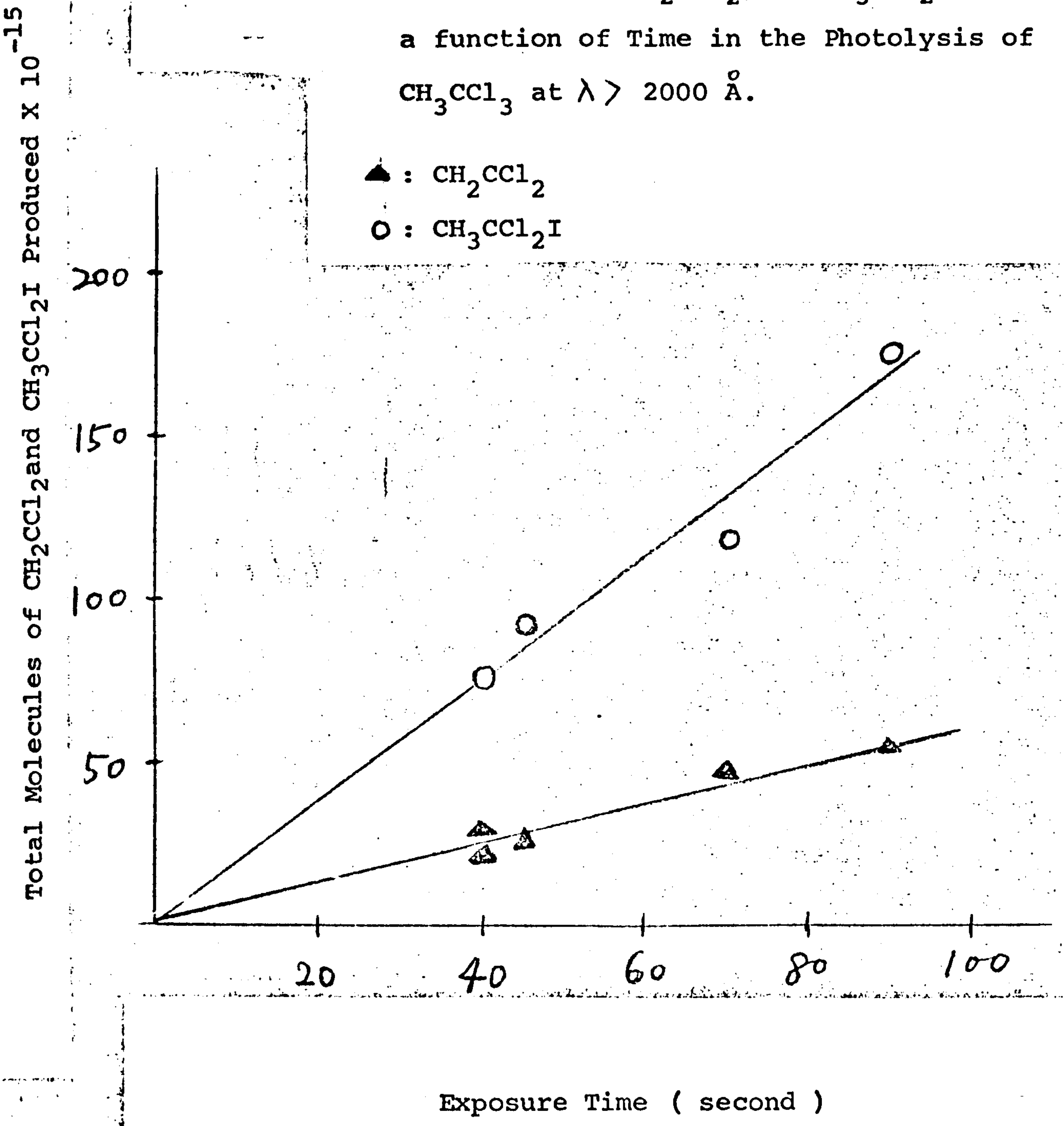


Figure 6. Production of CH_2CCl_2 and CH_3CCl_2I as a Function of Time in the Photolysis of CH_3CCl_3 at $\lambda > 2200$ Å

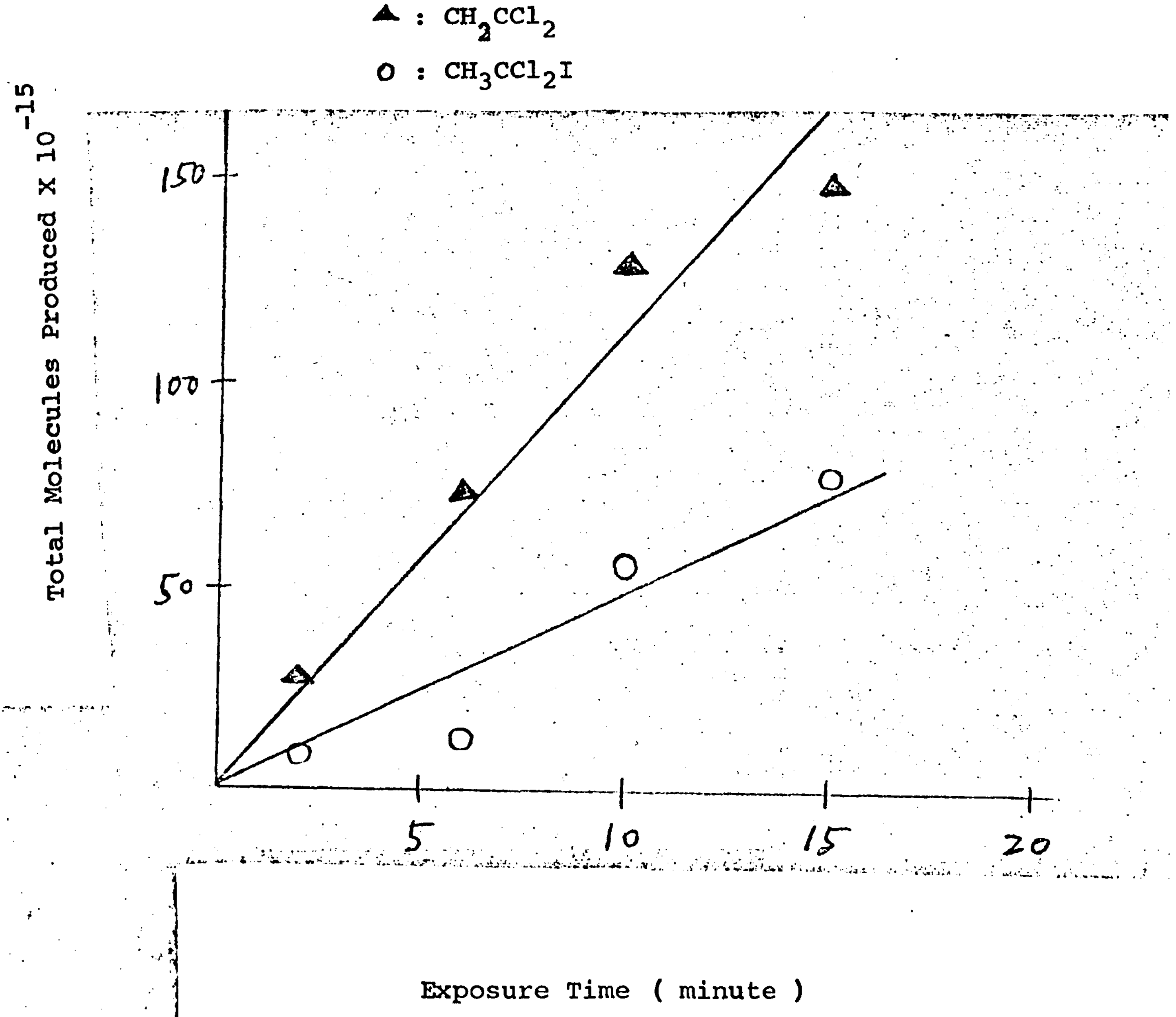
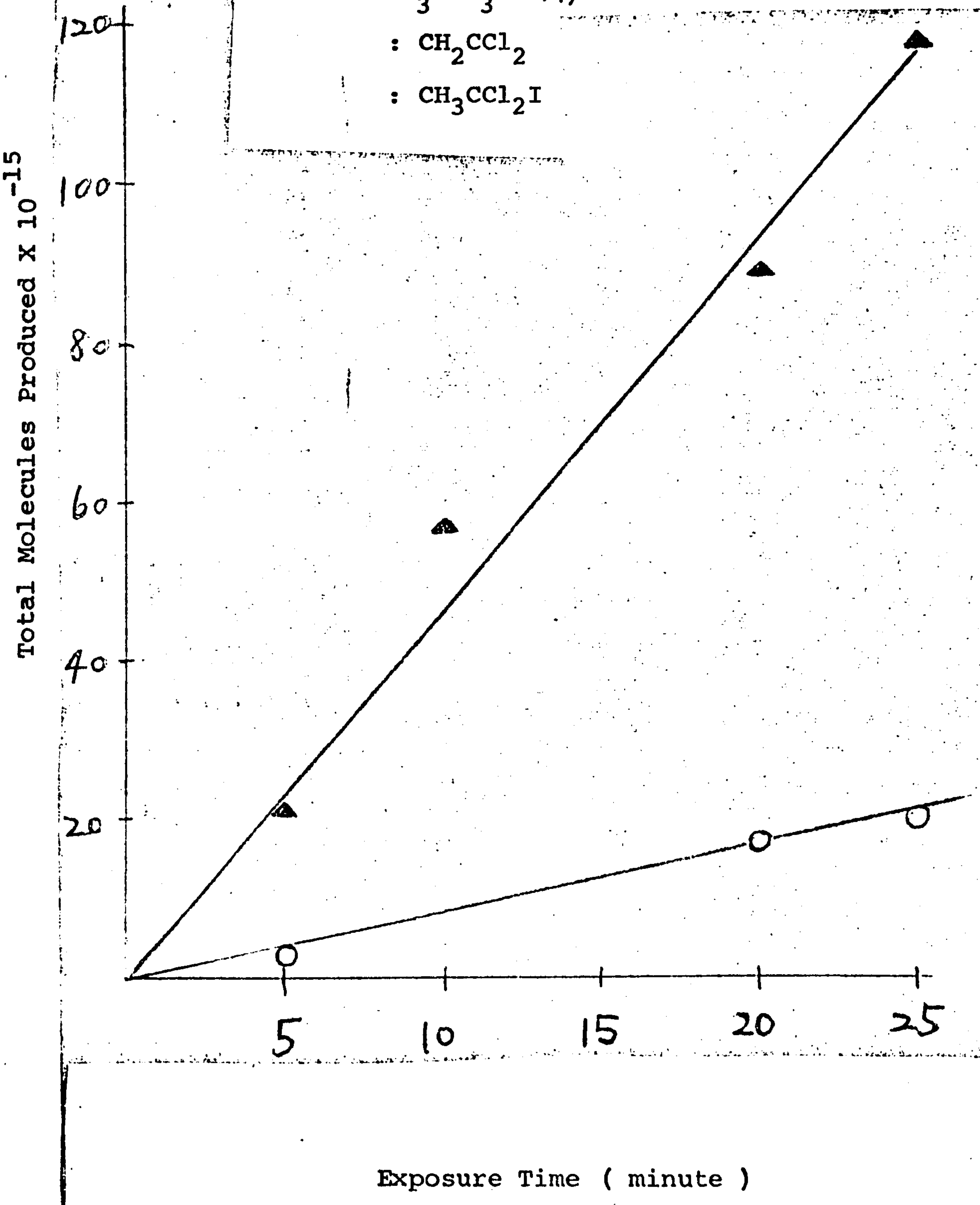


Figure 7. Production of CH_2CCl_2 and CH_3CCl_2I as a Function of Time in the Photolysis of CH_3CCl_3 at $\lambda > 3400$ Å



CH_3CCl_3 molecule.

C. Energetic considerations regarding the decomposition of 1,1,1-trichloroethane :

As we mentioned previously, the photolysis of 1,1,1-trichloroethane in the presence of I_2 yields 1,1-$C_2H_2Cl_2$ and the $CH_3CCl_2{}^{\circ}$ radical, which is scavenged by I_2 to give CH_3CCl_2I.

In the production of 1,1-$C_2H_2Cl_2$, a H and a Cl atom are lost by the 1,1,1-trichloroethane molecule. Either they can leave as a HCl molecule or as H and as Cl atoms.

The possible reactions for the photolysis of 1,1,1-CH_3CCl_3 are ;

$$1,1,1\text{-}CH_3CCl_3 + h\nu \longrightarrow 1,1,1\text{-}CH_3CCl_3{}^{*} \tag{1}$$

$$1,1,1\text{-}CH_3CCl_3{}^{*} \longrightarrow 1,1\text{-}CH_2CCl_2 + HCl \tag{2a}$$

$$\text{or} \longrightarrow 1,1\text{-}CH_2CCl_2 + H\cdot + Cl\cdot \tag{2b}$$

$$1,1,1\text{-}CH_3CCl_3{}^{*} \longrightarrow CH_3CCl_2\cdot + Cl\cdot \tag{3}$$

$$1,1,1\text{-}CH_3CCl_3{}^{*} \longrightarrow CCl_3CH_2\cdot + H\cdot \tag{4}$$

Analysis of the energetic requirements for the individual reactions from bond energies will give information regarding its probability and even its possibility. In table II, bond energies in kilocalories per mole are given for the compounds of interest to this discussion.

TABLE II

Bond energy in Kcal/mole

Cl-Cl	58.0	C-H	98.7	C-C	82.6
H-Cl	103.2	C-Cl	81	C=C	145.8
H-I	71.4	C-I	51	I-I	36.1

From the data in table II, it is possible to calculate the minimum energy required for the reactions given above.

To form 1,1-$C_2H_2Cl_2$ the following bonds must be broken : C-Cl; C-H and the C-C bond. The bonds formed are H-Cl and C=C for reaction 2a and only C=C for reaction 2b. The energies involved in these steps are giving below,

Bonds broke		Bonds formed (reaction 2a)		Bonds formed (reaction 2b)	
C-H	98.7	H-Cl	103.2	C=C	145.8
C-Cl	81.0	C=C	145.8		
C-C	82.6				
	262.3		249.0		145.8

Thus, reaction 2a requires a minimum input of 262.3 - 249.0 = 13.3 Kcal/mole, while reaction 2b requires a minimum of 262.3 - 145.8 = 116.5 Kcal/mole. The corresponding wavelength for reaction 2a is 21,504 Å, while reaction 2b is 2455 Å.

The experimental data (see table I) from the photolysis with 3400 Å (corning filter 0-54) clearly indicate that CH_2CCl_2 is produced at wavelength longer than 2650 Å. Thus at $\lambda > 2650$ Å CH_2CCl_2 is produced exclusively by reaction 2a.

The production of $CH_3CCl_2\cdot$ radicals, as indicated by reaction 3, requires a minimum of 81 Kcal/mole, the energy necessary to break up the carbon-chlorine bond. This energy corresponds to 3530 Å. Thus, reaction 3 is a process which could be observed under all experimental conditions.

Reaction 4, the formation of $CCl_3CH_2\cdot$ radical requires a minimum of 98.7 Kcal/mole, the energy necessary to break up the carbon-hydrogen bond. This energy corresponds to 2890 Å. The fact we did not observe CH_2ICCl_3 is not surprising since C-H bond rupture are not common in the wavelength regions of this investigation.

D. Deactivated study with 1,1,1-trichloroethane :

In order to obtain further information regarding the nature of the excited states, two series of experiments were carried out in which the product rates were examined as a function of initial CH_3CCl_3 pressure. These experiments were carried out in the wavelength region 2000 Å to 4000 Å and 2200 Å to 4000 Å. The data of these experiments are reported in table IIIA and IIIB.

Another series of experiments were carried out with Octafluorocyclobutane (OFCB) as inert deactivator. In these experiments the CH_3CCl_3 pressure was kept constant at 20 torr while the pressure of OFCB was being varied. These experiments were also carried out in the wavelength region 2000 Å to 4000 Å and 2200 Å to 4000 Å. The data are given in table IVA and IVB.

The rate of production of CH_2CCl_2 and CH_3CCl_2I with respect to initial CH_3CCl_3 pressure are plotted in figure 8 for the data obtained in the range of 2000 Å to 4000 Å. The marked difference in behavior between CH_2CCl_2 and CH_3CCl_2I is clearly visible in this figure. The rate of production of

CH_2CCl_2 increases with increasing CH_3CCl_3 pressure to reach a maximum at about 40 torr and decreases rapidly with further increasing CH_3CCl_3 pressure. The initial increase in the rate of CH_2CCl_2 production is undoubtedly due to an increase in light absorption with increasing CH_3CCl_3 pressure. The decrease of rate of production of CH_2CCl_2 at pressure over 40 torr may be caused by self-quenching of the excited state producing CH_2CCl_2. The production of CH_3CCl_2I reaches a maximum at a much lower CH_3CCl_3 pressure, about 10 torr, and does not show a decrease even at CH_3CCl_3 pressure of 80 torr. The fact that the maxima in product rates are obtained at different pressures indicates that light of different wavelength regions is absorbed to produce two different excited state with different life times. The excited state yielding CH_2CCl_2 can, but the excited state yielding CH_3CCl_2I can not, be deactivated by the pressures used in this investigation. These data confirm therefore that we are indeed dealing with at least two different excited states.

A similiar plot for the rate of production of CH_2CCl_2 and CH_3CCl_2I with respect to the initial CH_3CCl_3 pressure for the wavelength region 2200 Å to 4000 Å is shown in figure 9.

TABLE IIIA & IIIB

Deactivation Study of CH_3CCl_3 with CH_3CCl_3 as Deactivator

Run No.	$P_{CH_3CCl_3}$ (10^{17} molec./c.c)	Exposure Time (minute)	Corning Filter	$R_{CH_2CCl_2}$ (10^{12} molec./c.c sec.	$R_{CH_3CCl_2I}$
A-29	1.6	25	9-54	0.07	0.05
A-30	1.6	35	9-54	0.07	0.05
A-27	3.2	10	9-54	/	0.10
A-28	3.2	20	9-54	0.14	0.09
A-23	6.4	10	9-54	0.64	0.29
A-24	6.4	15	9-54	0.56	0.50
A-25	12.8	10	9-54	0.14	0.57
A-26	12.8	15	9-54	/	0.13
A-31	19.2	20	9-54	0.19	0.08
A-32	19.2	30	9-54	0.19	/
B-20	3.2	3	None	0.28	5.13
B-19	3.2	5	None	0.35	3.67
B-15	6.4	4	None	0.99	5.65
B-16	6.4	8	None	0.98	5.74
B-12	12.8	5	None	1.33	5.28
B-11	12.8	10	None	1.80	4.66

TABLE IIIB - CONTINUED

Run No.	$P_{CH_3CCl_3}$	Exposure Time	Corning Filter	$R_{CH_2CCl_2}$	$R_{CH_3CCl_2I}$
B-17	19.2	5	None	0.46	7.52
B-18	19.2	8	None	0.79	3.34
B-13	25.6	5	None	0.52	6.75
B-14	25.6	8	None	0.52	/
B-21	25.6	8	None	0.21	5.25

@ Scavenger: I_2

TABLE IVA & IVB

Deactivation Study of CH_3CCl_3 with OFCB as Deactivator

Run No.	P_{OFCB} (10^{17} molec./cc)	Exposure Time (minute)	Corning Filter	$R_{CH_2CCl_2}$ (10^{12} molec./cc sec.	$R_{CH_3CCl_2I}$
A-17	0	25	9-54	0.41	0.17
A-19	2.24	25	9-54	0.40	0.13
A-20	10.88	25	9-54	0.33	0.12
A-21	18.24	25	9-54	0.25	0.11
A-18	27.20	25	9-54	0.25	/
B-7	0	5	None	1.33	4.77
B-5	4.8	5	None	1.33	4.78
B-6	4.8	5	None	1.21	3.02
B-10	10.24	5	None	0.91	4.23
B-8	16.0	5	None	0.52	4.30
B-9	21.44	5	None	0.43	3.79

@ Pressure of CH_3CCl_3 = 20 torr Scavenger: I_2

Figure 8. Variation of Product Rate as a Function of Initial CH_3CCl_3 Pressure at λ > 2000 Å.

▲ : CH_2CCl_2

○ : CH_3CCl_2I

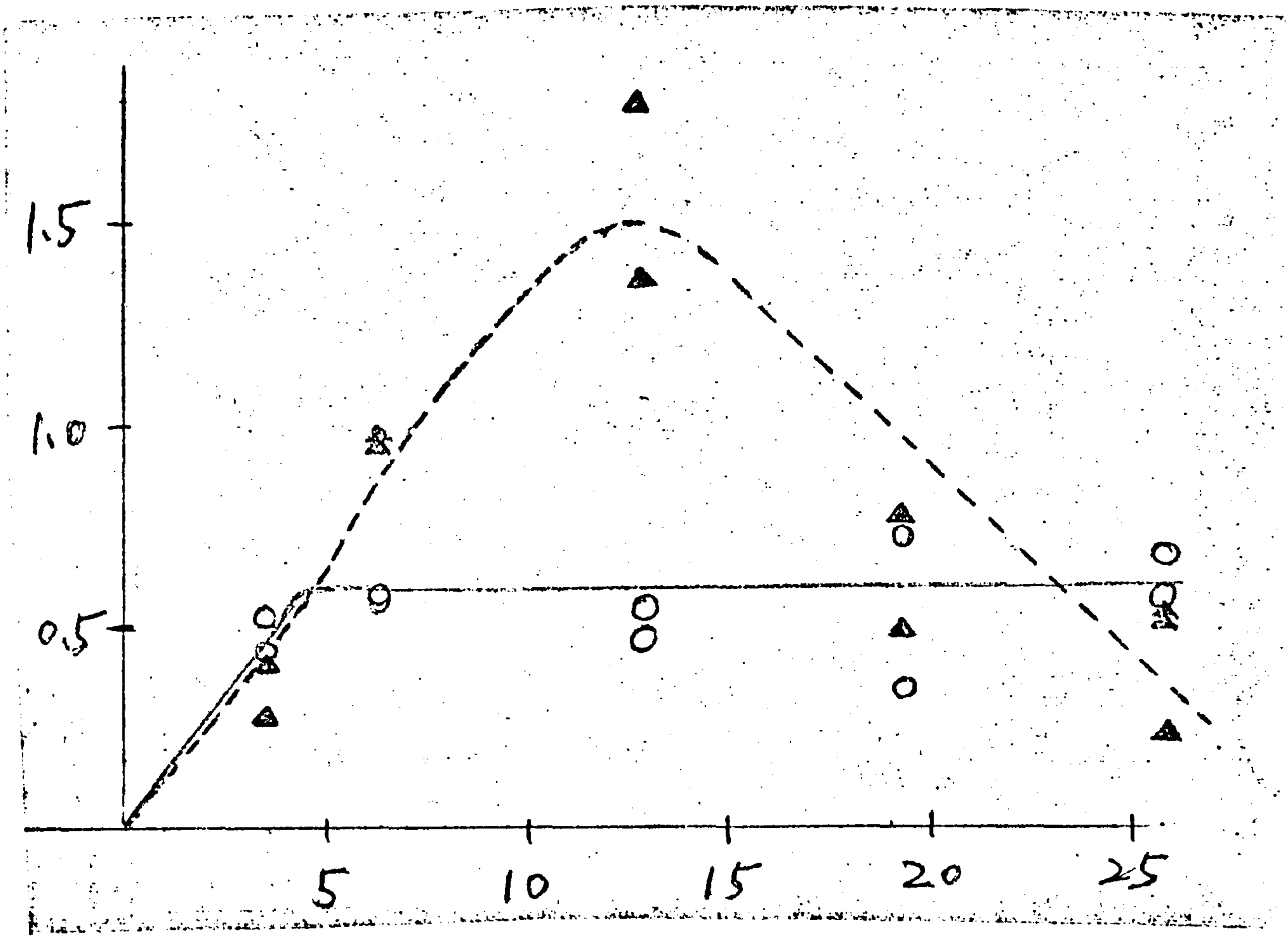
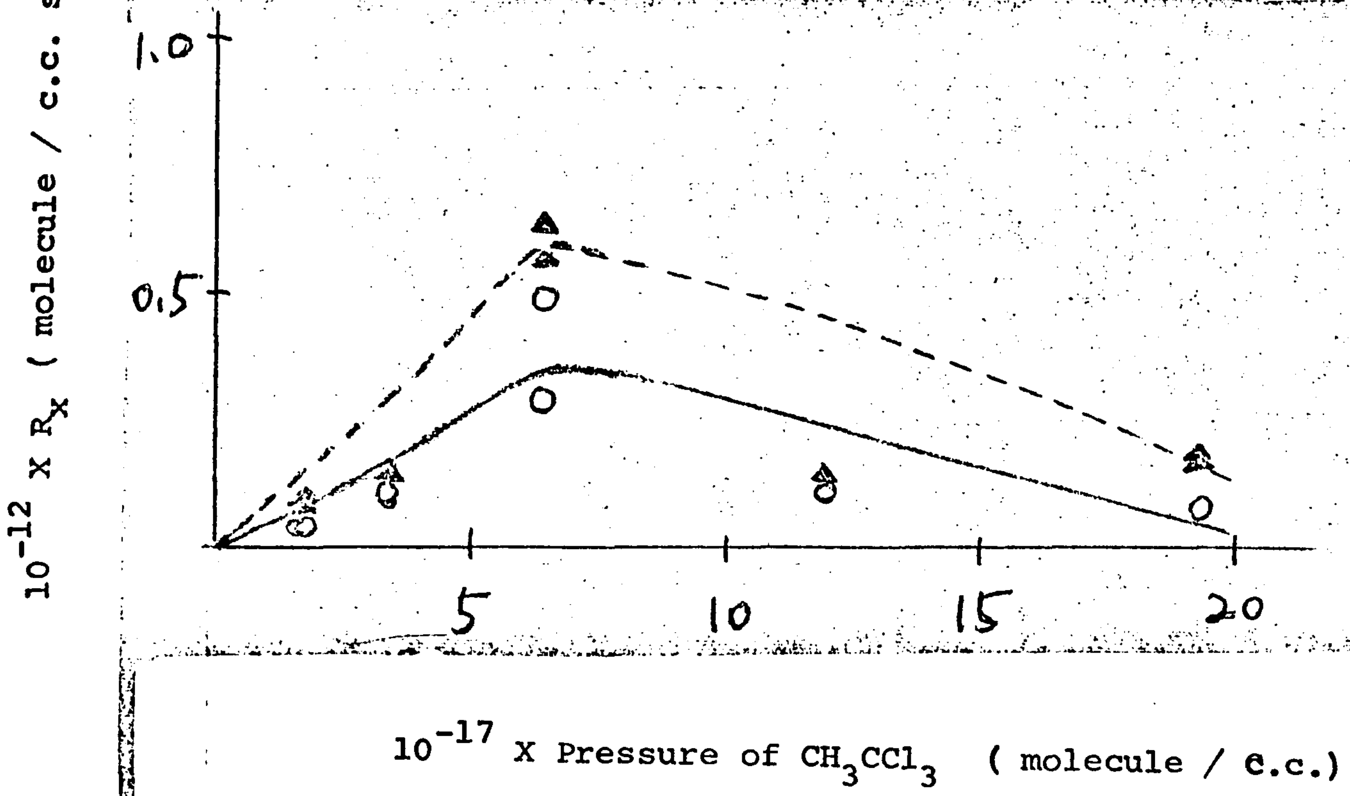


Figure 9. Variation of Product Rate as a Function of Initial CH_3CCl_3 Pressure $\lambda > 2200$ Å.

▲ : CH_2CCl_2

○ © CH_3CCl_2I



Even though the data are somewhat scattered, the results indicate that in this wavelength region both CH_2CCl_2 and CH_3CCl_2I reach a maximum at identical CH_3CCl_3 pressure, about 20 torr. This observation may be explained by accepting one single excited state as a common precursor to both CH_2CCl_2 and CH_3CCl_2I in the long wavelength region and that in the short wavelength regions additional CH_3CCl_2I may originate from a different excited state. Accepting temporarily this idea, we propose the following mechanism ;

$$
\begin{array}{lll}
CH_3CCl_3 + h\nu & \longrightarrow CH_3CCl_3\,^{*} & 1 \\
CH_3CCl_3 + h\nu' & \longrightarrow CH_3CCl_3\,^{**} & 2 \\
CH_3CCl_3\,^{*} & \longrightarrow CH_2CCl_2 + HCl & 3a \\
CH_3CCl_3\,^{*} & \longrightarrow CH_3CCl_2\cdot + Cl\cdot & 3b \\
CH_3CCl_3\,^{*} + CH_3CCl_3 & \longrightarrow \text{Deactivation} & 4a \\
CH_3CCl_3\,^{*} + \text{OFCB} & \longrightarrow \text{Deactivation} & 4b \\
CH_3CCl_3\,^{**} & \longrightarrow CH_3CCl_2\cdot + Cl\cdot & 5 \\
CH_3CCl_2\cdot + I_2 & \longrightarrow CH_3CCl_2I + I\cdot & 6
\end{array}
$$

The life time of the " two star " excited state is so short that it can not be deactivated under the experimental conditions of the present investigation.

The CH_3CCl_3 * is the excited state produced predominantly at $\lambda > 2200$ Å and CH_3CCl_3 ** is the excited state produced mainly at $\lambda < 2200$ Å. In agreement with the observation made from figures 8 and9 we are suggesting that only the lower excited state, CH_3CCl_3* can be deactivated by the pressures used in this investigation. Reaction 3a and 3b represent the decomposition reaction of the single star excited state via molecular detachment of HCl and via C-Cl bond rupture respectively. Reaction 4a represents the deactivation by CH_3CCl_3 itself and 4b represents the deactivation by OFCB. However, it is now interesting to test whether the above mechanism also agrees in a quantitative manner with the data.

According to the above proposed mechanism;

$$R_{CH_2CCl_2} = K_{3a} \, (CH_3CCl_3 \, *) \qquad \text{I}$$

In order to obtain the concentration of the excited molecules the steady state approximation must be used.

For any species, once the excited state reaches its steady state concentration, the rate of production is equal to its rate of disappearance. Thus,

$$d\ (\ CH_3CCl_3\ *\ ) = -\ d\ (\ CH_3CCl_3\ *\ ) \qquad \mathrm{II}$$

The rate of formation of the single star excited 1,1,1-trichloroethane is directly proportional to the amount of light absorbed per unit time,

$$d\ (\ CH_3CCl_3\ *\ ) = \alpha \cdot I_{abs}$$

where α is the proportion of light absorbed which leads to the one star excited state and I_{abs} is the amount of light absorbed. In the absence of OFCB, the disappearance of the excited CH_3CCl_3 is accounted for by decomposition reactions 3a and 3b, and deactivation 4a,

$$-\ d\ (\ CH_3CCl_3\ *\ ) = k_{3a}(\ CH_3CCl_3\ *\ ) + k_{3b}(\ CH_3CCl_3\ *\ ) + k_{4a}(\ CH_3CCl_3\ *\ )(\ CH_3CCl_3\ )$$

Substitution of these equations for the rate of appearance and of disappearance of the excited molecule in equation II gives the following ;

$$\alpha \cdot I_{abs} = (\ k_{3a} + k_{3b}\ )(\ CH_3CCl_3\ *\ ) + k_{4a}\ (\ CH_3CCl_3)(\ CH_3CCl_3\ *\ )$$

The concentration of the excited species is;

$$(CH_3CCl_3 *) = \frac{\mathcal{L}\cdot I_{abs}}{(k_{3a} + k_{3b}) + k_{4a} (CH_3CCl_3)}$$

Thus,

$$R_{CH_2CCl_2} = \frac{\mathcal{L}\cdot k_{3a}\ I_{abs}}{(k_{3a} + k_{3b}) + k_{4a} (CH_3CCl_3)} \qquad \text{III}$$

The intensity of the absorbed light is related to the concentration of absorbing species by Beer's law;

$$I/I_o = e^{-abc} \qquad \text{IV}$$

where I_o is the incident indensity of light, I is the intensity of light transmitted, c is the concentration of the absorbing species, b is the path length of the light through the absorbing species, and a is a constant dependent upon the absorbing species.

Changing equation IV so that it may be expressed as a function of light absorbed, I_{abs}, rather than light transmitted yields,

$$I_{abs} = I_o (1 - e^{-abc})$$

However for a variable exponent of e, there is a Taylor expansion series,

$$e^{-x} = 1 - x + x^2/2! - x^3/3! +$$

For small values of x, in this case a low absorbance of light, e^{-x} may be approximated by (1 - x), so that,

$$I_{abs} = I_o \left[1 - (1 - abc) \right] \quad , \text{where } x = abc$$

or, $$I_{abs} = I_o \, abc$$

This may be written as,

$$I_{abs} = \beta \, I_o \, (CH_3CCl_3) \qquad \text{V}$$

which β is the absorption coefficient, a·b.

As long as the incident light is kept constant and the limitations of the approximation are not exceeded, equation V may be applied to this work. In the extreme, it is obvious that an increase in 1,1,1-trichloroethane pressure (concentration) will not cause I_{abs} to change if all available light already is absorbed at the low pressure.

By substitution of equation V into equation III, the expression for the rate of 1,1-dichloroethylene production becomes,

$$R_{CH_2CCl_2} = \frac{\alpha \cdot \beta \cdot I_o k_{3a} (CH_3CCl_3)}{(k_{3a} + k_{3b}) + k_{4a} (CH_3CCl_3)}$$

if I_o is kept constant, then this equation may be simplified by placing $\alpha \cdot \beta \cdot I_o = \gamma$. Thus, we obtain,

$$R_{CH_2CCl_2} = \frac{\gamma \cdot k_{3a} \, (CH_3CCl_3)}{(k_{3a} + k_{3b}) + k_{4a} \, (CH_3CCl_3)} \qquad \text{or}$$

$$\frac{1}{R_{CH_2CCl_2}} = \frac{k_{4a}}{\gamma \cdot k_{3a}} + \frac{(k_{3a} + k_{3b})}{\gamma \cdot k_{3a}} \times \frac{1}{(CH_3CCl_3)} \qquad \text{VI}$$

In similiar way, an expression may be derived for the rate of CH_3CCl_2I production which is given in equation VII.

$$\frac{1}{R_{CH_3CCl_2I}} = \frac{k_{4a}}{\gamma \cdot k_{3b}} + \frac{(k_{3a} + k_{3b})}{\gamma \cdot k_{3b}} \times \frac{1}{(CH_3CCl_3)} \qquad \text{VII}$$

Using the data in table IIIA and IIIB equations VI and VII have been plotted in figure 10 for the results obtained with $\lambda > 2200$ Å and in figure 11 for the data obtained with $\lambda > 2000$ Å. As we mentioned earlier, equations VI and VII are applicable only in the region where the light absorption is small or for experiments carried out at low initial CH_3CCl_3 pressures. In figure 10 and 11 only those experiments were plotted in which the initial CH_3CCl_3 pressure did not exceed 13×10^{15} molecule/c.c.

Figure 10. $1/R_x$ versus $1/P_{CH_3CCl_3}$ at λ > 2200 Å.

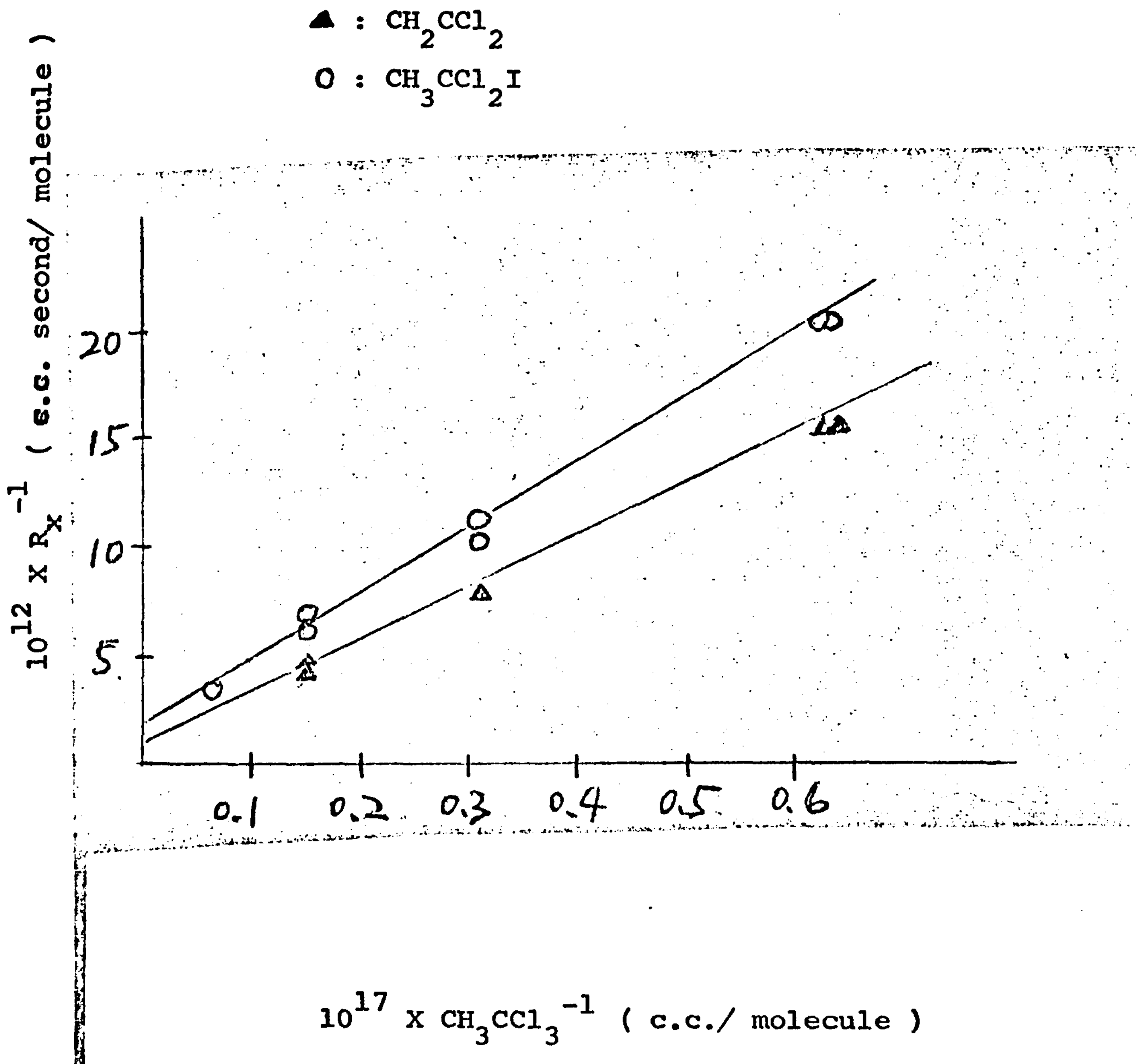
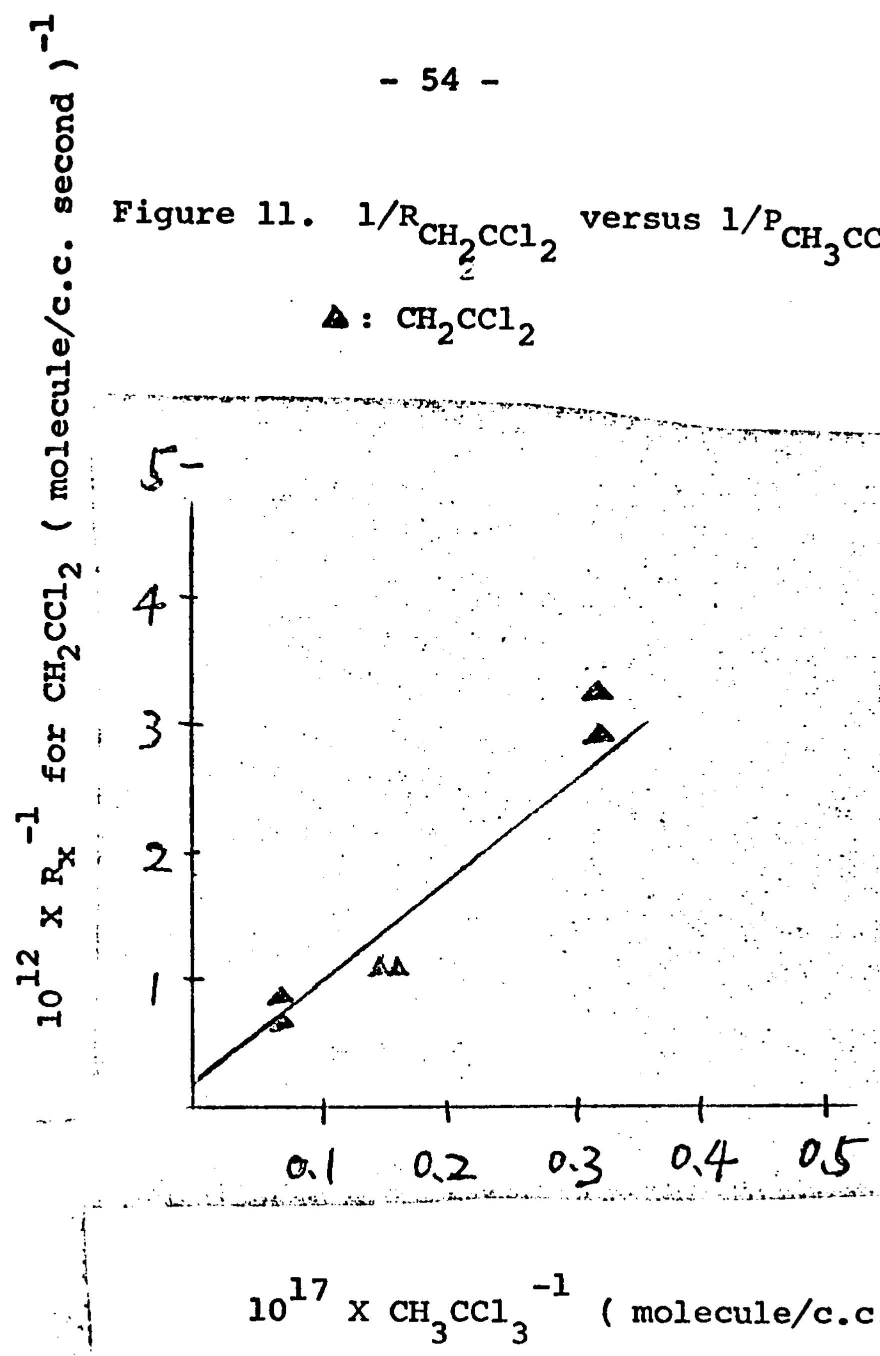


Figure 11. $1/R_{CH_2CCl_2}$ versus $1/P_{CH_3CCl_3}$ at $\lambda > 2000$ Å.

▲ : CH_2CCl_2



From figure 10 the following approximate ratios of rate constants are obtained;

$k_{4a} / (k_{3a} + k_{3b}) = 0.03 \times 10^{-17}$ (molecule/c.c.)$^{-1}$ (from the CH_3CCl_2I data)

$k_{4a} / (k_{3a} + k_{3b}) = 0.04 \times 10^{-17}$ (molecule/c.c.)$^{-1}$ (from the CH_2CCl_2 data)

These values are within experimental error identical indicating that the region $\lambda > 2200$ Å CH_2CCl_2 and CH_3CCl_2I originate mainly, if not exclusively from the same excited state.

In the region $\lambda > 2000$ Å it was only possible to plot the data for CH_2CCl_2 (see figure 11) and this plot yielded;

$k_{4a} / (k_{3a} + k_{3b}) = 0.01 \times 10^{-17}$ (molecule/c.c.)$^{-1}$

This value varies considerably from the above ratio obtained with corning filter 9-54 and may indicate that the CH_2CCl_2 production at low wavelength (absence of filter) is not correctly represented by our mechanism.

In the presence of OFCB as a inert deactivator, the following equation were derived form the proposed reaction mechanism;

$$1/R_{CH_2CCl_2} = \left[k_{3a} + k_{3b} + k_{4a}\,(CH_3CCl_3\,)\right] / k_{3a}\cdot\alpha\cdot I_{abs} + k_{4b}\,(OFCB)\,/\,k_{3a}\cdot\alpha\cdot I_{abs} \qquad \text{VIII}$$

If indeed CH_3CCl_2I is produced at $\lambda > 2200$ Å from CH_3CCl_3 *, then we may obtain a similiar equation in regard to the CH_3CCl_2I data,

$$1/R_{CH_3CCl_2I} = \left[k_{3a} + k_{3b} + k_{4a}\,(CH_3CCl_3\,)\right] / k_{3b}\cdot\alpha\cdot I_{abs} + k_{4b}\,(OFCB)\,/\,k_{3b}\cdot\alpha\cdot I_{abs} \qquad \text{IX}$$

In figure 12 $1/R_{CH_2CCl_2}$ and $1/R_{CH_3CCl_2I}$ are plotted versus OFCB pressure for the data obtained with corning filter 9-54 ($\lambda > 2200$ Å) and the data obtained in the absence of a filter ($\lambda > 2000$ Å) in figure 13.

It is clear that equation IX should not hold for both the CH_3CCl_2I data obtained at $\lambda > 2200$ Å and for those at $\lambda < 2200$ Å. Since our mechanism proposes different excited states as the precursors to CH_3CCl_2I dependent upon the energy of the incident light. It is gratifying to observe that the two plots of $1/R_{CH_3CCl_2I}$ are indeed quite different. In the absence of a filter (figure 13) $1/R_{CH_3CCl_2I}$ is independent of OFCB pressure

Figure 12. Plots of $1/R_x$ versus Pressure of OFCB at $\lambda > 2200$ Å.

▲ : CH_2CCl_2

○ : CH_3CCl_2I

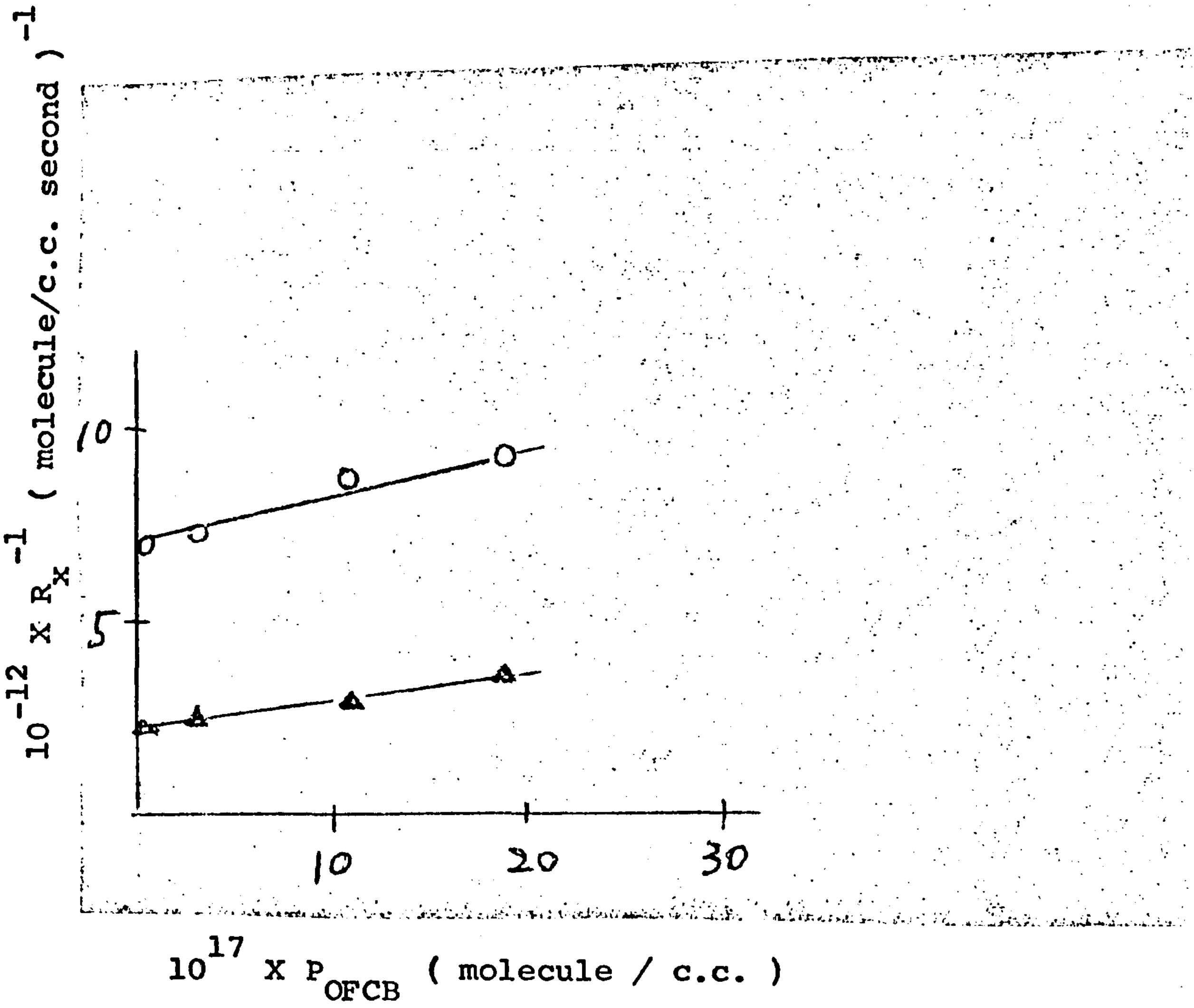
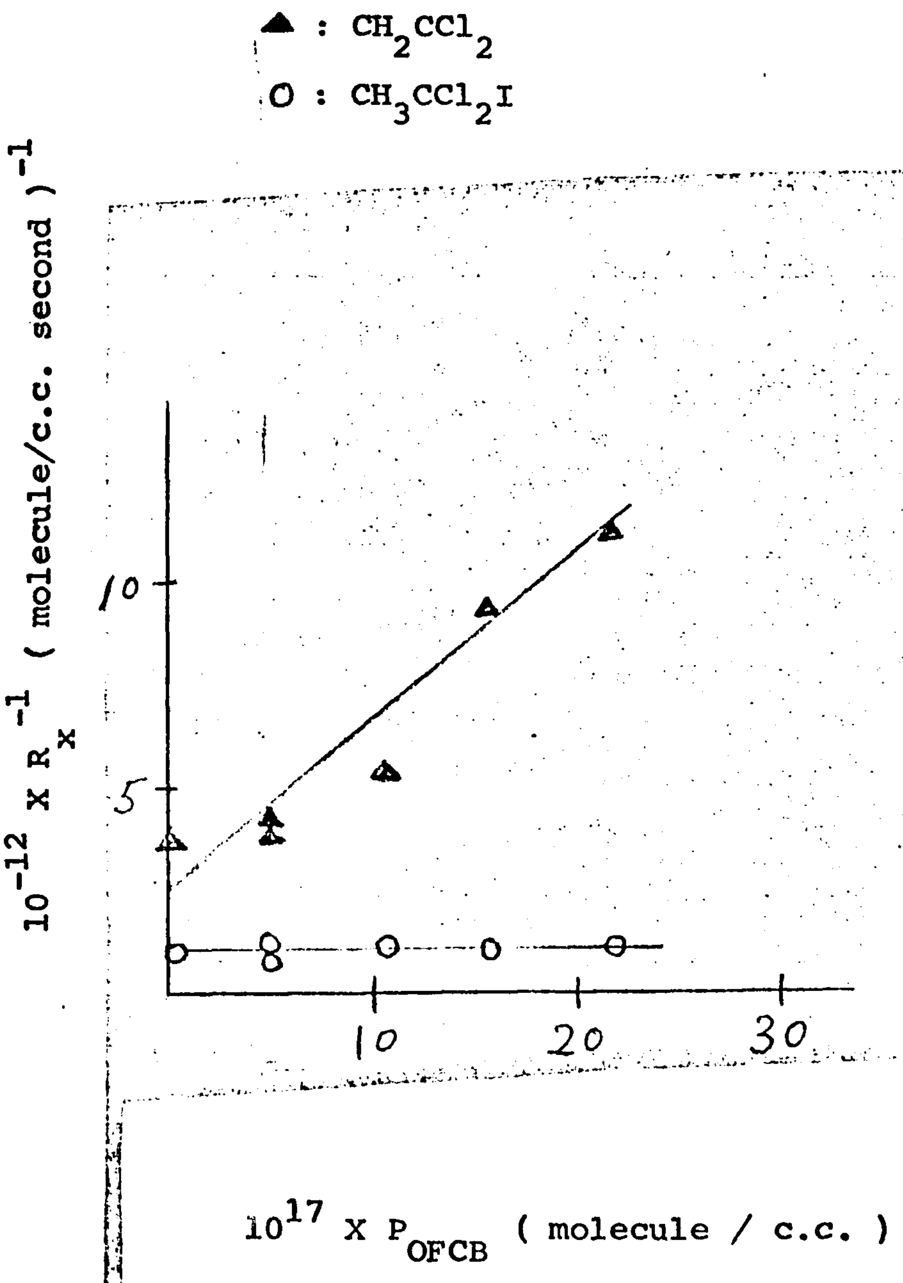


Figure 13. Plots of $1/R_x$ versus Pressure of OFCB at $\lambda > 2000$ Å.



indicating that the excited state producing CH_3CCl_2I in the absence of a filter ($\lambda > 2000$ Å) is so short lived that it can not be deactivated. This confirms our data obtained at different CH_3CCl_3 pressures and thus confirms our mechanism which proposes that CH_3CCl_2I is produced from different excited states at short wavelength of our investigation.

From figure 12 and 13 we can obtain the following rate constant ratios;

$k_{4b} / \left[k_{3a} + k_{3b} + k_{4a} (CH_3CCl_3) \right] = 0.03 \times 10^{-17}$ (molecule/c.c.) from both CH_2CCl_2 data and CH_3CCl_2I data at $\lambda > 2200$ Å . This ratio equals 0.3×10^{-17} (molecule/c.c.) from CH_2CCl_2 data at $\lambda > 2000$ Å.

By these ratios for rate constant and using the average value of the ratios for rate constant for $k_{4a} / (k_{3a} + k_{3b}) = 0.035 \times 10^{-17}$ $(\text{molecule/c.c.})^{-1}$ one can easily calculate out the ratio of $k_{4b} / (k_{3a} + k_{3b}) = 0.036 \times 10^{-17}$ $(\text{molecule/c.c.})^{-1}$ in the $\lambda > 2200$ Å. (since we have always keep the initial CH_3CCl_3 pressure at 20 torr: 6.4×10^{15} molecule/c.c. for the deactivated study of OFCB).

K_{4a} /(k_{3a} + k_{3b}) represents the rate of deactivation / rate of decomposition by CH_3CCl_3 molecule and k_{4b} /(k_{3a} + k_{3b}) represents the rate of deactivation / rate of decomposition by OFCB molecule. These two ratios are within experimental error identical indicating that OFCB and CH_3CCl_3 are equally effective as deactivator for the excited CH_3CCl_3 molecule.

The fact that at $\lambda > 2200$ Å both CH_2CCl_2 and CH_3CCl_2I data give an identical value for k_{4b} /(k_{3a} + k_{3b}) agrees with the mechanism suggesting a common presursor, CH_3CCl_3 *, for these products.

Not in agreement with our proposed mechanism are the widely divergent data varying by a factor of 10 for k_{4b} /(k_{3a} + k_{3b}) obtained from CH_2CCl_2 data at $\lambda > 2200$ Å and at $\lambda < 2200$ Å. This disagreement will be discussed later.

In any case it is quite clear that at longer wavelength ($\lambda > 2200$ Å) the mechanism is correctly represented by the following reactions sequence ;

$$CH_3CCl_3 + h\nu \longrightarrow CH_3CCl_3{}^* \tag{1}$$

$$CH_3CCl_3{}^* \longrightarrow CH_2CCl_2 + HCl \tag{3a}$$

$$CH_3CCl_3{}^* \longrightarrow CH_3CCl_2\cdot + Cl\cdot \tag{3b}$$

$$CH_3CCl_3{}^* + CH_3CCl_3 \longrightarrow \text{deactivation} \tag{4a}$$

$$CH_3CCl_3{}^* + \text{OFCB} \longrightarrow \text{deactivation} \tag{4b}$$

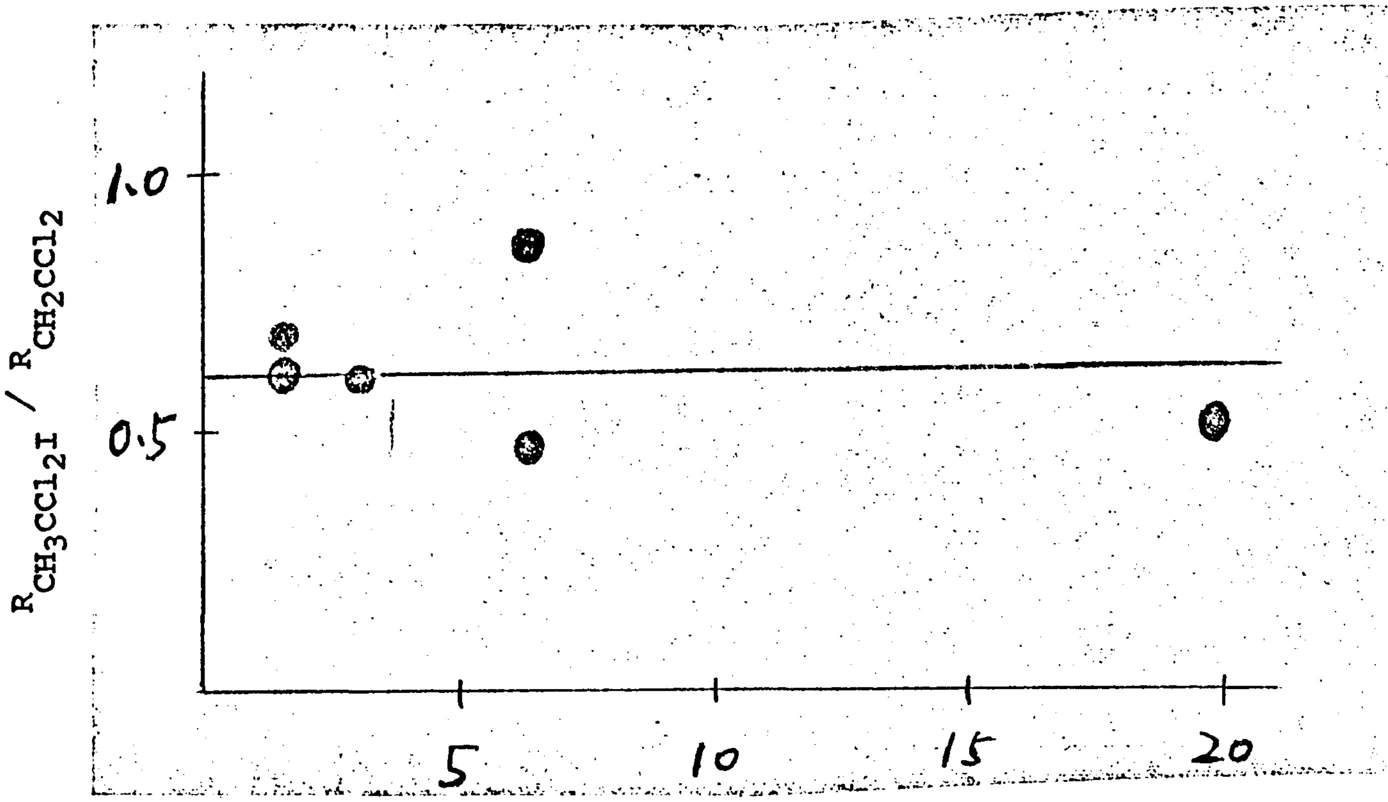
This mechanism requires that $R_{CH_3CCl_2I} / R_{CH_2CCl_2}$ must be constant regardless of the initial pressure of CH_3CCl_3 and of OFCB. In figure 14 and 15 this ratio is plotted versus CH_3CCl_3 and OFCB pressure respectively. Within experimental error a constant value is obtained for the above ratio proving that CH_2CCl_2 and CH_3CCl_2I originate, at $\lambda > 2200$ Å, mainly, if not exclusively from the same excited state.

Now the data in the absence of filter ($\lambda > 2000$ Å). There is no doubt - since it is not possible to deactivate the excited state producing CH_3CCl_2I - that this compound must be produced from an excited state different from the one being producing at $\lambda > 2200$ Å in agreement with our previous suggestion;

$$CH_3CCl_3 + h\nu' \longrightarrow CH_3CCl_3{}^{**} \tag{2}$$

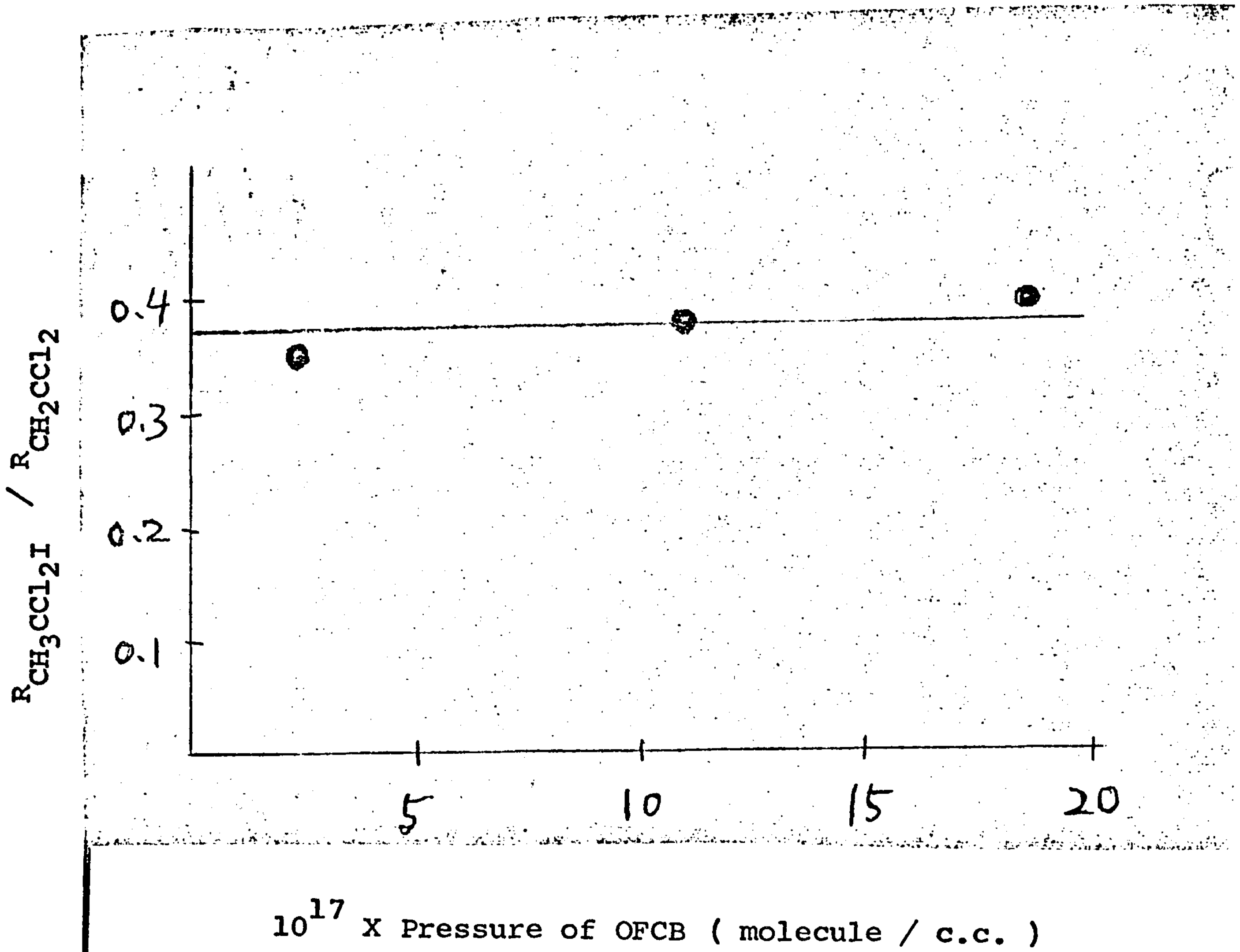
$$CH_3CCl_3{}^{**} \longrightarrow CH_3CCl_2\cdot + Cl\cdot \tag{5a}$$

Figure 14. $R_{CH_3CCl_2I}$ / $R_{CH_2CCl_2}$ versus Initial Pressure of CH_3CCl_3 at $\lambda > 2200$ Å



10^{17} X Pressure of CH_3CCl_3 (molecule/c.c.)

Figure 15. $R_{CH_3CCl_2I} / R_{CH_2CCl_2}$ versus Pressure of OFCB at $\lambda >$ 2200 Å.



There is a problem regarding the production of CH_2CCl_2 in the absence of a filter. If CH_2CCl_2 were produced exclusively from the same one star excited state regardless of the wavelength of the absorbed light then the ratios of rate constants should be identical. But the following data were obtained :

$$k_{4a} / (k_{3a} + k_{3b}) = 0.04 \times 10^{-17} \text{ (molecule/c.c.)}^{-1} \quad \lambda > 2200 \text{ Å}$$
$$k_{4a} / (k_{3a} + k_{3b}) = 0.01 \times 10^{-17} \text{ (molecule/c.c.)}^{-1} \quad \lambda > 2000 \text{ Å}$$
$$k_{4b} / (k_{3a} + k_{3b}) = 0.036 \times 10^{-17} \text{ (molecule/c.c.)}^{-1} \quad \lambda > 2200 \text{ Å}$$
$$k_{4b} / (k_{3a} + k_{3b}) = 0.36 \times 10^{-17} \text{ (molecule/c.c.)}^{-1} \quad \lambda > 2000 \text{ Å}$$

Although the data for $k_{4a} / (k_{3a} + k_{3b})$ are perhaps the same regardless of the energy of the incident light, those for $k_{4b} / (k_{3a} + k_{3b})$ are definitely not. Thus, the data indicate that CH_2CCl_2 does not originate from an excited state common to both wavelength regions. We have no information to explain this behaviour except that at shorter wavelengths perhaps additional CH_2CCl_2 may be produced by a reaction of the type,

$$CH_3CCl_3^{**} \longrightarrow CH_2CCl_2 + Cl\cdot + H\cdot \qquad 5b$$

where this reaction may occur directly or via an excited $C_2H_3Cl_2\cdot^{o}$ radical as intermediate. Evidence for this type of reactions in other halogenated compounds will be discussed later.

E. Photolysis of CH_3CCl_3 in the presence of HI as free radical scavenger :

Some experiments were carried out with HI rather than I_2 as a free radical scavenger. As expected two reaction products were observed, CH_2CCl_2 as in the case of I_2 as a free radical scavenger and CH_3CCl_2H. The last compound is of course similar to CH_3CCl_2I formed in the presence of I_2 . Since the $CH_3CCl_2\cdot$ radical formed by reactions 3b and 5 will now react with HI according to reaction 6b,

$$CH_3CCl_2\cdot + HI \longrightarrow CH_3CCl_2H + I\cdot \qquad 6b$$

The experiments carried out with HI are reported in table V. Series VA is a summary of 7 experiments at different exposure times in the presence of 5 % HI. The ratio $R_{CH_2CCl_2} / R_{CH_3CCl_2H} = 0.12$. The I_2 experiments gave a value of 0.3 for the equivalent ratio $R_{CH_2CCl_2} / R_{CH_3CCl_2I}$ in the $\lambda > 2000$ Å.

Series VB shown the influence of increasing pressures of OFCB upon the reaction products in the presence of HI. It is clear that the rate of production of CH_3CCl_2H decreases with increasing OFCB pressure. In figure 16 a plot of $1/R_{CH_3CCl_2H}$

TABLE VA, VB & VC

Photolysis of CH_3CCl_3 with HI

VA: Time Study, No Filter, $P_{CH_3CCl_3}$ = 20 torr

Run No.	P_{OFCB} (10^{17} molec./cc)	% of HI	$R_{CH_2CCl_2}$ (10^{12} molecule/c.c sec.)	$R_{CH_3CCl_2I}$ (10^{12} molecule/c.c sec.)
	0	5	1.5	13

VB: Deactivation Study with OFCB

$P_{CH_3CCl_3}$ = 20 torr, No Filter

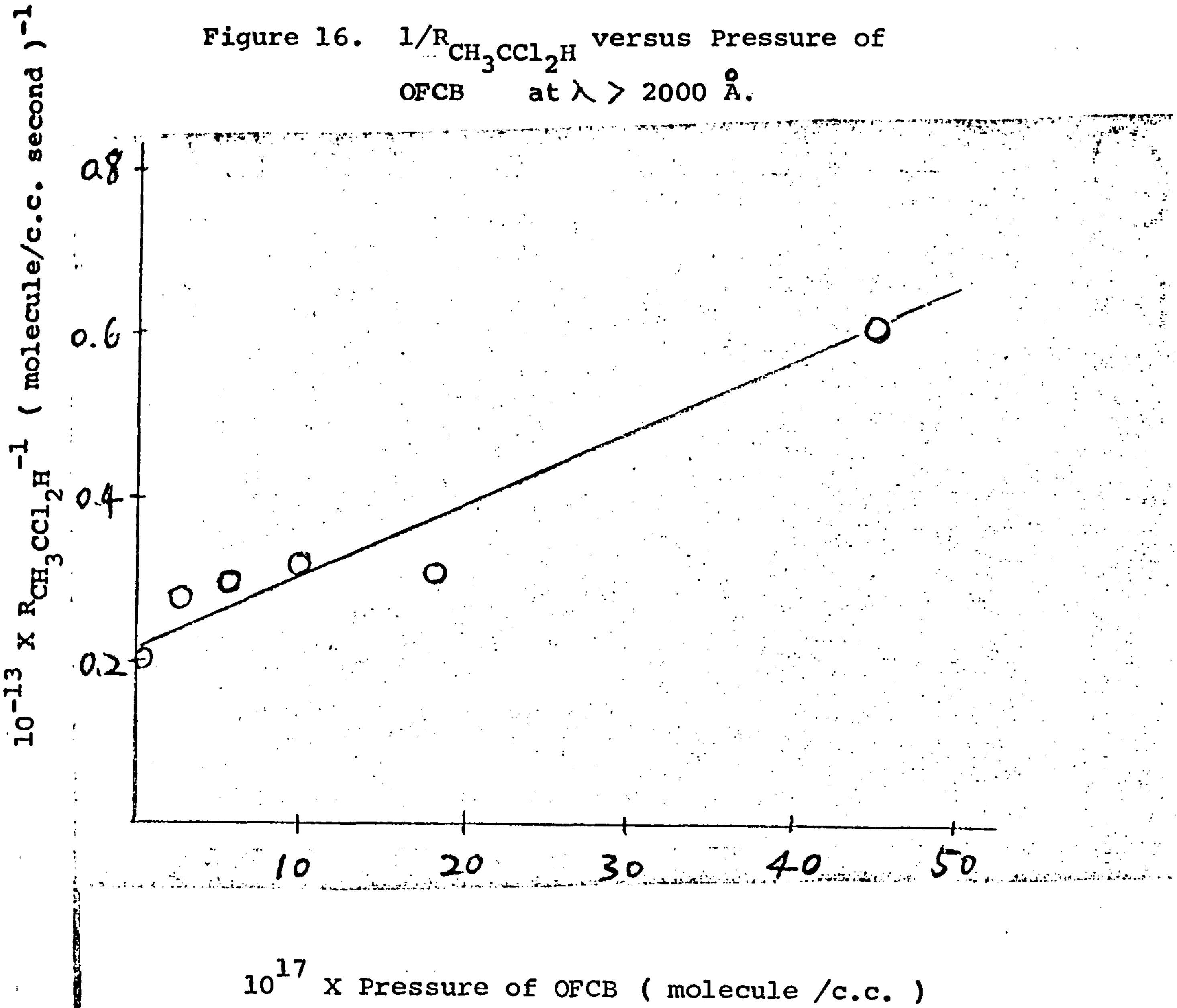
Run No.	P_{OFCB} (10^{17} molec./cc)	% of HI	$R_{CH_2CCl_2}$ (10^{12} molecule/c.c sec.)	$R_{CH_3CCl_2I}$ (10^{12} molecule/c.c sec.)
0-13	0	6	8.3	44.7
0-19	3.2	6	9.1	36.7
0-15	5.4	6	5.5	35.5
0-18	9.9	6	7.2	31.9
0-20	17.9	6	1.9	33.7
0-17	44.2	6	/	16.7

VC: Study with Varies % of HI, $P_{CH_3CCl_3}$ = 20 t

Corning Filter 9-54

Run No.	P_{OFCB} (10^{17} molec./cc)	% of HI	$R_{CH_2CCl_2}$ (10^{12} molecule/c.c sec.)	$R_{CH_3CCl_2I}$ (10^{12} molecule/c.c sec.)
0-25	0	2	0.19	1.6
0-26	0	2	0.17	1.6
0-22	0	5	0.15	2.1
0-23	0	5	0.17	2.5
0-34	0	10	0.23	4.7

Figure 16. $1/R_{CH_3CCl_2H}$ versus Pressure of OFCB at λ > 2000 Å.



versus OFCB pressure is given. The following approximate values are obtained from this plot.

$$\text{intercept} = \frac{k_{3a} + k_{3b} + k_{4a}\ (\mathrm{CH_3CCl_3})}{k_{3a}\cdot\alpha\cdot I_{abs}} = 2.0 \times 10^{-12} \text{ c.c. sec./molec.}$$

$$\text{slope} = \frac{k_{4b}}{k_{3a}\cdot\alpha\cdot I_{abs}} = 0.1 \times 10^{-29} \text{ c.c.}^2 \text{ sec./molecule}^2$$

From this we calculate an approximate value of 0.05×10^{-17} (molecule/c.c.)$^{-1}$ for $k_{4b} / [(k_{3a} + k_{3b} + k_{4a}\ (\mathrm{CH_3CCl_3})]$ in the $\lambda > 2000$ Å. This value is considerably less than the value of 0.3×10^{-17} (molecule/c.c.)$^{-1}$ which is obtaied from I_2 data. In studying the data carried out with HI, one other observation should be made; The ratio of $R_{\mathrm{CH_2CCl_2}} / R_{\mathrm{CH_3CCl_2H}}$ is consistently smaller than the ratio of $R_{\mathrm{CH_2CCl_2}} / R_{\mathrm{CH_3CCl_2I}}$ observed with I_2 as a scavenger. All the above results leads us to believe that in the presence of HI some secondary reactions may have occurred either increasing the $\mathrm{CH_3CCl_2H}$ production or decreasing the $\mathrm{CH_2CCl_2}$ production. For this reason we have carried out a study of the effect of different concentrations of HI upon the rate of production of these compounds. Data are reported in table VC and the rate of $\mathrm{CH_3CCl_2H}$ and $\mathrm{CH_2CCl_2}$ versus per cent of HI are plotted in figure 17. The figure clearly indicates that the rate of CH_2CCl_2 is independent of HI concentration but that CH_3CCl_2H increase with increasing HI concentration. An increase in CH_3CCl_2H production might be caused by the reaction sequence :

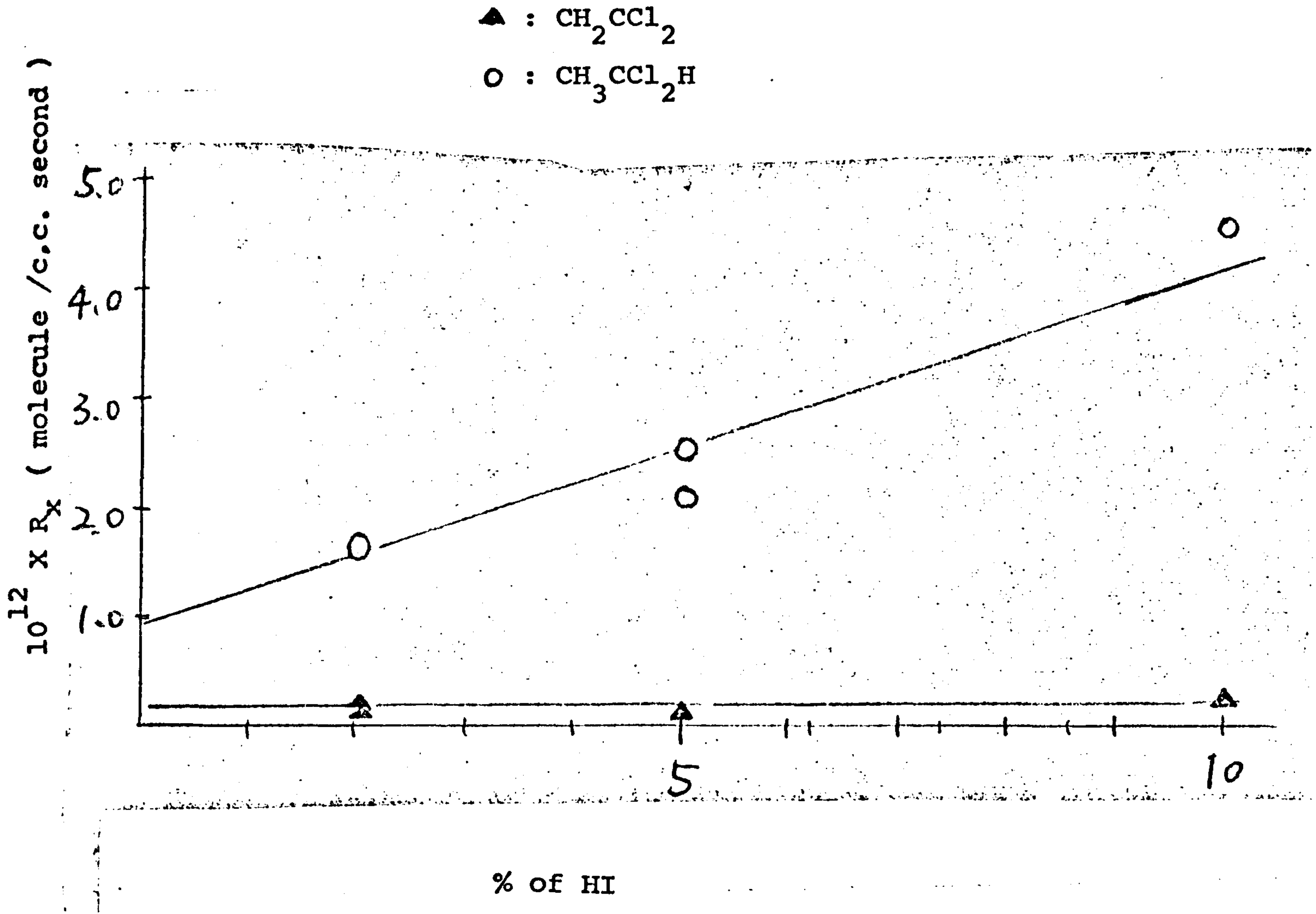
$$HI + h\nu \longrightarrow H\cdot + I\cdot \qquad 8$$

$$H\cdot + CH_3CCl_3 \longrightarrow CH_3CCl_2\cdot + HCl \qquad 9$$

$$CH_3CCl_2\cdot + HI \longrightarrow CH_3CCl_2H + I\cdot \qquad 10$$

In any case this observation explains why the HI experiments do not agree with those obtained with I_2 as free radical scavenger and furthermore, clearly indicate that the data in the presence of I_2 must be preferred.

Figure 17. Rate of Production of CH_3CCl_2H and CH_2CCl_2 versus % of HI



II. PHOTOLYSIS OF 1,1,2,2-TETRACHLOROETHANE

A. Introduction :

1,1,2,2-tetrachloroethane has been photolyzed in the presence of I_2 as a free radical scavenger. The reaction products observed are 1,1-dichloroethylene, trans 1,2 and cis 1,2-dichloroethylene, trichloroethylene, tetrachloroethylene and 1-iodo,1,2,2-trichloroethane.

Essentially the same types of experiments were carried out in this investigation as was the case with 1,1,1-trichloroethane. There was, however, one large difference. The maximum pressure of 1,1,2,2-tetrachloroethane at room temperature is only 5 torr. It was, therefore, not possible to carry out studies at different 1,1,2,2-tetrachloroethane pressures in order to observe a possible self-quenching of the excited states produced by the absorption of light. Deactivation studies were carried out exclusively with OFCB as inert deactivator.

B. Time Study :

Again, we have carried out a time study for 1,1,2,2-$CHCl_2CHCl_2$ in order to make sure that the obtained data are in the region of primary reaction.

Two series of experiments, (a) and (b), were carried out in the presence of I_2 as free radical scavenger.

(a) Photolysis in the absence of a filter (the light absorbed by 1,1,2,2-$CHCl_2CHCl_2$ ranges from 2000 Å to 4000 Å), using the direct light of Hanovia medium pressure arc.

(b) Photolysis in which Corning filter 0-54 (transmitting above 3000 Å) was inserted between reaction cell and arc.

All data are shown in table VI. It should be mentioned that the C_2HCl_3 , C_2Cl_4 and $CHCl_2CHClI$ data show some scattering due to the fact that these compounds are produced in relatively small amounts compared to the amounts of trans and cis 1,2-dichloroethylene. Also, the total decomposition of 1,1,2,2-$CHCl_2CHCl_2$ was kept to less than 0.5 % of the starting material, Thus making it difficult to analyse for compounds produced in these trace amount.

TABLE VI

Time Study of 1,1,2,2-$CHCl_2CHCl_2$ with I_2 , No Filter

$P_{CHCl_2CHCl_2}$ = 5 torr

Run No.	Exposure Time (minute)	$R_{CH_2CCl_2}$	$R_{t-1,2-C_2H_2Cl_2}$	$R_{c-1,2-C_2H_2Cl_2}$	$R_{C_2HCl_3}$	$R_{C_2Cl_4}$	R_{CHCl_2CHClI}
		(10^{12} molecule/c.c. second)					
A-2	5	/	0.27	0.69	/	/	/
A-1	10	/	0.33	0.51	/	/	/
A-9	10	0.05	0.22	0.36	0.09	0.17	/
A-3	20	0.04	0.30	0.43	/	0.15	/
A-10	20	/	0.21	0.34	0.06	/	/
A-5	30	/	0.24	0.41	0.08	0.04	0.01
A-7	30	0.02	0.23	0.37	0.07	0.03	0.02
A-8	30	0.02	0.17	0.30	0.07	0.06	0.01
A-4	60	0.03	0.20	0.32	0.04	/	0.01
A-6	120	0.03	0.05	0.16	0.03	/	/

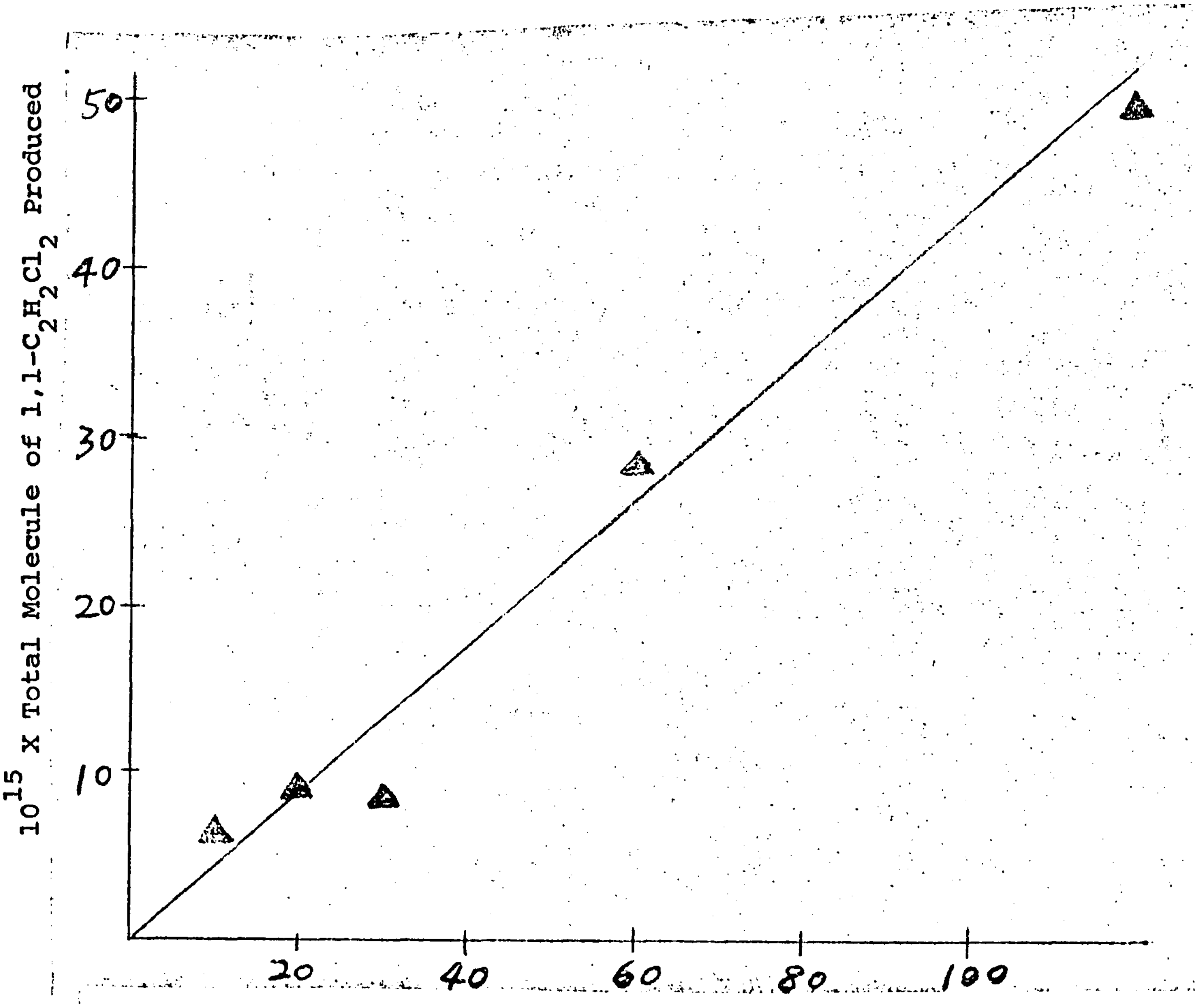
TABLE VI - CONTINUED

Time Study of 1,1,2,2-$CHCl_2CHCl_2$ with I_2 , Corning Filter 0-54
$P_{CHCl_2CHCl_2}$ = 5 torr

(unit: 10^{12} molecule/c.c. secomd)

Run No.	Exposure Time (hour)	$^R CH_2CCl_2$	$^R t\text{-}1,2\text{-}C_2H_2Cl_2$	$^R c\text{-}1,2\text{-}C_2H_2Cl_2$	$^R C_2HCl_3$	$^R C_2Cl_4$	$^R CHCl_2CHClI$
B-18	10.5	0.15	0.57	1.96	0.43	0.43	/
B-11	17.7	/	0.87	1.60	/	0.42	0.29
B-17	20	0.12	0.45	0.79	0.19	/	/
B-12	24	/	0.83	1.40	0.37	/	/
B-16	45.7	0.07	0.29	0.68	0.13	/	0.30
B-13	46.5	/	0.23	0.47	0.12	/	0.14
B-14	65	/	0.19	0.56	0.07	/	0.11
B-15	66.4	0.06	0.23	0.86	0.15	/	0.22

Figure 18. Production of 1,1-$C_2H_2Cl_2$ as a Function of Time in the Photolysis of 1,1,2,2-$CHCl_2CHCl_2$ at $\lambda > 2000$ Å.



Exposure Time (minute)

Figure 19. Production of C_2HCl_3 as a Function of Time in the Photolysis of 1,1,2,2-$CHCl_2CHCl_2$ at λ > 2000 Å.

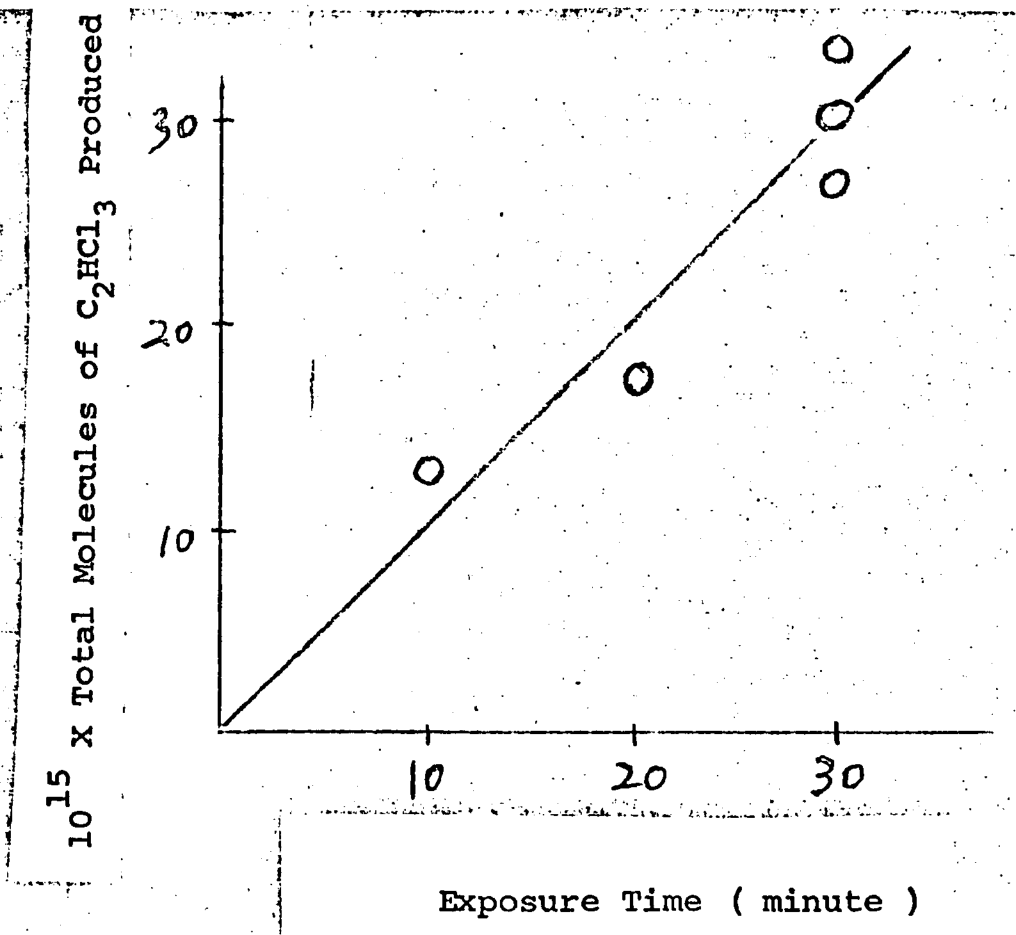


Figure 20. Production of $CHCl_2CHClI$ as a Function of Time in the Photolysis of 1,1,2,2-$CHCl_2CHCl_2$ at $\lambda > 2000$ Å

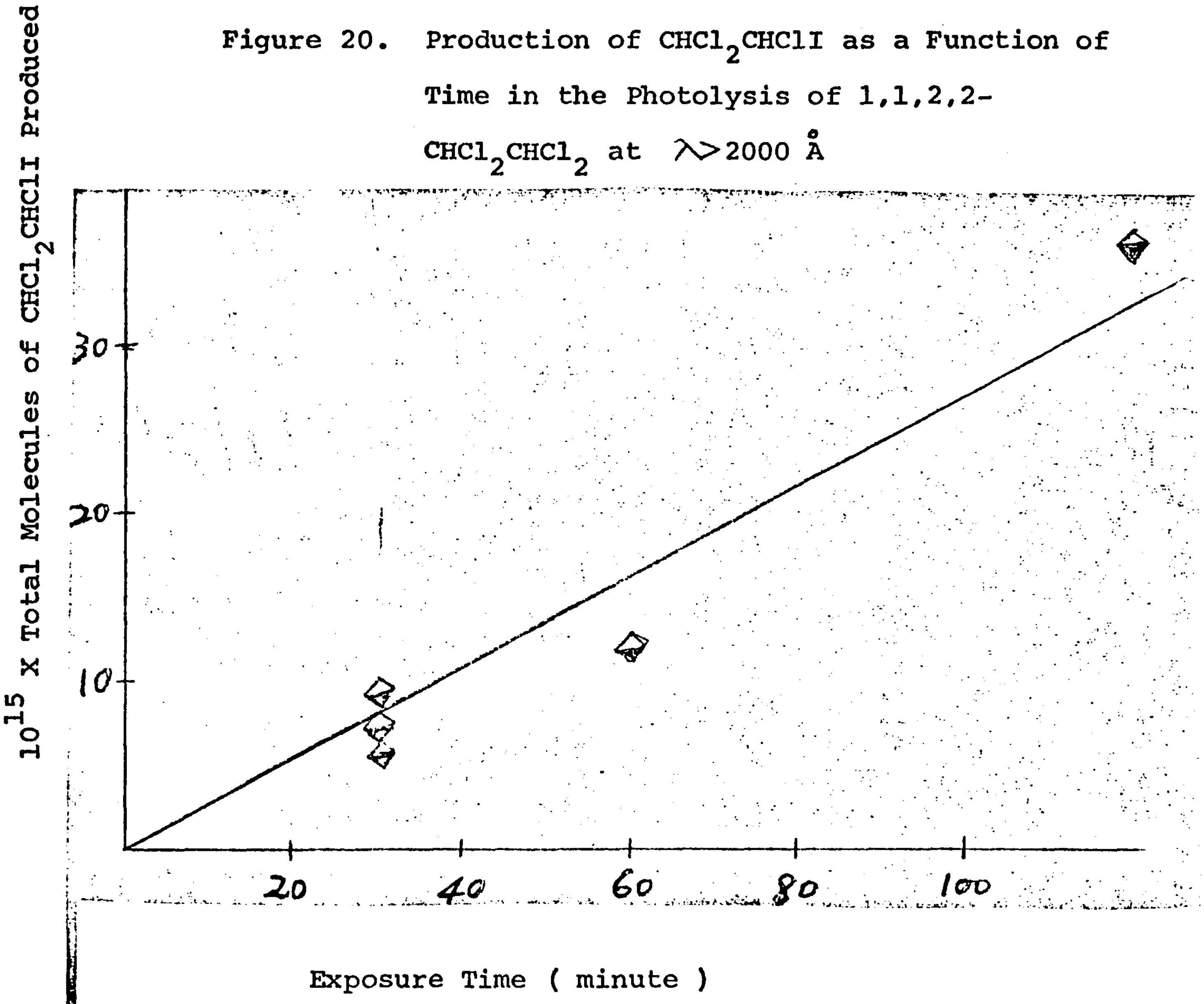


Figure 21. Production of Trans and Cis 1,2-$C_2H_2Cl_2$ as a Function of Time in the Photolysis of 1,1,2,2-$CHCl_2CHCl_2$ at $\lambda > 2000$ Å.

△: Trans 1,2-$C_2H_2Cl_2$

⊖: Cis 1,2-$C_2H_2Cl_2$

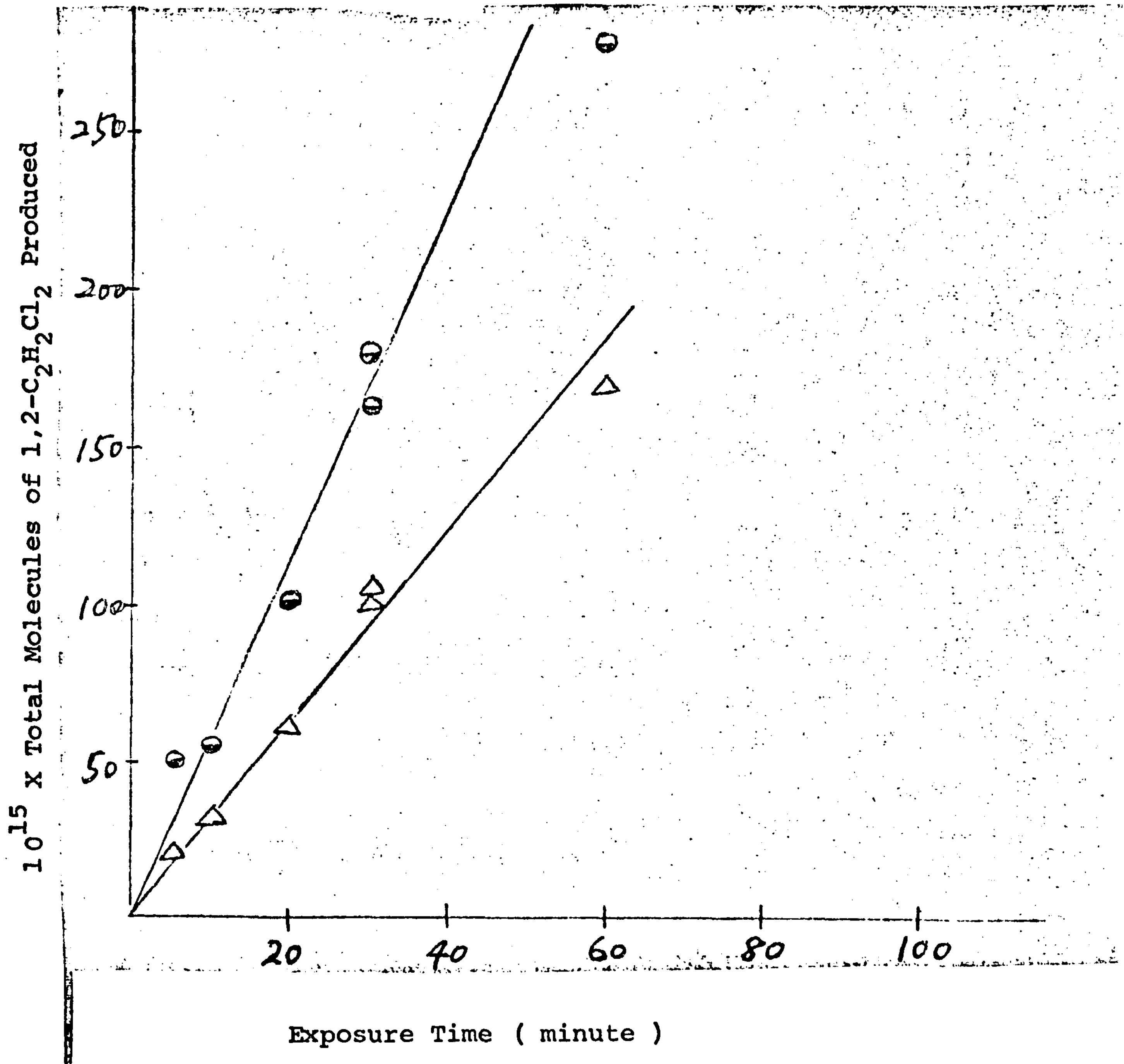


Figure 22. Production of 1,1-$C_2H_2Cl_2$ as a Function of Time in the Photolysis of 1,1,2,2-$CHCl_2CHCl_2$ at $\lambda > 3000$ Å

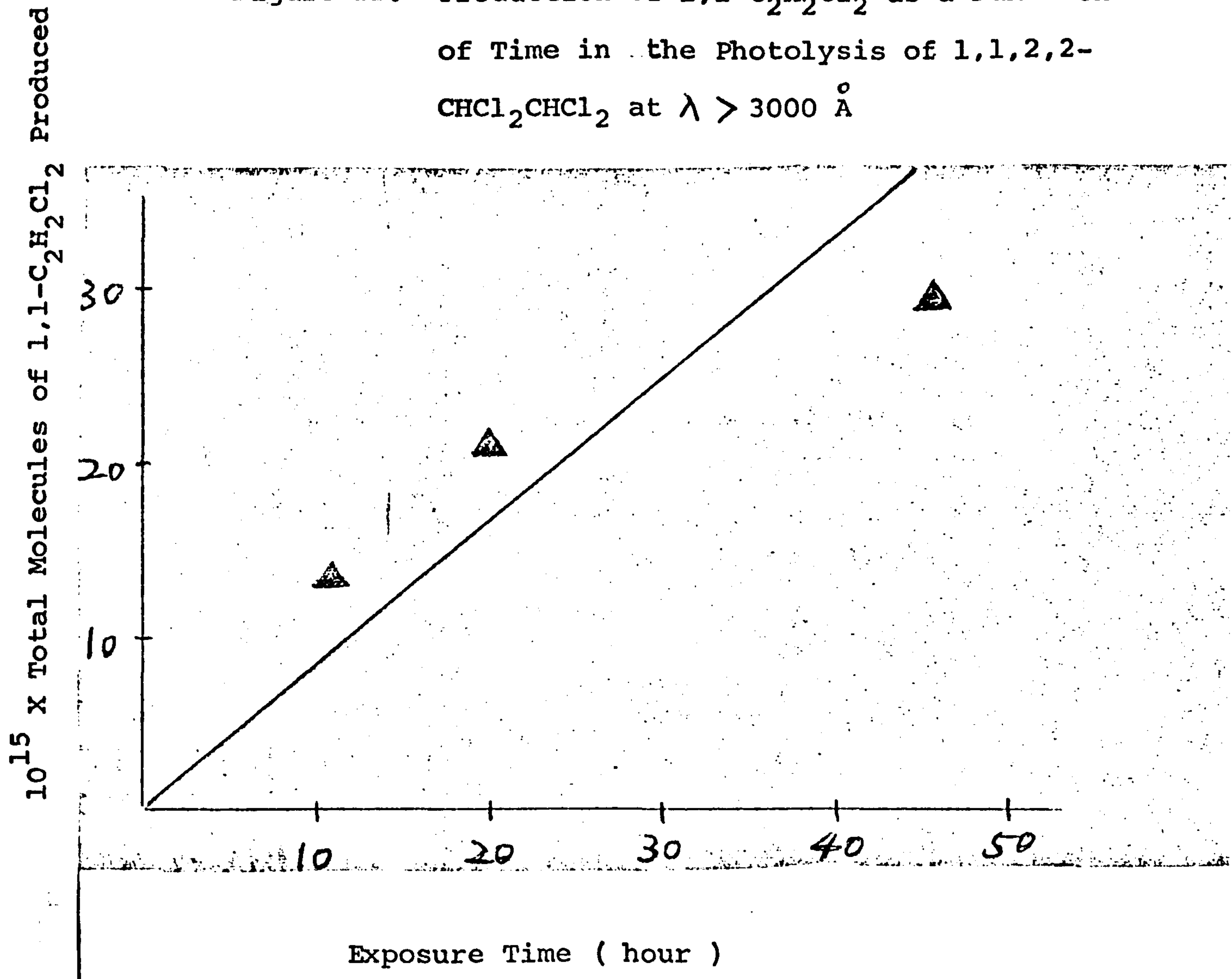
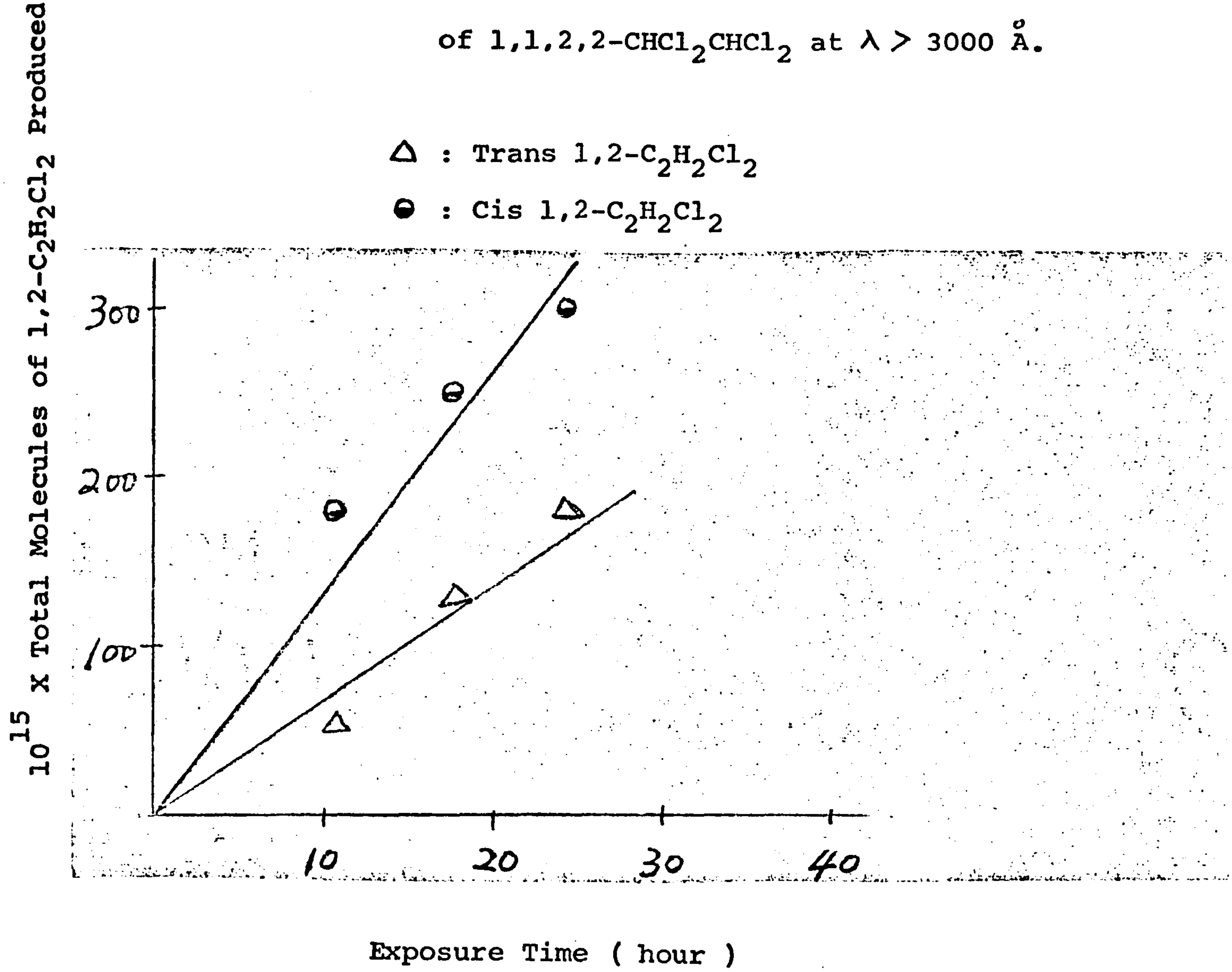


Figure 23. Production of Trans and Cis 1,2-$C_2H_2Cl_2$ as a Function of Time in the Photolysis of 1,1,2,2-$CHCl_2CHCl_2$ at $\lambda > 3000$ Å.



The results are plotted as the amounts produced versus exposure time in figures 18, 19, 20, 21 for the runs at $\lambda > 2000$ Å except C_2Cl_4 and figures 22, 23 for the experiments at $\lambda > 3000$ Å for 1,1, cis 1,2 and trans 1,2-$C_2H_2Cl_2$ only.

C. Energetic consideration in the photolysis of 1,1,2,2-$CHCl_2CHCl_2$:

It was mentioned earlier, the photolysis of 1,1,2,2-$CHCl_2CHCl_2$ in the presence of I_2, yields 1,1-$C_2H_2Cl_2$, cis-1,2-$C_2H_2Cl_2$, trans 1,2-$C_2H_2Cl_2$, C_2HCl_3 , C_2Cl_4 and $CHCl_2CHClI$.

As done in the case of CH_3CCl_3 it was again interesting to study the energetics of the individual reactions.

There are two possible pathways by which the observed dichloroethylenes may be produced.

$$\text{1,1,2,2-}CHCl_2CHCl_2 + h\nu \longrightarrow \text{1,1,2,2-}CHCl_2CHCl_2^* \qquad (11)$$

$$\text{1,1,2,2-}CHCl\ CHCl\ ^* \longrightarrow \text{1,1-, trans 1,2- or cis 1,2-}C_2H_2Cl_2 + Cl_2 \qquad (12a)$$

$$\longrightarrow \text{1,1-, trans 1,2- or cis 1,2-}C_2H_2Cl_2 + 2Cl\cdot \qquad (12b)$$

The change in bonds between the reactant and products are as follow (unit in Kcal/mole)

Bonds broke		Bonds formed (reaction 12a)		Bonds formed (reaction 12b)	
C-C	82.6	C=C	145.8	C=C	145.8
C-Cl	81	Cl-Cl	58		
C-Cl	81				
	244.6		203.8		145.8

Thus reaction (12a) requires a minimum input of 244.6-203.8 = 40.8 Kcal/mole, while reaction (12b) requires a minimum of 244.6-145.8 = 98.8 Kcal/mole. The corresponding wavelength for reaction (12a) and (12b) are 7010 Å and 2895 Å respectively. The experimental data (table VI) from the photolysis with Corning filter 0-54 (at $\lambda > 3000$ Å) clearly indicate that all three types of dichloroethylene are produced. Thus, in this wavelength region all the dichloroethylenes are produced exclusively via reaction (12a).

Trichloroethylene may be produced in a similar manner, the possible mechanisms are ;

$$1,1,2,2\text{-}CHCl_2CHCl_2^* \longrightarrow C_2HCl_3 + HCl \qquad (13a)$$

$$\text{or} \qquad \longrightarrow C_2HCl_3 + H\cdot + Cl\cdot \qquad (13b)$$

Reaction (13a) requires 13.3 Kcal/mole corresponding to a wavelength of 21,504 Å. Reaction (13b) requires a energy of about 116.5 Kcal/mole corresponds to a maximum wavelength of 2455 Å. This indicates that trichloroethylene produced at wavelength greater than 2455 Å is exclusively by HCl elimination, as shown in reaction (13a).

The possible mechanisms for producing C_2Cl_4 are :

$$1,1,2,2\text{-}CHCl_2CHCl_2^* \longrightarrow C_2Cl_4 + H_2 \qquad (14a)$$

$$\text{or} \qquad \longrightarrow C_2Cl_4 + 2\ H\cdot \qquad (14b)$$

Reaction (14a) requires 30 Kcal/mole, a wavelength of 9533 Å, while reaction (14b) requires 134.2 Kcal/mole or a wavelength of 2131 Å. This indicates that in the range $\lambda > 3000$ Å, tetrachloroethylene was produced exclusively from reaction (14a).

At this point, no consideration shall be given whether they are produced in part from different excited states.

The above energetic considerations and these preliminary experiments suggest the existence of 5 primary reactions at $\lambda >$ 3000 Å.

$$1,1,2,2\text{-}CHCl_2CHCl_2 + h\nu \longrightarrow 1,1\ C_2H_2Cl_2 + Cl_2 \qquad (11)$$

$$\longrightarrow \text{trans \& cis } 1,2\text{-}C_2H_2Cl_2 + Cl_2 \qquad (12)$$

$$\longrightarrow C_2HCl_3 + HCl \qquad (13)$$

$$\longrightarrow C_2Cl_4 + H_2 \qquad (14)$$

$$\longrightarrow CHCl_2CHCl\cdot + Cl\cdot \qquad (15)$$

D. Results and Interpretation of Data :

Accepting temporarily reaction (11) to (15), it becomes necessary to investigate whether all products originate from the same or from different excited states. For this purpose experiments with light of different wavelength regions were carried out.

Using the data in table VI we can calculate the ratio $R_{C_2HCl_3} / R_{CHCl_2CHClI}$ for $\lambda > 2000$ Å and $\lambda > 3000$ Å. Even though the data shows some scatter, the results yield an average value of about 6 ± 2 for $\lambda > 2000$ Å and 0.6 ± 0.2 for $\lambda >$ 3000 Å. This indicate that these two products do not originate from the same excited state.

In figure 24 $R_{C_2HCl_3} / R_{(\text{cis+trans } 1,2\text{-}C_2H_2Cl_2)}$ is plotted as a function of exposure time for the data obtained at λ>2000 Å and λ>3000 Å. A constant value of $R_{C_2HCl_3} / R_{(\text{cis+trans } 1,2\text{-}C_2H_2Cl_2)} = 0.14$ is obtained. Thus, the production of C_2HCl_3 and of cis/trans 1,2-$C_2H_2Cl_2$ occurs from the same excited state. Similiary $R_{CH_2CCl_2} / R_{(\text{cis+trans } 1,2\text{-}C_2H_2Cl_2)}$ versus exposure time is plotted in figure 25 for the data at λ>2000 Å and λ > 3000 Å. Again within experimental error an identical value 0.05 is found, indicating that CH_2CCl_2 and cis/trans 1,2-$C_2H_2Cl_2$ originate from the same excited state. The average value for $R_{CHCl_2CHClI} / R_{(\text{cis+trans } 1,2\text{-}C_2H_2Cl_2)}$ is 0.025 at λ>2000 Å and is 0.2 at λ>3000 Å, indicating these products originate from different excited states. The average value for $R_{C_2Cl_4} / R_{(\text{cis+trans } 1,2\text{-}C_2H_2Cl_2)}$ is about 0.15 for experiments at λ>3000 Å. This ratio is somewhat random for runs at λ> 2000 Å, nevertheless, average out equals to 0.25±0.05, indicating at least part of C_2Cl_4 originate from different excited state from cis & trans 1,2-C_2H_2Cl .

The ratio of $R_{\text{cis } 1,2\text{-}C_2H_2Cl_2} / R_{\text{trans } 1,2\text{-}C_2H_2Cl_2}$ versus exposure time is plotted in figure 26 for experiments at λ> 2000 Å and figure 27 for experiments at λ>2600 Å and λ>3000 Å.

Figure 24. $R_{C_2HCl_3} / R_{cis+trans\ 1,2-C_2H_2Cl_2}$ Versus Exposure Time at λ > 2000 Å and λ > 3000 Å.

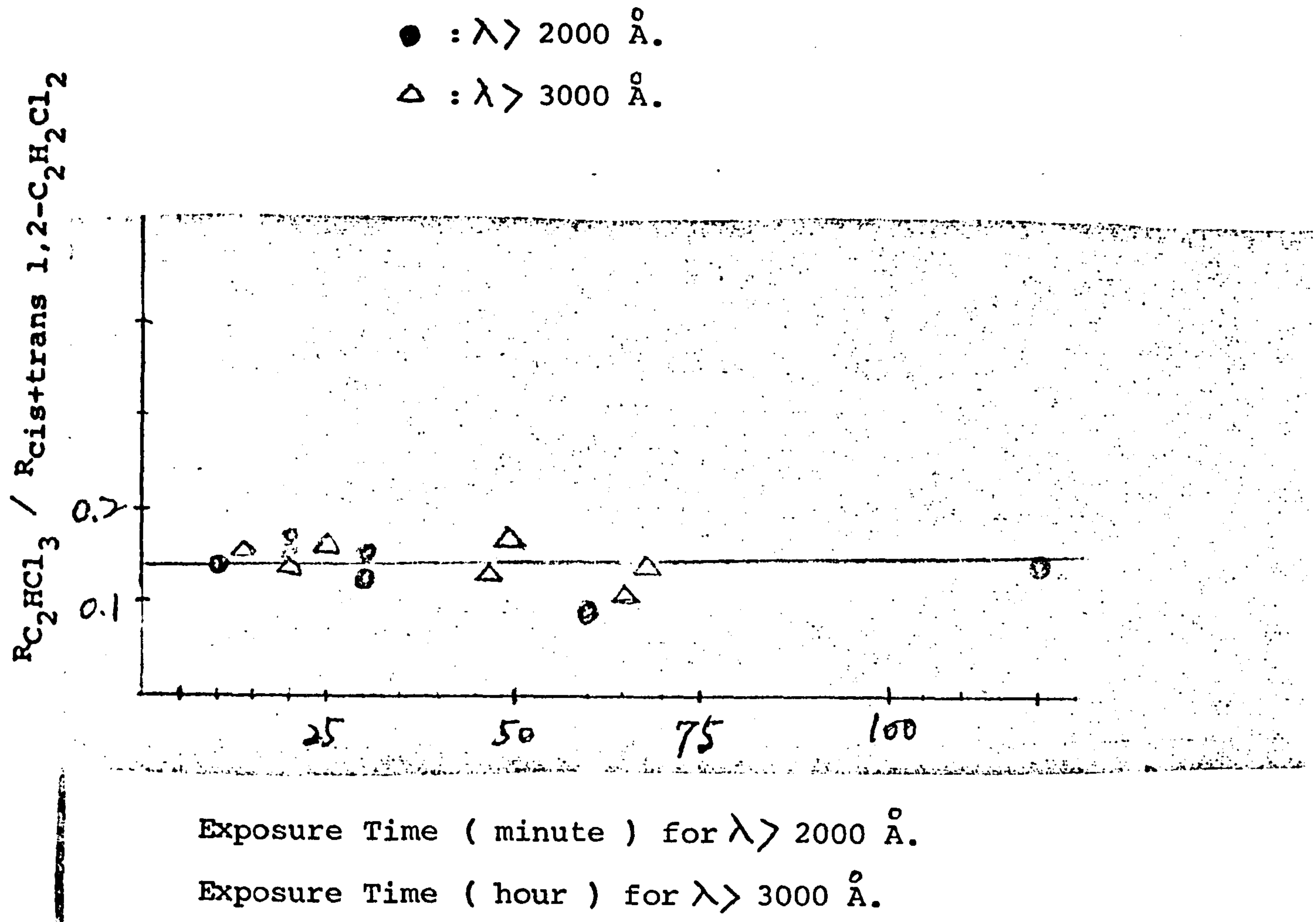
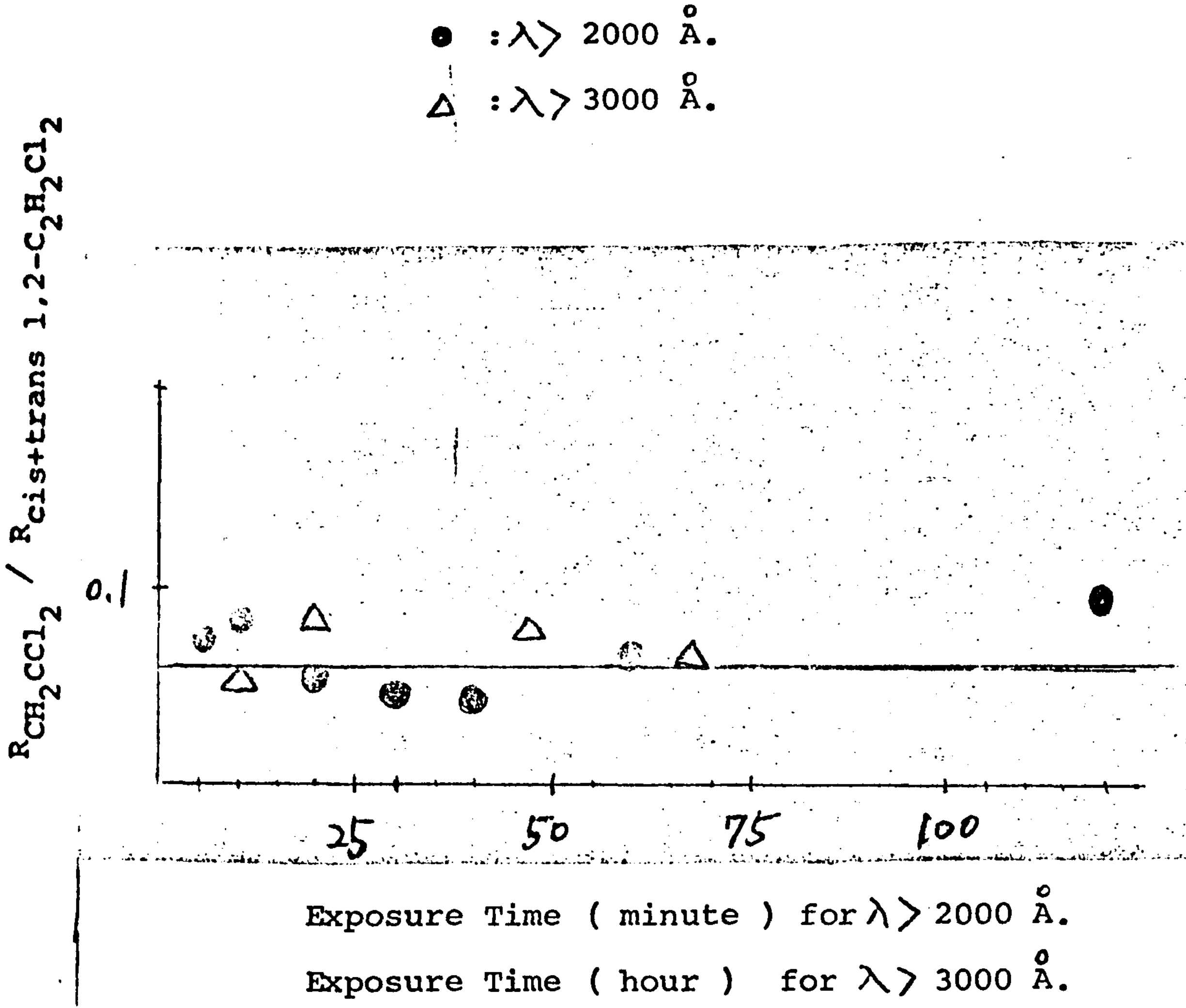


Figure 25. $R_{CH_2CCl_2}$ / $R_{cis+trans\ 1,2-C_2H_2Cl_2}$ Versus Exposure Time at $\lambda > 2000$ Å and $\lambda > 3000$ Å.



Figures 26 and 27 clearly indicate that at zero time the ratio of cis 1,2-$C_2H_2Cl_2$ / trans 1,2-$C_2H_2Cl_2$ is approximately unity, indicating that the excited precursor yields both isomers in a one to one ratio. With increasing exposure time the ratio increases, indicating that some cis-trans isomerization processes do occur.

E. Pressure Study with OFCB as inert deactivator :

In order to gain more information regarding the nature of the excited states, experiments were carried out at various octafluorocyclobutane (OFCB) pressures but at a constant pressure of 1,1,2,2-$CHCl_2CHCl_2$ in the presence of I_2. These experiments were performed in the nature of time studies in order to make certain that the data obtained are the results of primary reactions.

Data shown in table VII are for the runs at $\lambda > 3000$ Å and in table VIII for runs at $\lambda > 2000$ Å. The results are plotted as total molecules produced versus exposure time. Figures 28, 29, 30, 31, 32 and 33 correspond to $\lambda > 3000$ Å. and figures 34,35, 36, 37, 38 and 39 are the runs at $\lambda > 2000$ Å. It was mentioned earlier that C_2Cl_4 was only produced in trace amounts and it was impossible to get accurate data. It is therefore not plotted here for the pressure studies of C_2Cl_4.

Figure 26. Ratio of Cis 1,2-$C_2H_2Cl_2$ / Trans 1,2-$C_2H_2Cl_2$ Versus Exposure Time at $\lambda > 2000$ Å.

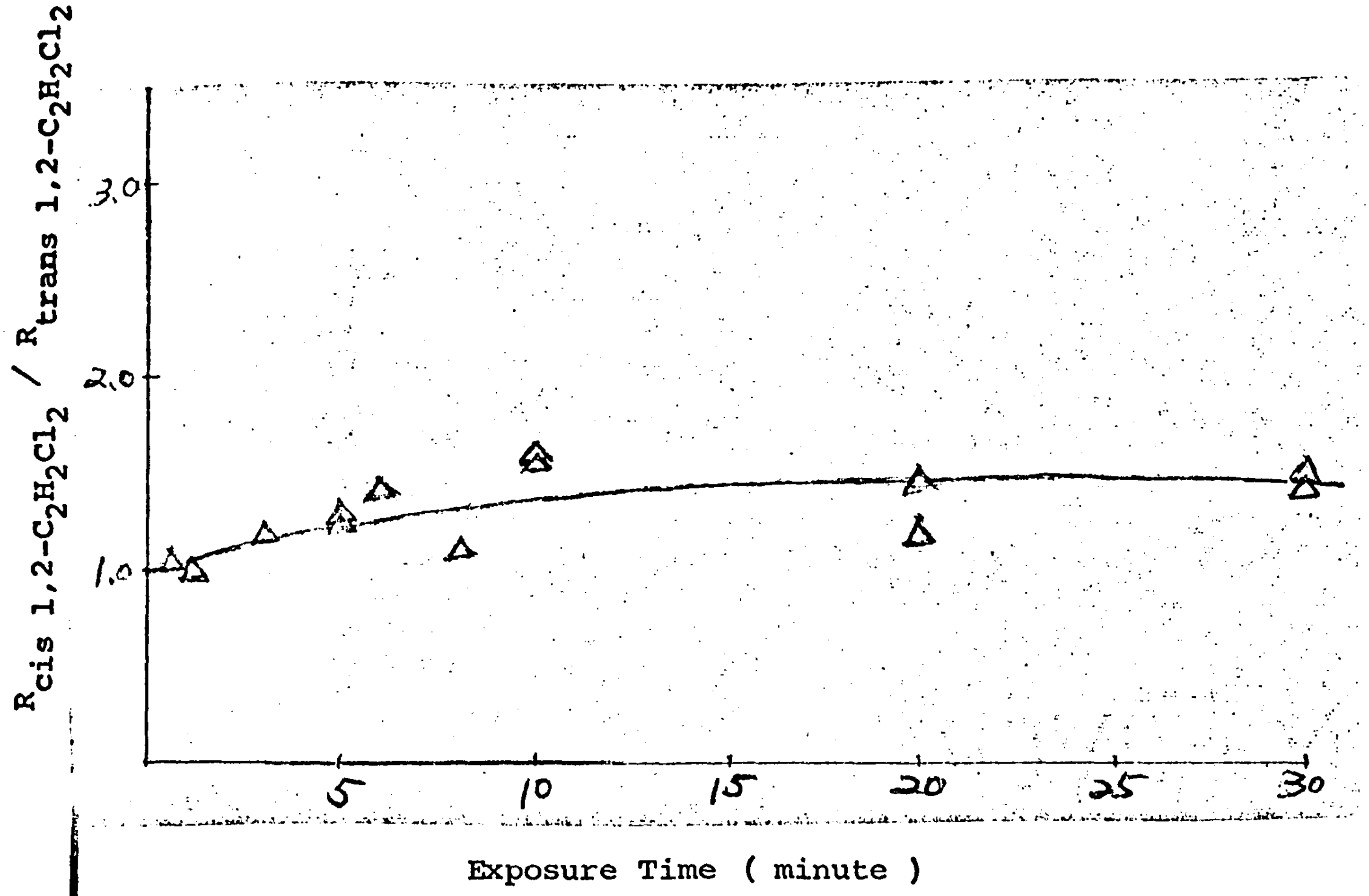


TABLE VII

Deactivation Study of $CHCl_2CHCl_2$ with OFCB as Deactivator
$P_{CHCl_2CHCl_2}$ = 5 torr, Cornig Filter 0-54

Run No.	P_{OFCB}	Exposure Time	$R_{CH_2CCl_2}$	$R_{t-1,2-C_2H_2Cl_2}$	$R_{c-1,2-C_2H_2Cl_2}$	$R_{C_2HCl_3}$	$R_{C_2Cl_4}$
	(10^{17} molec./cc)	(hour)	(10^{10} molecule/c.c. second)				
C-18	7.04	12.5	/	0.55	0.67	0.09	/
C-19	7.04	15.3	0.03	0.40	0.52	0.08	0.06
C-15	7.04	22.5	0.04	0.57	0.77	0.10	0.07
C-16	7.04	43.4	0.04	0.39	0.67	0.06	0.04
C-23	16.64	18	0.03	0.36	0.47	0.09	0.07
C-22	16.644	28	0.02	0.38	0.45	0.10	0.05
C-20	32.24	15	0.02	0.12	0.14	0.06	0.05
C-21	32.24	2401	0.01	0.16	0.18	0.05	0.03

Figure 27. Ratio of Cis 1,2-$C_2H_2Cl_2$/ Trans 1,2-$C_2H_2Cl_2$ Versus Exposure Time

△ : $\lambda > 2600$ Å.

O : $\lambda > 3000$ Å.

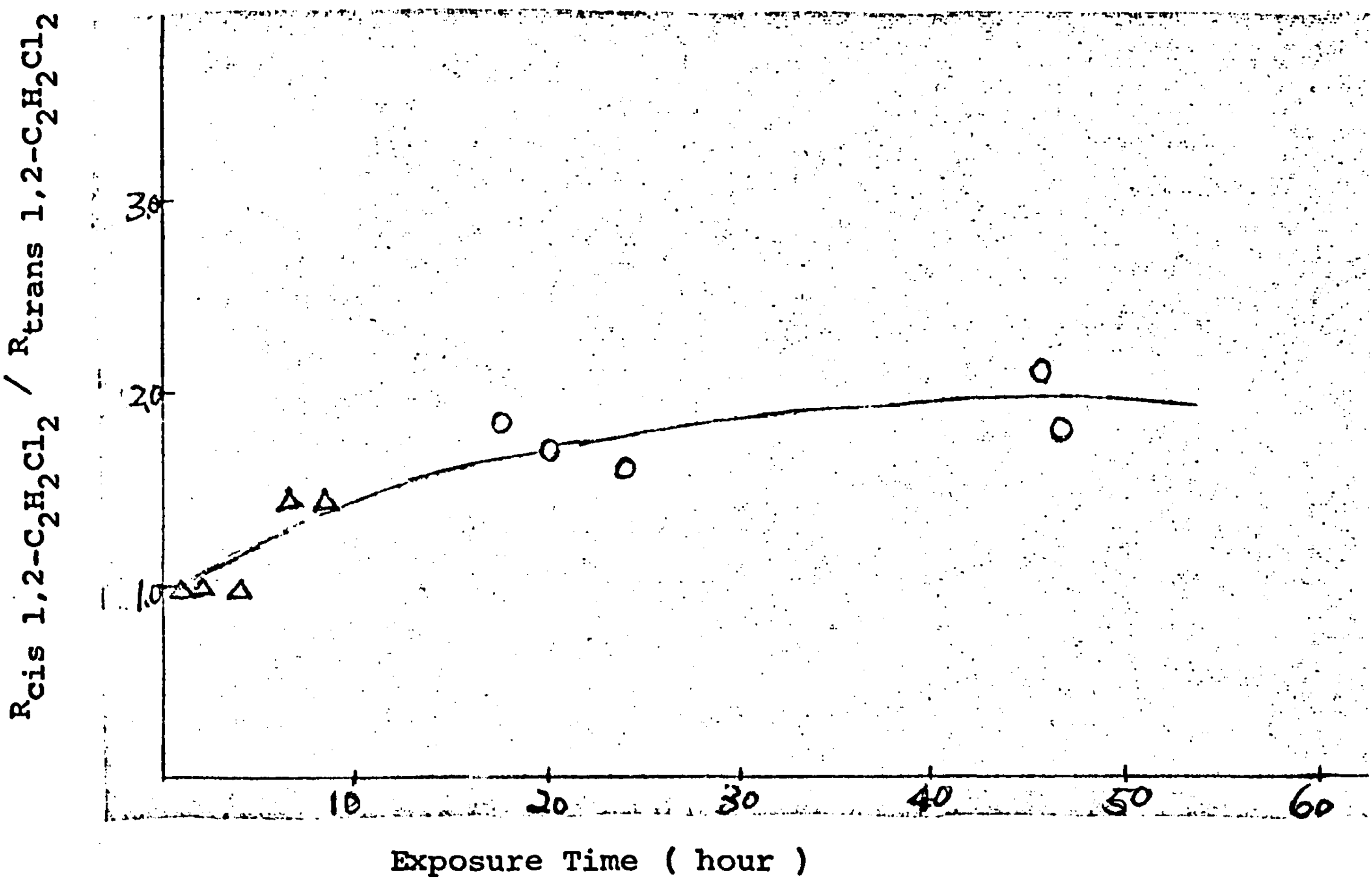


TABLE VIII

Deactivation Study of $CHCl_2CHCl_2$ with OFCB as Deactivator
$P_{CHCl_2CHCl_2}$ = 5 torr, No Filter

Run No.	P_{OFCB}	Exposure Time	$R_{CH_2CCl_2}$	$R_{t-1,2-C_2H_2Cl_2}$	$R_{c-1,2-C_2H_2Cl_2}$	$R_{C_2HCl_3}$	$R_{C_2Cl_4}$
	(10^{17} molec./cc)	(minute)	(10^{12} molecule / c.c. second)				
C-26	7.04	20	0.014	0.19	0.29	0.05	/
C-27	7.04	30	0.008	0.27	0.30	0.02	/
C-25	16.64	10	/	0.13	0.15	0.06	/
C-28	16.64	25	0.015	0.14	0.17	/	/
C-29	16.64	40	0.010	0.17	0.20	0.03	0.04
C-31	32.24	30	0.010	0.20	0.25	0.024	/
C-30	32.24	42	0.010	0.18	0.19	0.02	0.02

Figure 28. Product Production as a Function of Time in the Photolysis of 1,1,2,2-$CHCl_2CHCl_2$ at $\lambda > 3000$ Å.

$P_{OFCB} = 7.04 \times 10^{17}$ moleculc / c.c.

▲: 1,1-$C_2H_2Cl_2$

○: C_2HCl_3

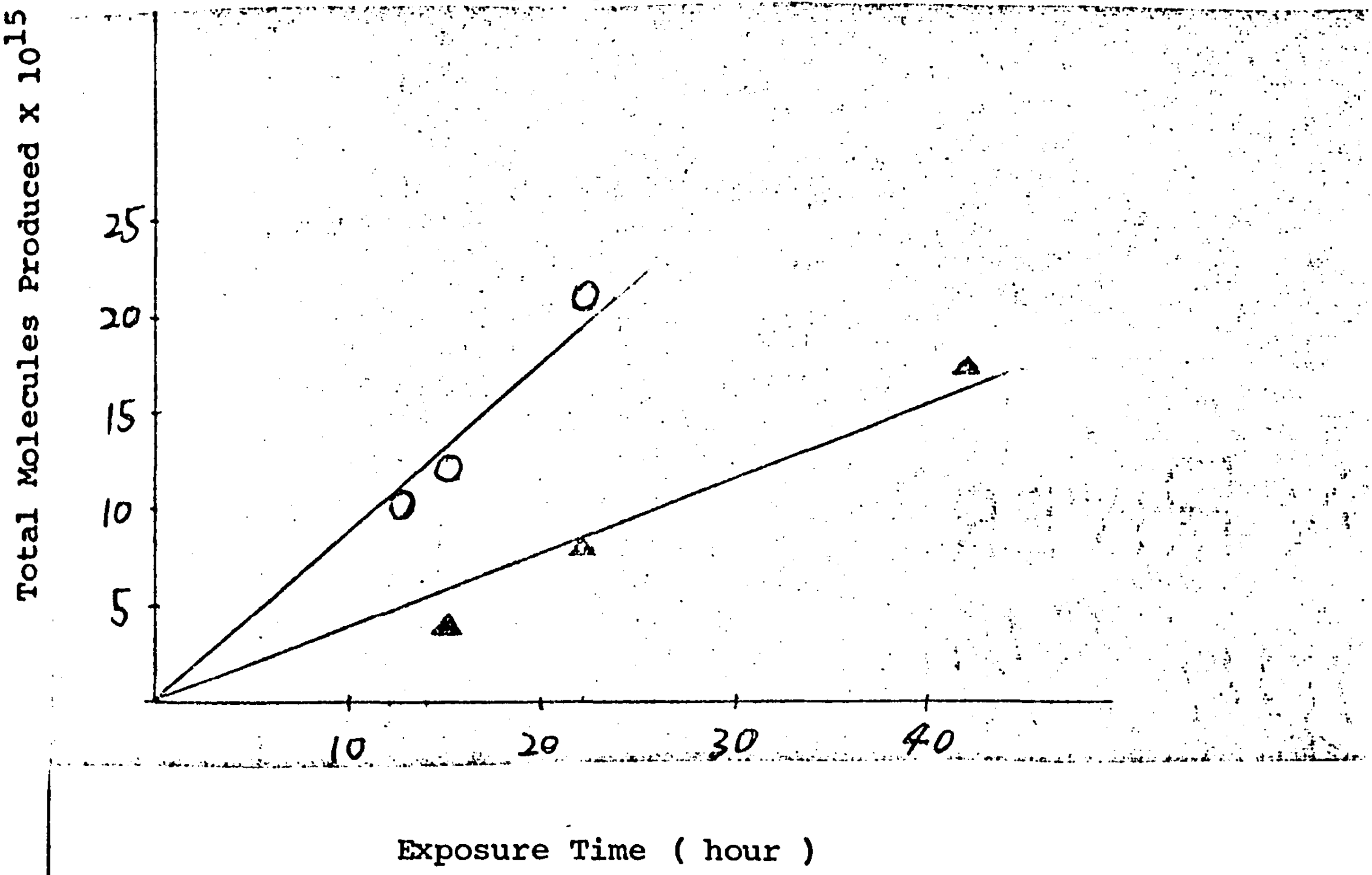


Figure 29. Product Production as a Function of Time in the Photolysis of 1,1,2,2-$CHCl_2CHCl_2$ at $\lambda > 3000$ Å. $P_{OFCB} = 7.04 \times 10^{17}$ molec./c.c.

△ : Trans 1,2-$C_2H_2Cl_2$

◒ : Cis 1,2-$C_2H_2Cl_2$

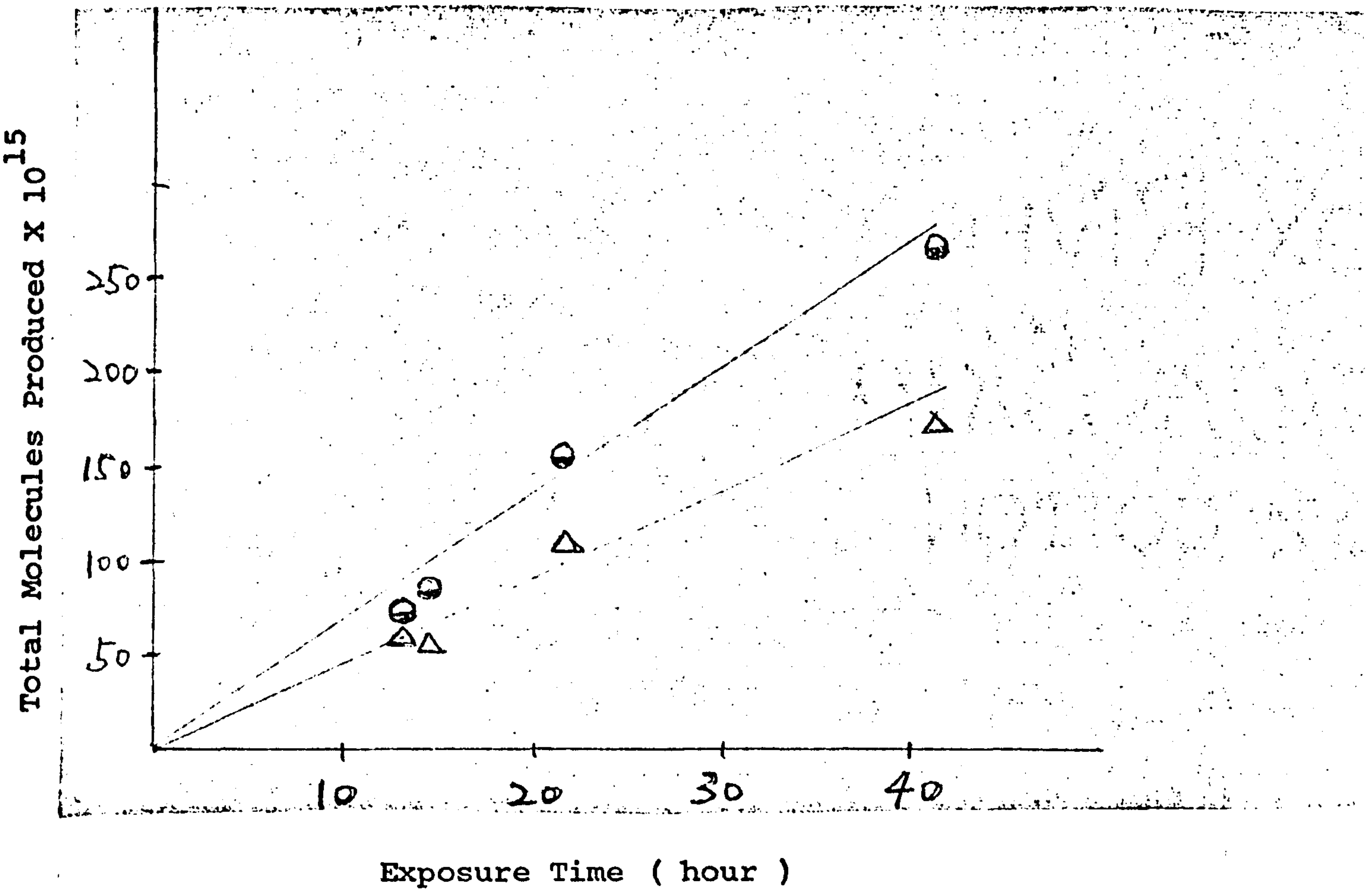


Figure 30. Product Production as Function of Time in the Photolysis of 1,1,2,2-$CHCl_2CHCl_2$ at $\lambda > 3000$ Å. Pressure of OFCB = 32.24×10^{17} molecule / c.c.

▲ : 1,1-$C_2H_2Cl_2$

○ : C_2HCl_3

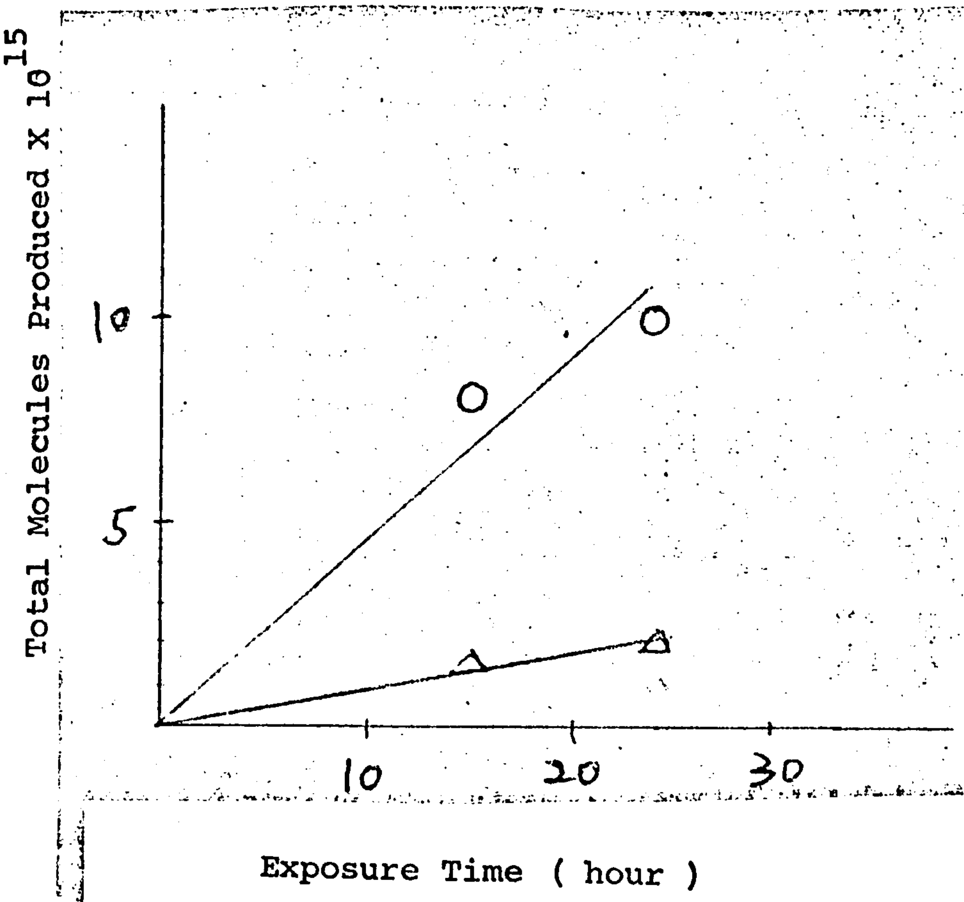


Figure 31. Product Production as a Function of Time in the Photolysis of 1,1,2,2-$CHCl_2CHCl_2$ at $\lambda > 3000$ Å. $P_{OFCB} = 32.24 \times 10^{17}$ molec./c.c.

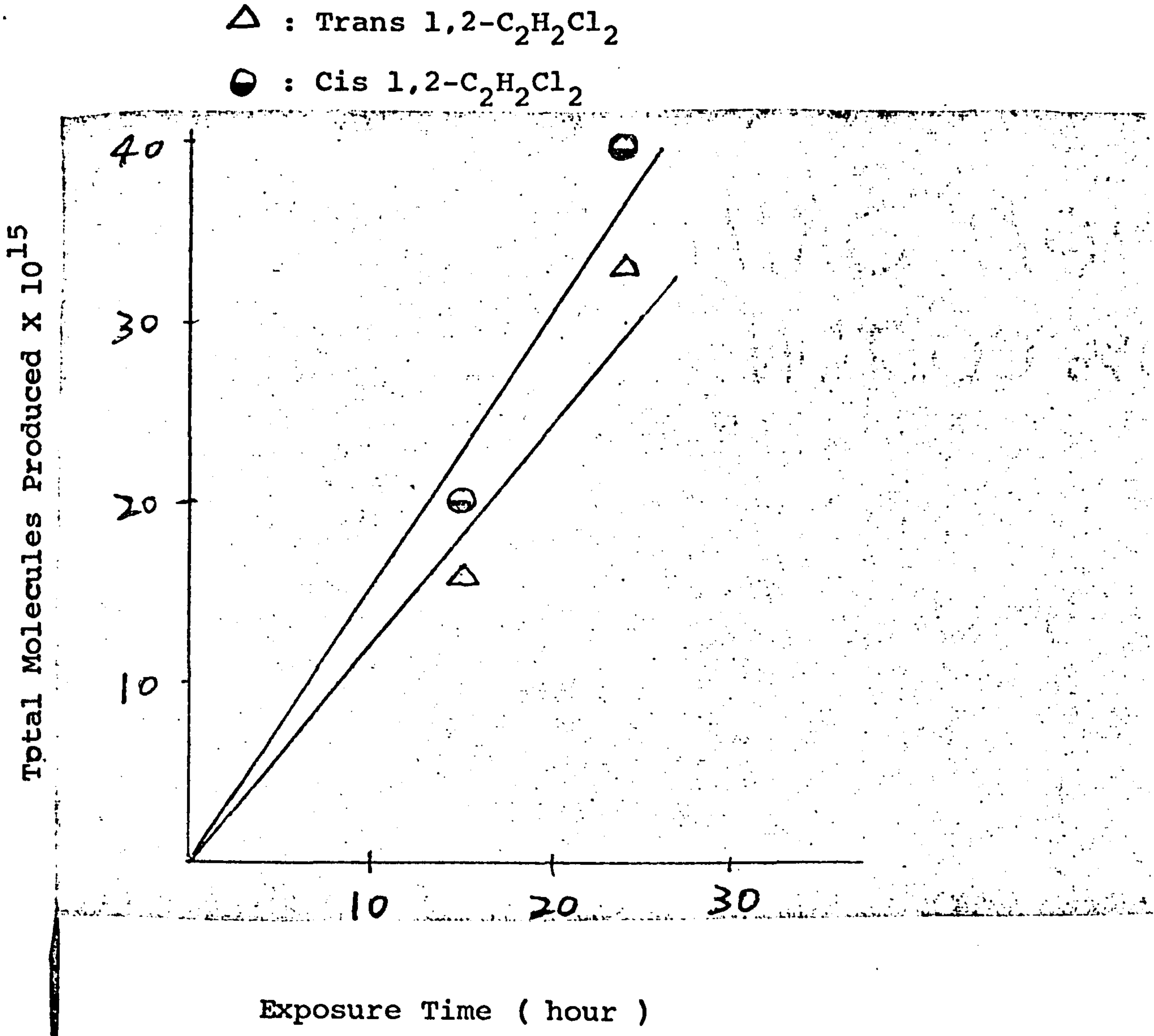


Figure 32. Product Production as a Function of Time in the Photolysis of 1,1,2,2-$CHCl_2CHCl_2$ at $\lambda > 3000$ Å. $P_{OFCB} = 16.64 \times 10^{17}$ molec./c.c.

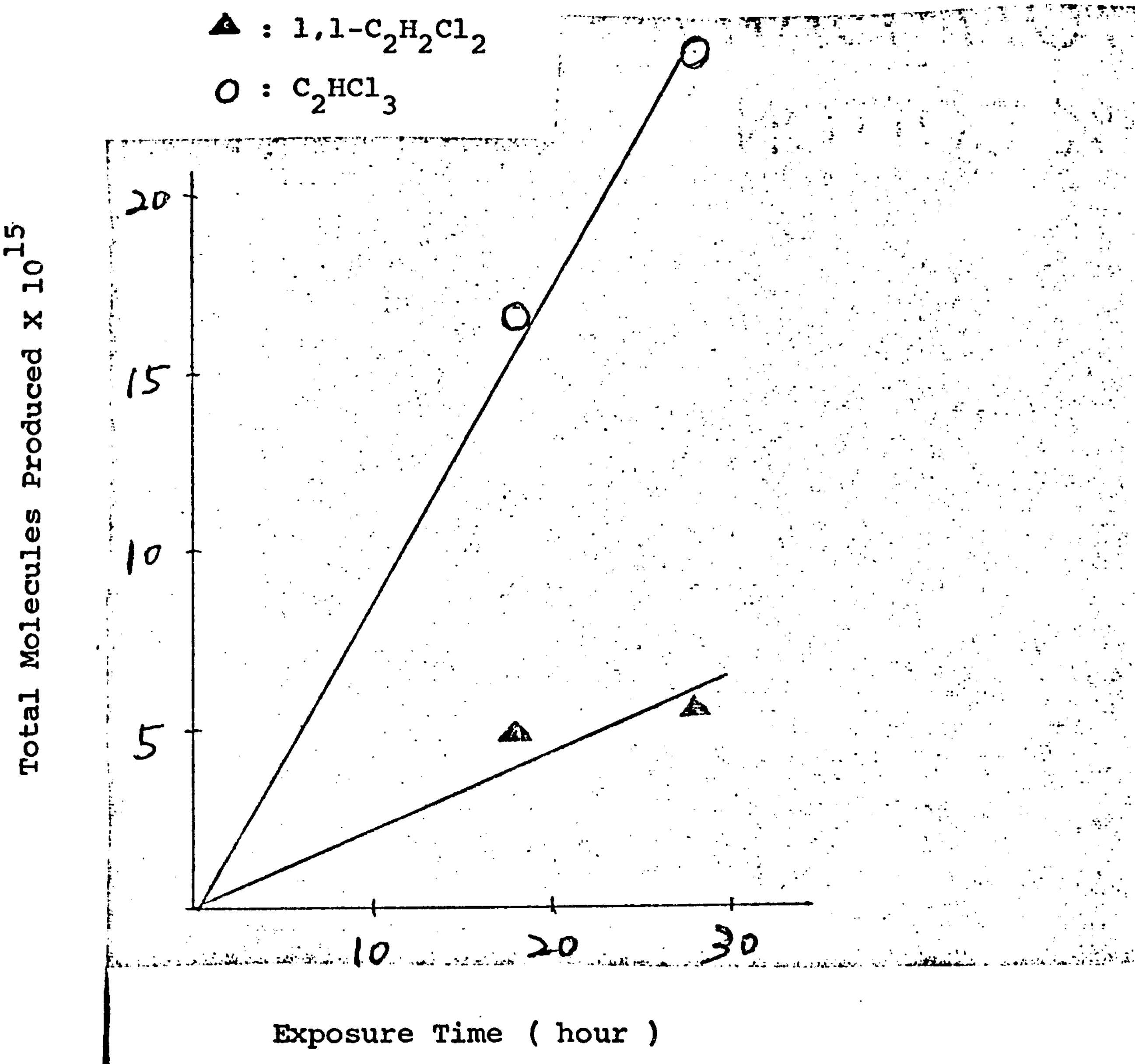


Figure 33. Product Production as a Function of Time in the Photolysis of 1,1,2,2-$CHCl_2CHCl_2$ at $\lambda > 3000$ Å. $P_{OFCB} = 16.64 \times 10^{17}$ molec./c.c.

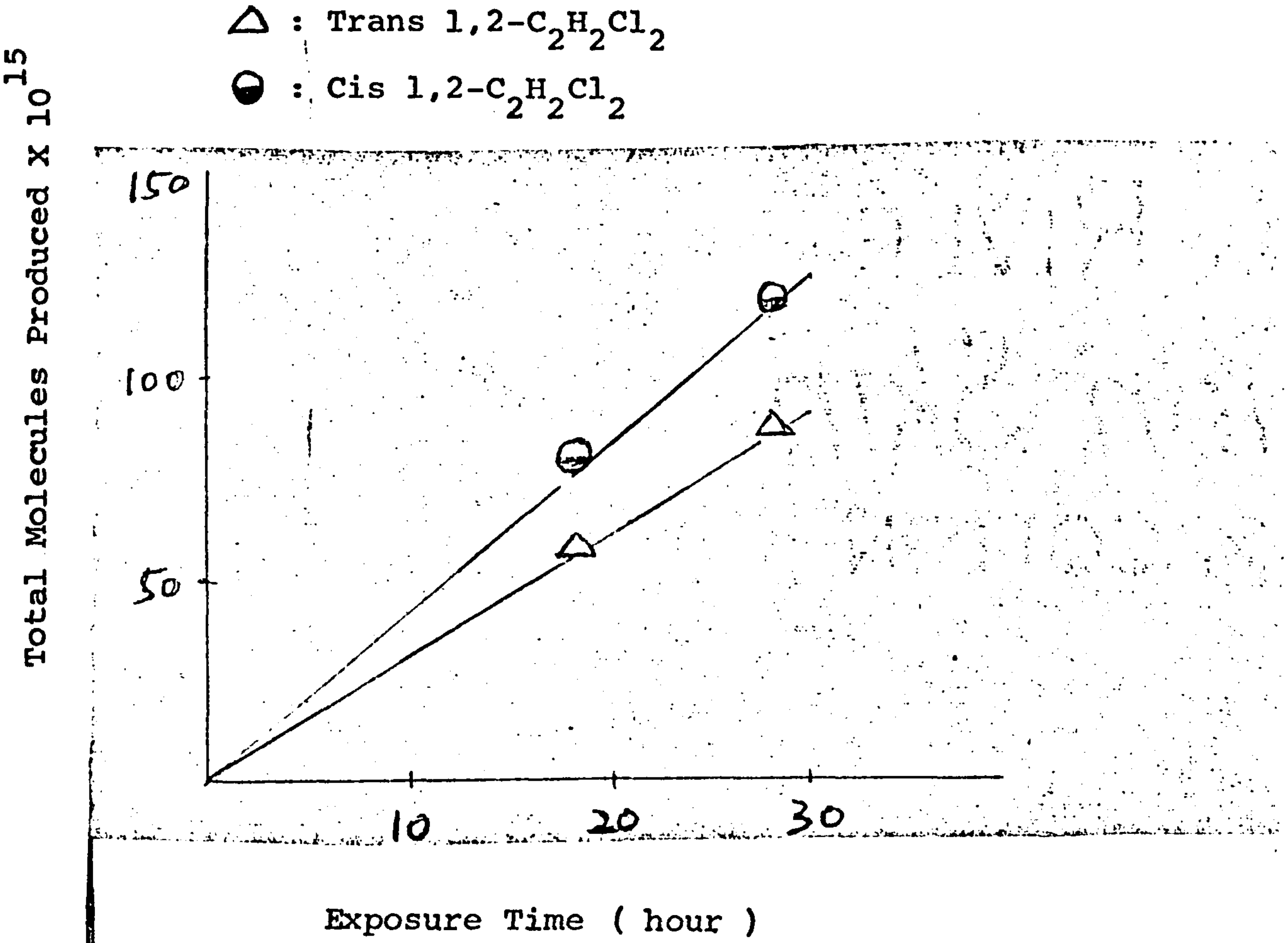


Figure 34. Product Production as a Function of Time in the Photolysis of 1,1,2,2-$CHCl_2CHCl_2$ at $\lambda > 2000$ Å. $P_{OFCB} = 7.04 \times 10^{17}$ molec./c.c.

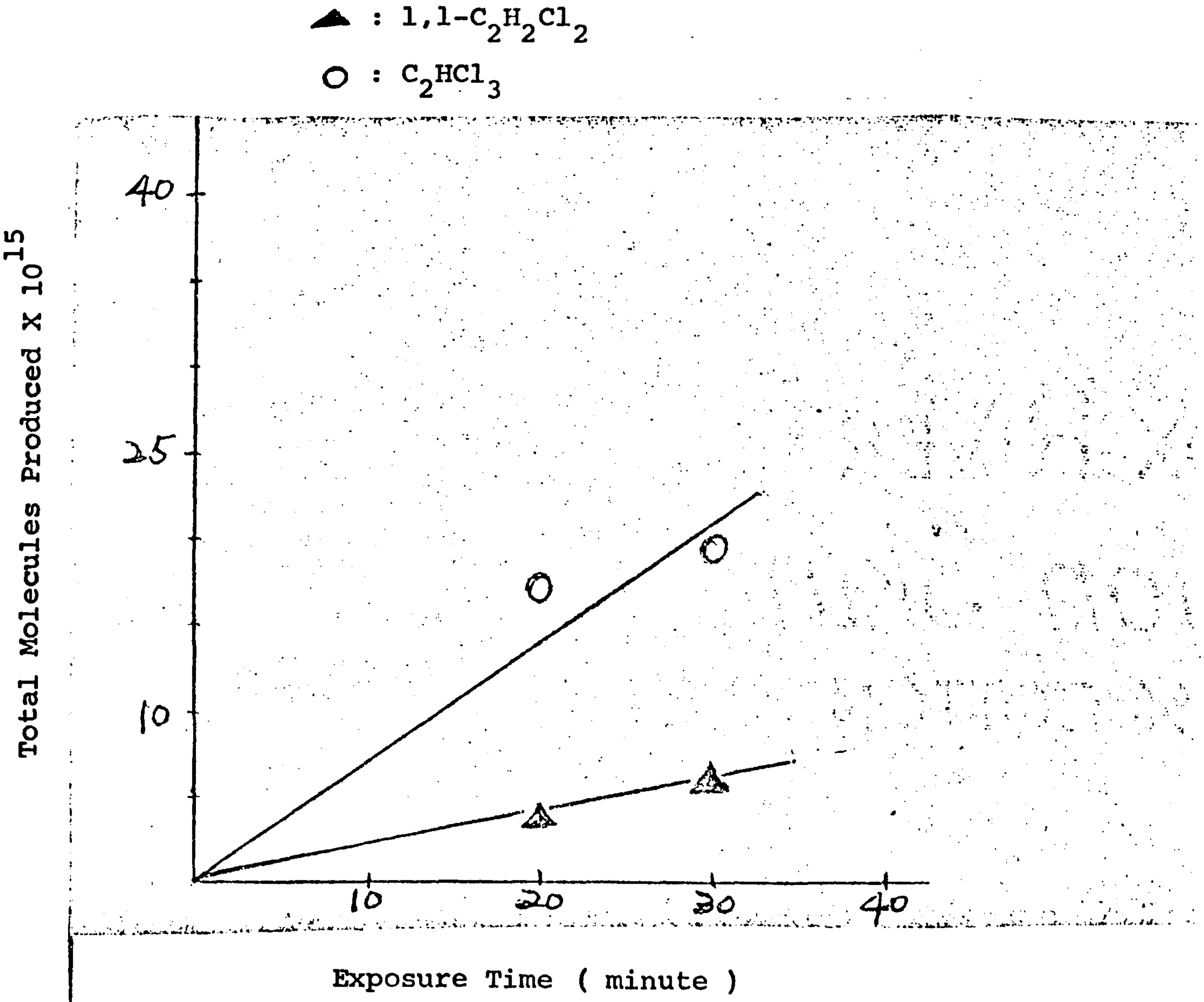


Figure 35. Product Production as a Function of Time in the Photolysis of 1,1,2,2-$CHCl_2CHCl_2$ at $\lambda >$ 2000 Å. P_{OFCB} = 7.04 X 10^{17} molec./c.c.

△ : Trans 1,2-$C_2H_2Cl_2$

● : Cis 1,2-$C_2H_2Cl_2$

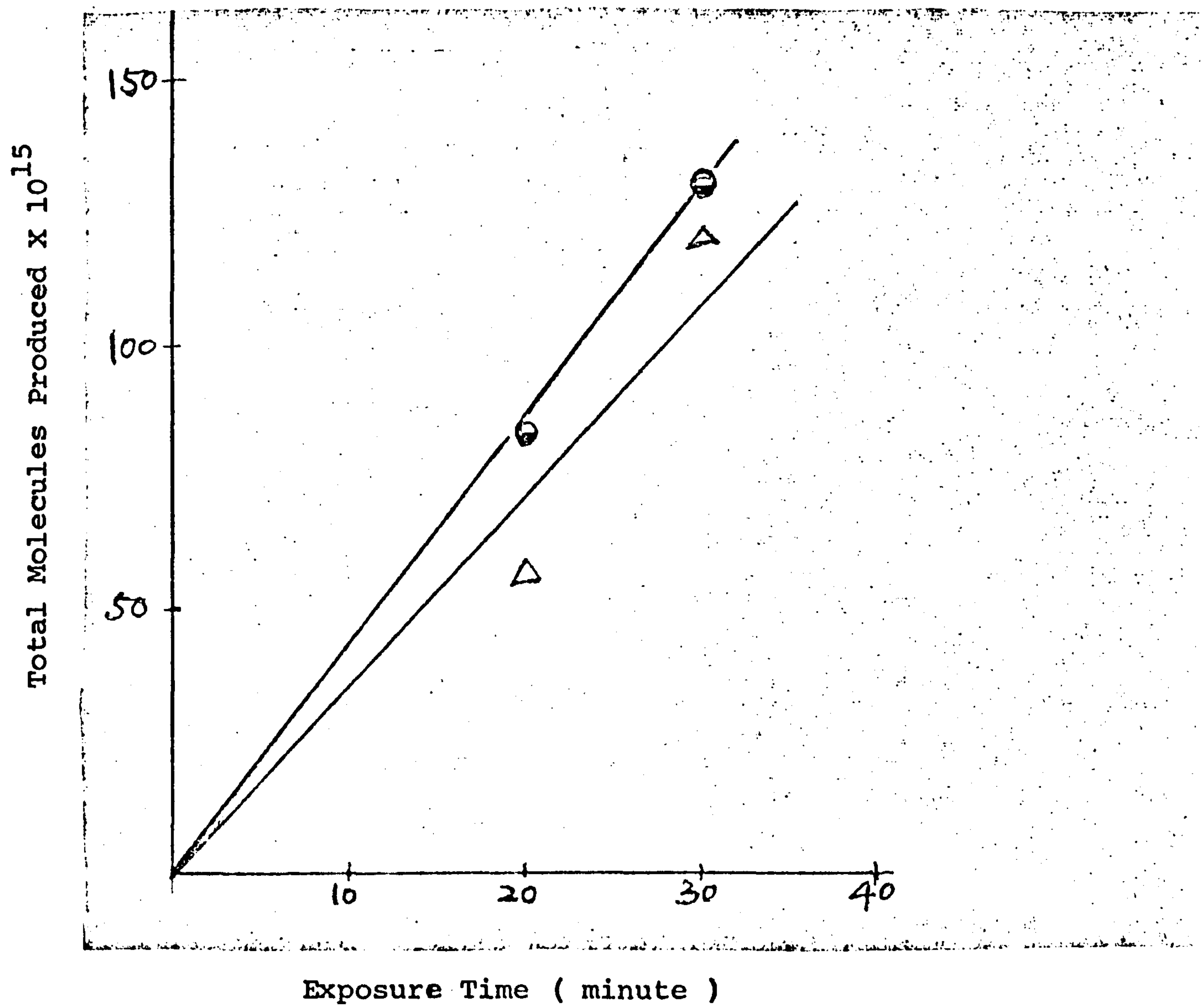


Figure 36. Product Production as a Function of Time in the Photolysis of 1,1,2,2-$CHCl_2CHCl_2$ at $\lambda >$ 2000 Å. P_{OFCB} = 16.64 X 10^{17} molec./c.c.

○ : C_2HCl_3

▲ : 1,1-$C_2H_2Cl_2$

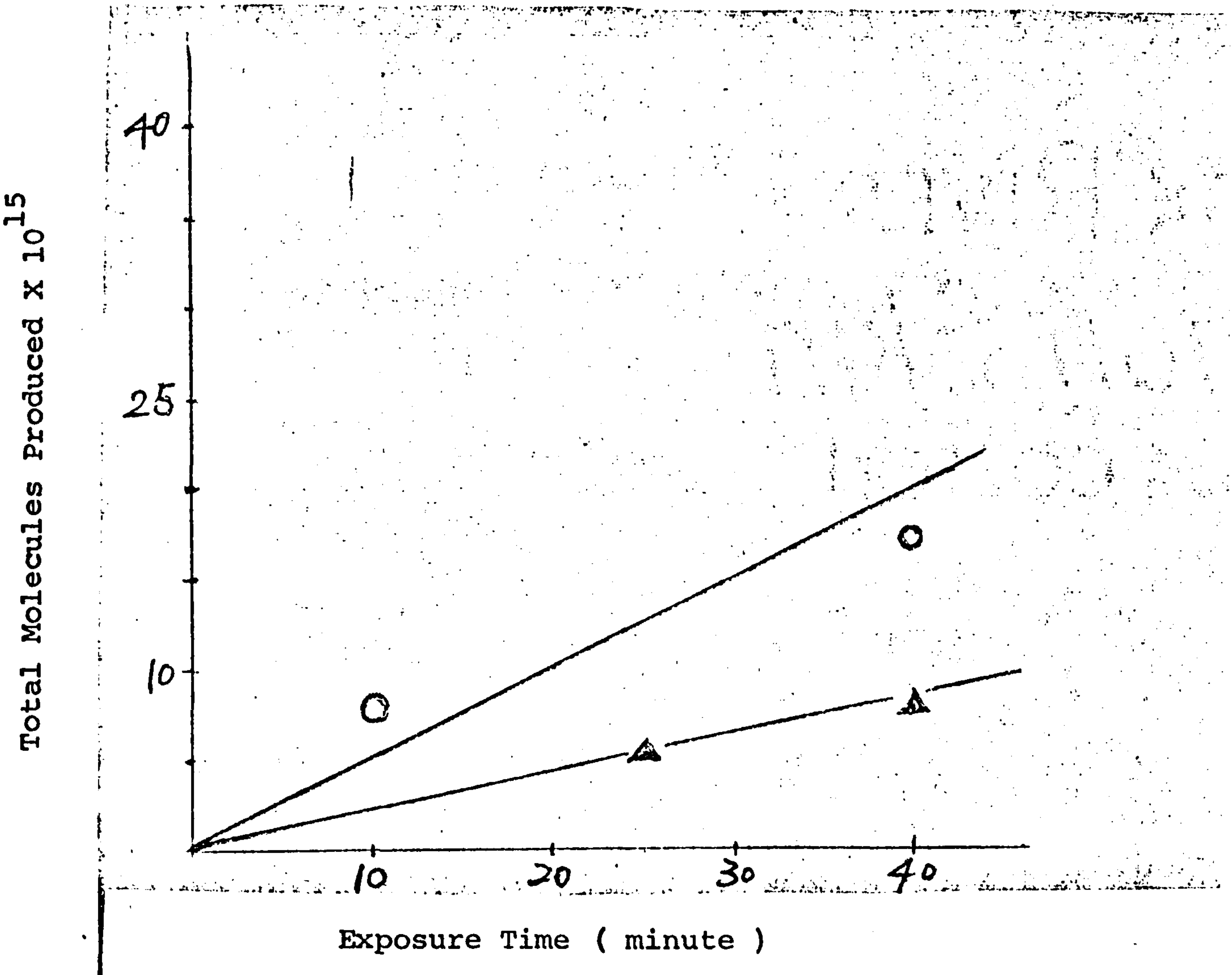


Figure 37. Product Production as a Function of Time in the Photolysis of 1,1,2,2-$CHCl_2CHCl_2$ at $\lambda > 2000$ Å. $P_{OFCB} = 16.64 \times 10^{17}$ molec./c.c.

△ : Trans 1,2-$C_2H_2Cl_2$

◒ : Cis 1,2-$C_2H_2Cl_2$

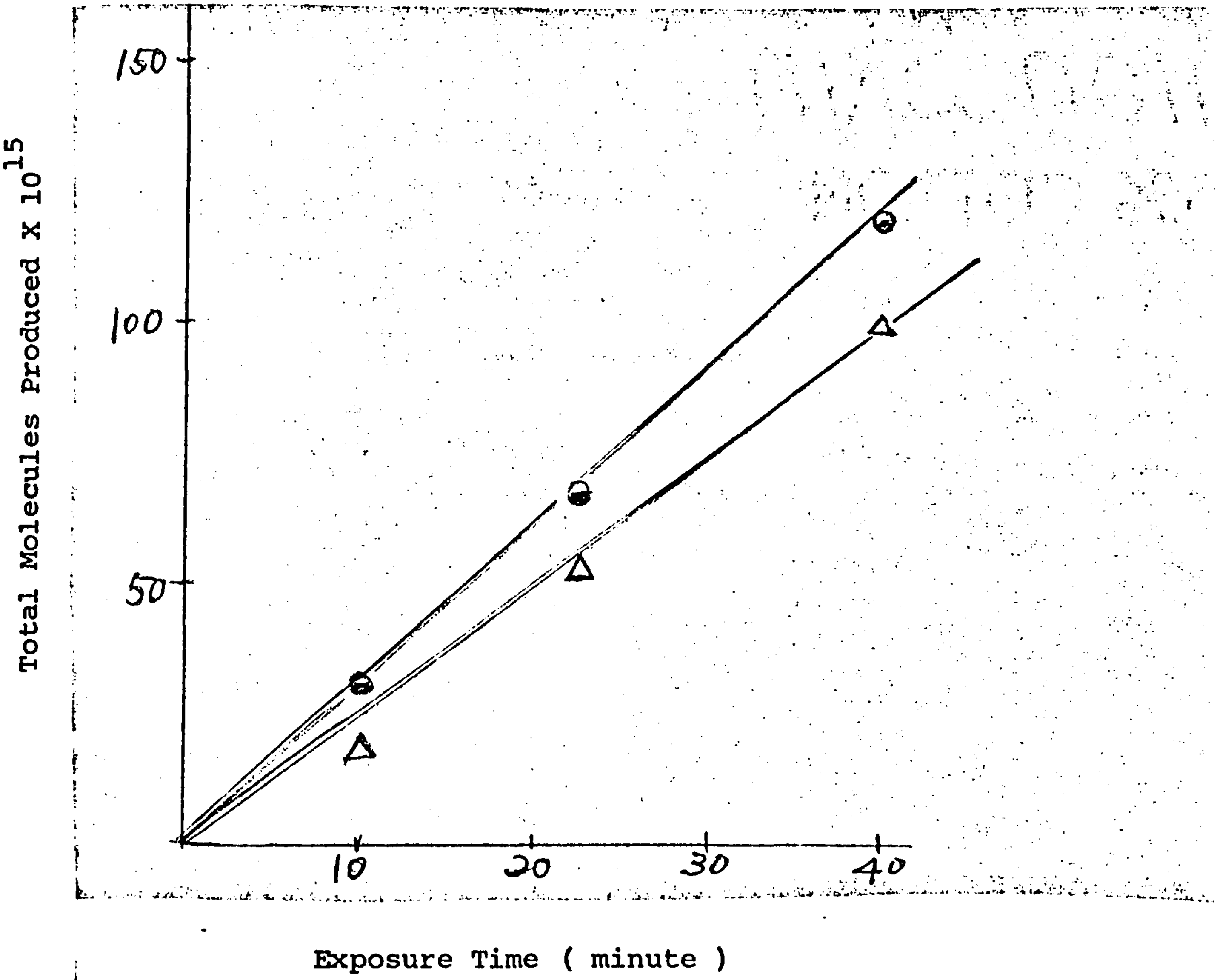


Figure 38. Product Production as a Function of Time in the Photolysis of 1,1,2,2-$CHCl_2CHCl_2$ at $\lambda > 2000$ Å. $P_{OFCB} = 32.24 \times 10^{17}$ molecules/ c.c.

▲ : 1,1-$C_2H_2Cl_2$

○ : C_2HCl_3

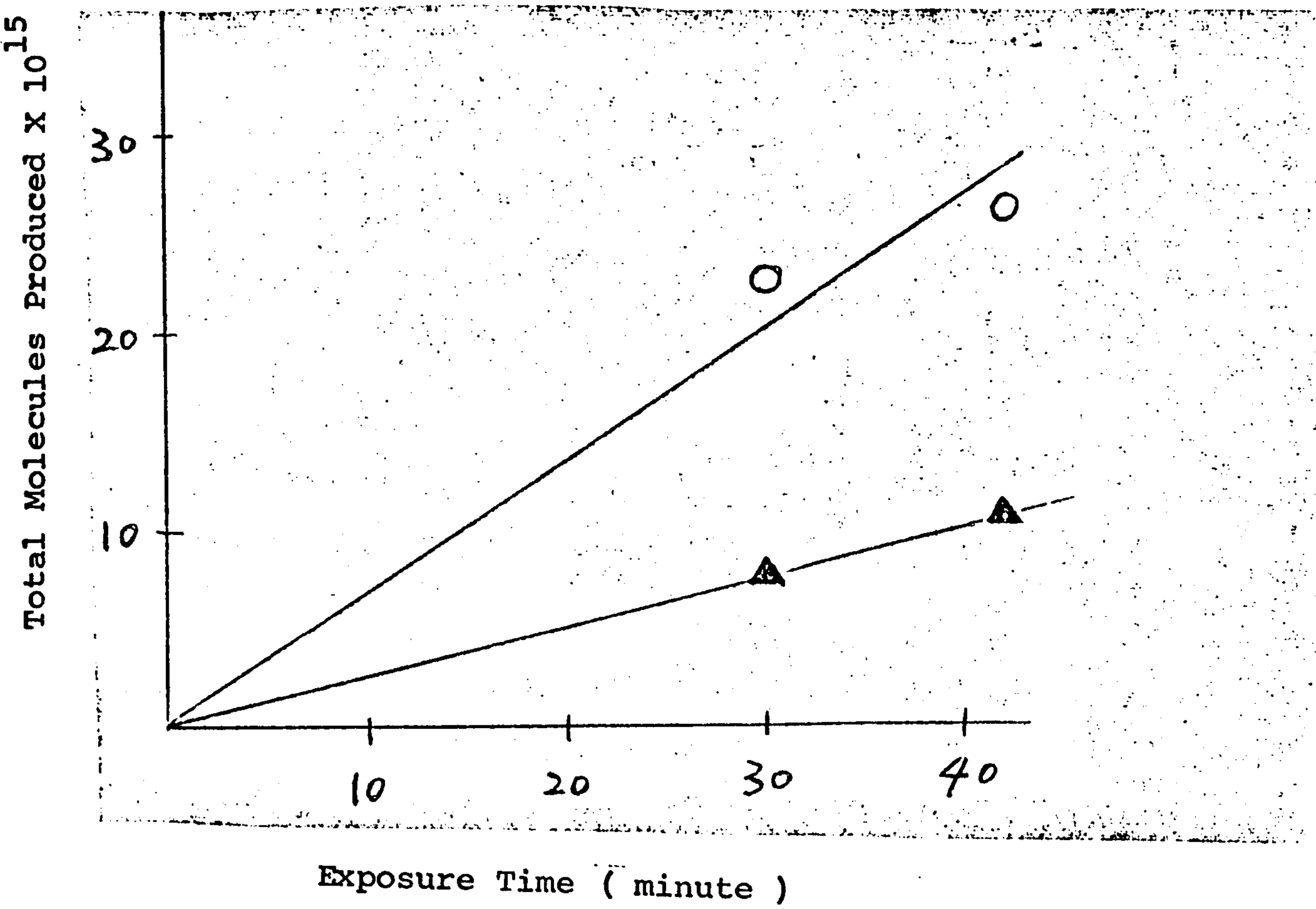
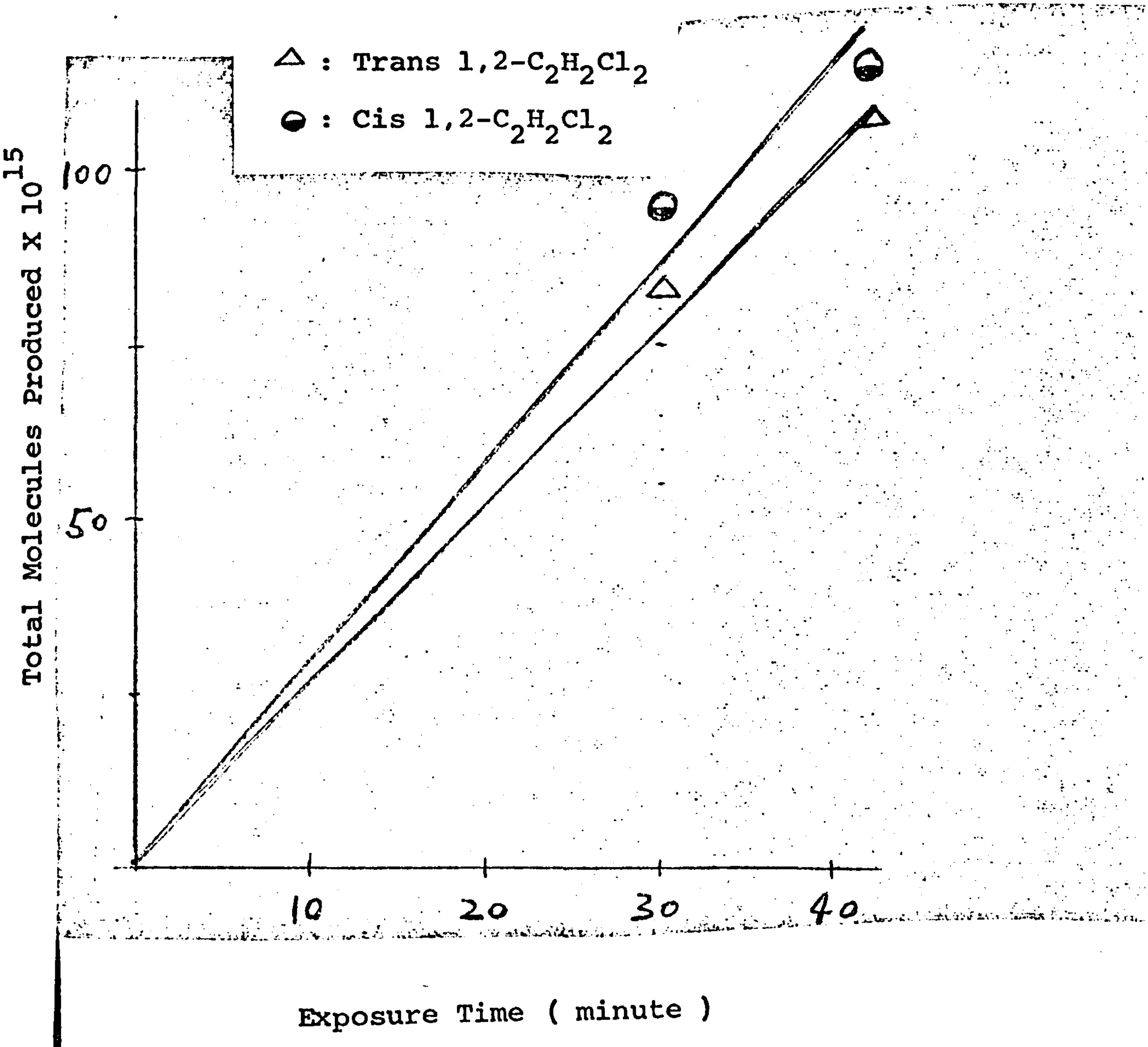


Figure 39. Product Production as a Function of Time in the Photolysis of 1,1,2,2-$CHCl_2CHCl_2$ at $\lambda > 2000$ Å. $P_{OFCB} = 32.24 \times 10^{17}$ molec./c.c.



In order to evaluate these deactivation studies, a reaction mechanism must be presented. Therefore the following mechanism is proposed which takes into account that 1,1 and cis and trans 1,2-C_2H_2Cl and C_2HCl_3 originate from the same excited state and C_2Cl_4 , $CHCl_2CHClI$ originate from the different excited states as was established by the previous wavelength study.

$$1,1,2,2\text{-}CHCl_2CHCl_2 + h\nu \longrightarrow CHCl_2CHCl_2{}^{*} \qquad (\ 11\ )$$

$$1,1,2,2\text{-}CHCl_2CHCl_2 + h\nu' \longrightarrow CHCl_2CHCl_2{}^{**} \qquad (\ 12\ )$$

$$1,1,2,2\text{-}CHCl_2CHCl_2 + h\nu'' \longrightarrow CHCl_2CHCl_2{}^{o} \qquad (\ 13\ )$$

$$CHCl_2CHCl_2{}^{*} \longrightarrow 1,1\text{-}C_2H_2Cl_2 + Cl_2 \qquad (\ 14\ )$$

$$CHCl_2CHCl_2{}^{*} \longrightarrow \text{cis \& trans } 1,2\text{-}C_2H_2Cl_2 + Cl_2 \qquad (\ 15\ )$$

$$CHCl_2CHCl_2{}^{*} \longrightarrow C_2HCl_3 + HCl \qquad (\ 16\ )$$

$$CHCl_2CHCl_2{}^{**} \longrightarrow C_2Cl_4 + H_2 \qquad (\ 17\ )$$

$$CHCl_2CHCl_2{}^{o} \longrightarrow CHCl_2CHCl\cdot + Cl\cdot \qquad (\ 18\ )$$

$$CHCl_2CHCl_2{}^{*} + OFCB \longrightarrow \text{deactivation} \qquad (\ 19\ )$$

$$CHCl_2CHCl_2{}^{**} + OFCB \longrightarrow \text{deactivation} \qquad (\ 20\ )$$

$$CHCl_2CHCl_2{}^{o} + OFCB \longrightarrow \text{deactivation} \qquad (\ 21\ )$$

In the above mechanism $CHCl_2CHCl_2{}^{*}$, $CHCl_2CHCl_2{}^{**}$, and $CHCl_2CHCl_2{}^{o}$ denote different excited states produced by the absorption of light.

If this mechanism is correct then the ratio of 1,1-$C_2H_2Cl_2$ / (cis+trans 1,2-$C_2H_2Cl_2$) and the ratio of C_2HCl_3 / (cis+trans 1,2-$C_2H_2Cl_2$) must be constant regardless of the pressure of OFCB. In figures 40 and 41 the ratio of 1,1-$C_2H_2Cl_2$ / (cis+trans 1,2-$C_2H_2Cl_2$) and C_2HCl_3 / (cis+trans 1,2-$C_2H_2Cl_2$) are plotted as function of OFCB pressure respectively for the data obtained at λ>3000 Å. The same ratios are plotted in figures 42 and 43 for the experiments at λ>2000 Å.

From these figures the following approximate ratios are obtained;

	3000 Å	2000 Å
1,1-$C_2H_2Cl_2$ / (cis+trans 1,2-$C_2H_2Cl_2$)	0.04	0.04
C_2HCl_3 / (cis+trans 1,2-$C_2H_2Cl_2$)	0.1	0.1

We see clearly that within experimental error the ratios of 1,1-$C_2H_2Cl_2$ /(cis+trans 1,2-$C_2H_2Cl_2$) and C_2HCl_3 /(cis+trans 1,2-$C_2H_2Cl_2$) are constant regardless of the pressure of OFCB and the wavelength of the incident light. It indicates without any doubt that 1,1-$C_2H_2Cl_2$, cis and trans 1,2-$C_2H_2Cl_2$,C_2HCl_3 originate mainly if not exclusively from the same excited state. Even though we did not have any good pressure study data for proving that $C_2Cl_4$and $CHCl_2CHClI$ come from the different excited states from the other products, nevertheless, this proposed mechanism is reasonable since the

Figure 40. Ratio of 1,1-$C_2H_2Cl_2$ to (Cis + Trans 1,2-$C_2H_2Cl_2$) Versus Pressure of OFCB at $\lambda >$ 3000 Å.

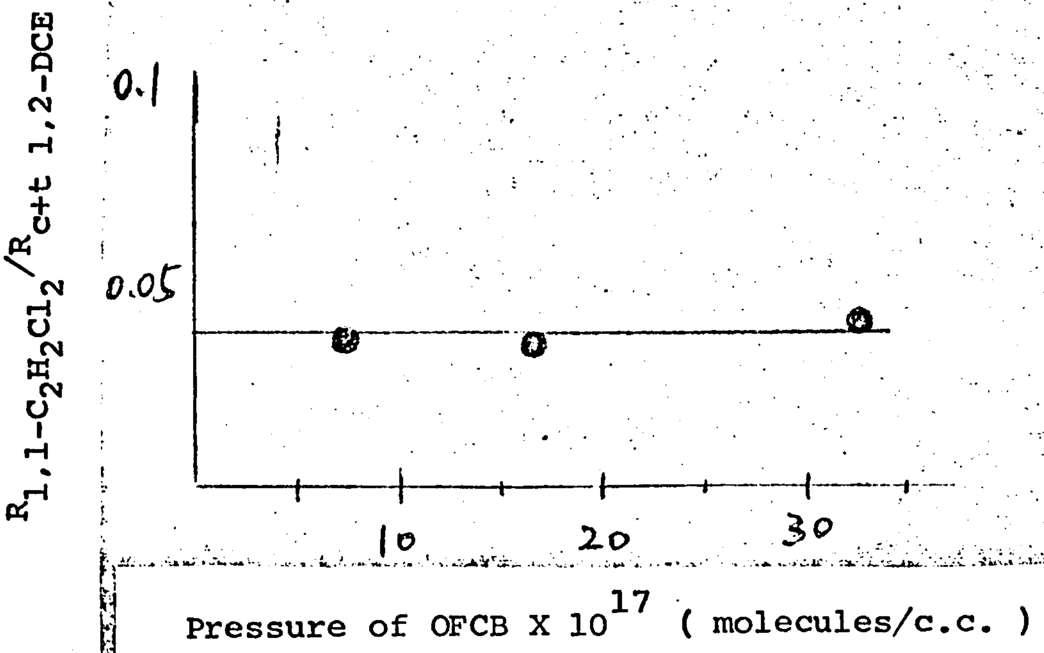
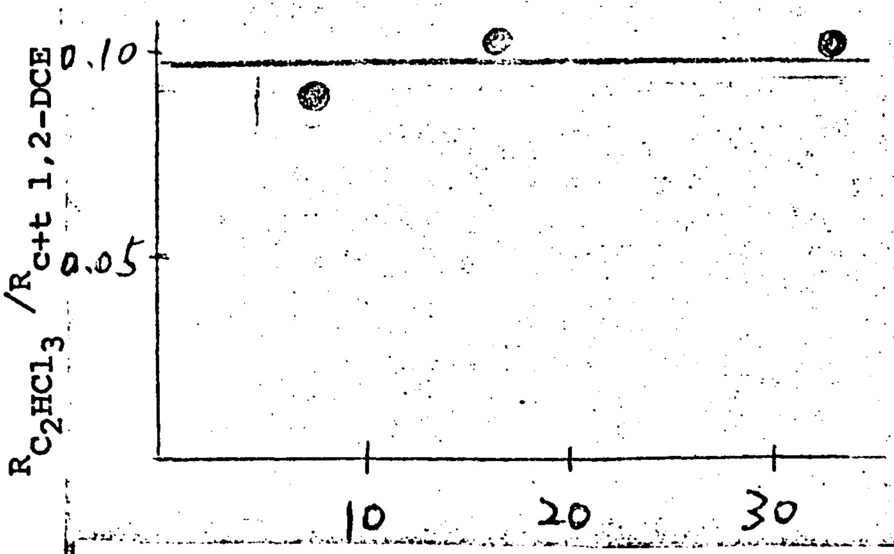


Figure 41. Ratio of C_2HCl_3 to (Cis + Trans 1,2-$C_2H_2Cl_2$) Versus Pressure of OFCB at $\lambda > 3000$ Å.



Pressure of OFCB X 10^{17} (molecules/c.c.)

Figure 42. Ratio of 1,1-$C_2H_2Cl_2$ to (Cis + Trans 1,2-$C_2H_2Cl_2$) Versus Pressure of OFCB at $\lambda > 2000$ Å.

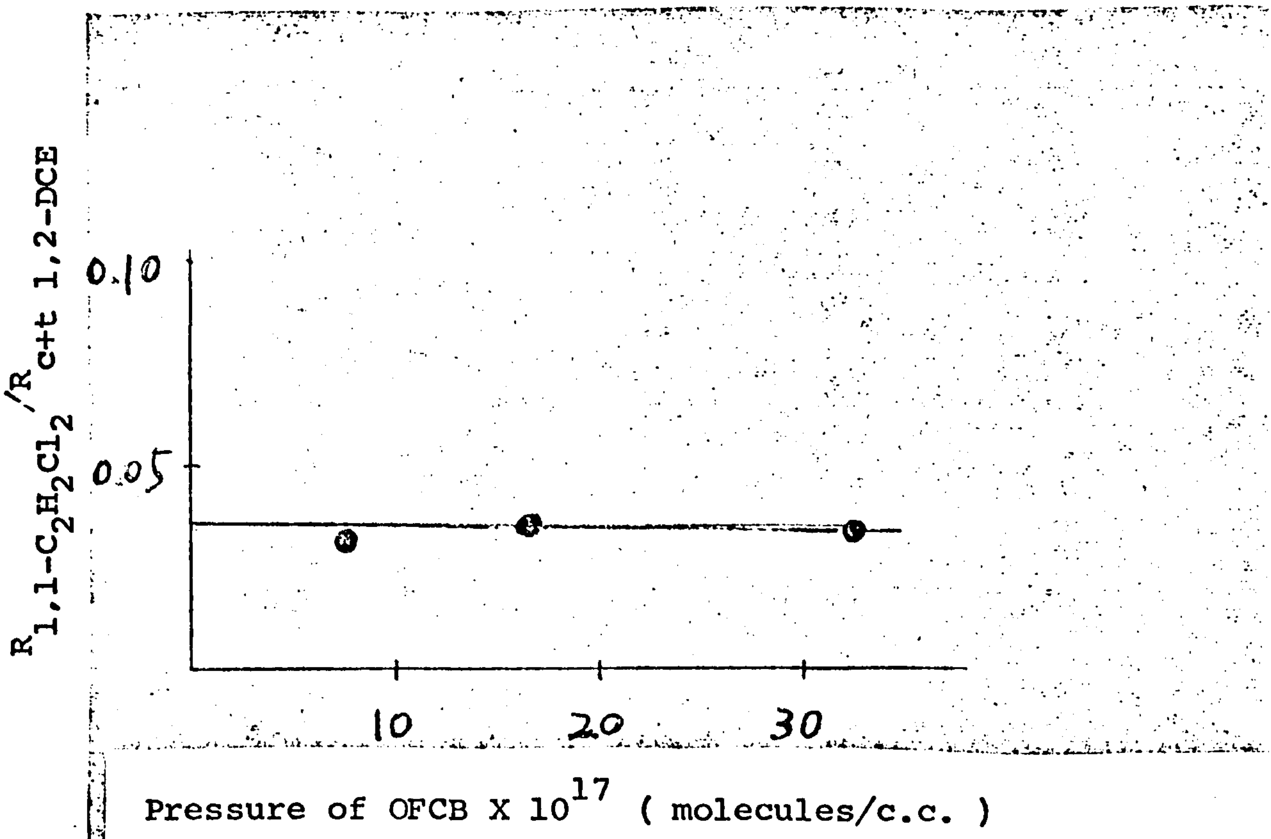
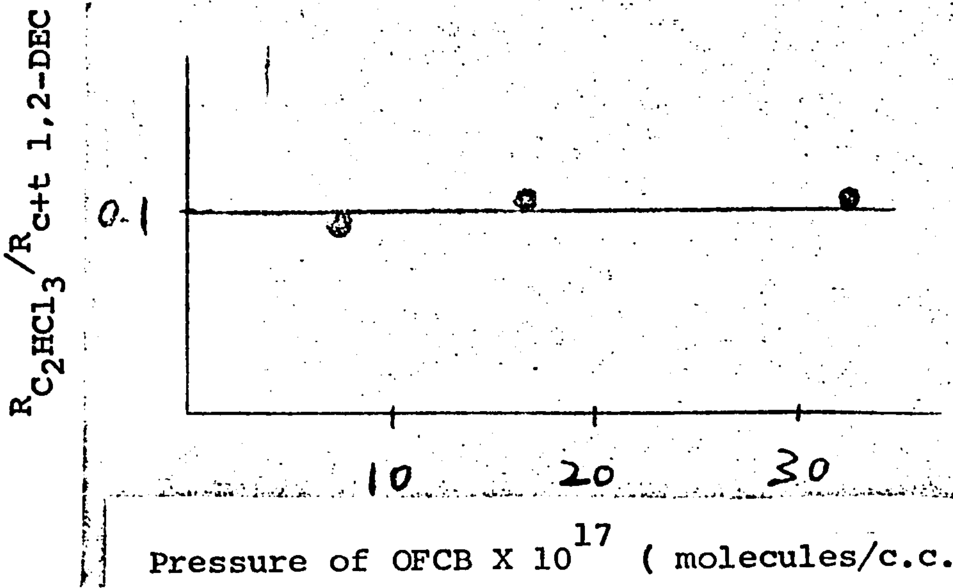


Figure 43. Ratio of C_2HCl_3 to (Cis + Trans 1,2-$C_2H_2Cl_2$) Versus Pressure of OFCB at $\lambda > 2000$ Å.



previous wavelength study already verified that C_2Cl_4 , $CHCl_2CHClI$ and cis & trans-1,2-$C_2H_2Cl_2$ originate from the different excited states. All the ratios are listed in table IX for comparison.

The ratio of cis 1,2-$C_2H_2Cl_2$ / trans 1,2-$C_2H_2Cl_2$ versus OFCB pressure is plotted in figure 44, for experiments at $\lambda > 3000$ Å and figure 45 for experiments at $\lambda > 2000$ Å. Figures 44 and 45 clearly indicate that as the OFCB pressure increases the cis/trans ratio approaches unity. This observation will be discussed later in the discussion.

TABLE IX

Without OFCB	$\frac{R_{CH_2CCl_2}}{R_{Cis+trans\ DCE}}$,	$\frac{R_{C_2HCl_3}}{R_{Cis+trans\ DCE}}$,	$\frac{R_{C_2Cl_4}}{R_{C+T\ DCE}}$,	$\frac{R_{CHCl_2CHClI}}{R_{Cis+trans\ DCE}}$
3000 Å	0.05	0.14	0.15	0.2
2000 Å	0.05	0.14	0.25 ± 0.05	0.025
With OFCB				
3000 Å	0.04	0.1	/	/
2000 Å	0.04	0.1	/	/

Figure 44. Ratio of Cis 1,2-$C_2H_2Cl_2$ to Trans 1,2-$C_2H_2Cl_2$ Versus Pressure of OFCB at $\lambda >$ 3000 Å.

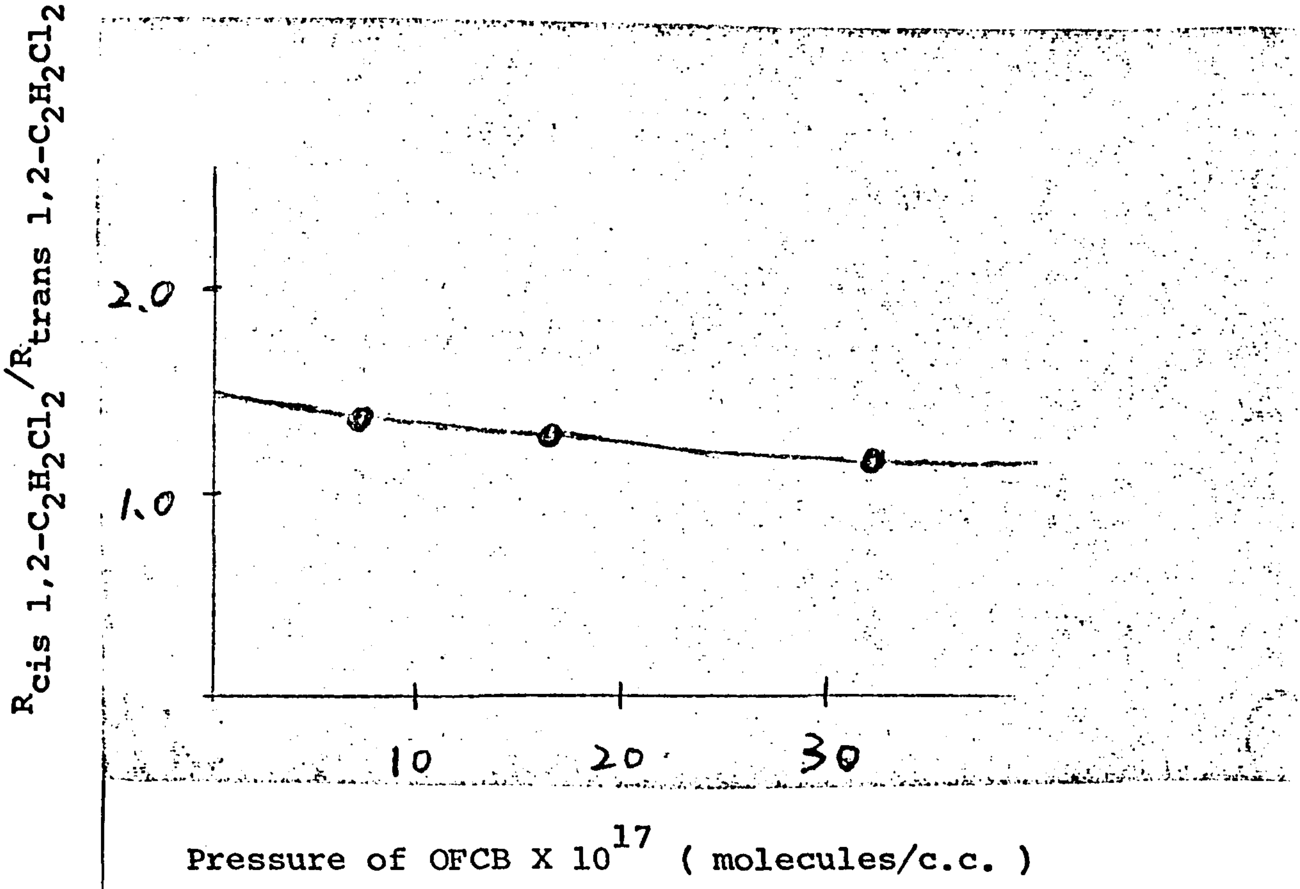
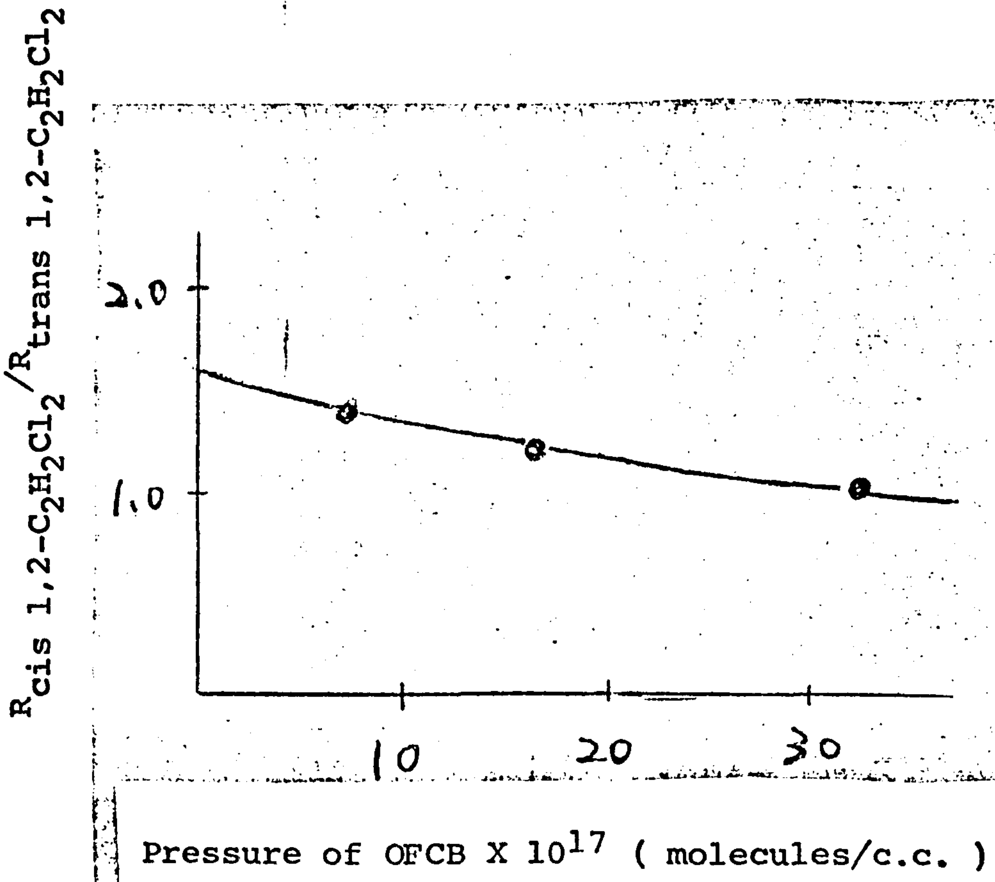


Figure 45. Ratio of Cis 1,2-$C_2H_2Cl_2$ to Trans 1,2-$C_2H_2Cl_2$ Versus Pressure of OFCB at $\lambda > 2000$ Å.



DISCUSSION OF THE RESULTS

The data clearly indicate that the following primary reactions occur in the photolysis of 1,1,1-CH_3CCl_3.

$CH_3CCl_3 + h\nu \longrightarrow CH_3CCl_3^*$ 1

$CH_3CCl_3 + h\nu' \longrightarrow CH_3CCl_3^{**}$ 2

$CH_3CCl_3^* \longrightarrow CH_2CCl_2 + HCl$ 3a

$CH_3CCl_3^* \longrightarrow CH_3CCl_2\cdot + Cl\cdot$ 3b

$CH_3CCl_3^* + CH_3CCl_3 \longrightarrow$ deactivation 4a

$CH_3CCl_3^* +$ OFCB $\longrightarrow$ deactivation 4b

$CH_3CCl_3^{**} \longrightarrow CH_3CCl_2\cdot + Cl\cdot$ 5a

$CH_3CCl_3^{**} \longrightarrow CH_2CCl_2 + H\cdot + Cl\cdot$ 5b

$CH_3CCl_2\cdot + I_2 \longrightarrow CH_3CCl_2I + I\cdot$ 6

The one star lower excited state is produced predominantly at $\lambda > 2200$ Å and the two star higher excited state is produced mainly at $\lambda < 2200$ Å. The life time of the two star excited state is so short that this state can not be deactivated under our experimental conditions. Reaction 5b may occur directly or via a excited $CH_3CCl_2^{o}$ radical as an intermediate.

No previous study of the photolysis of CH_3CCl_3 in this wavelength region has been carried out. However, recently Salomon, Kirk and Tschuikow-Roux (21) photolysed CH_3CCl_3 at 1470 Å. It is interesting to compare their results with ours .

The major products observed in the 1470 Å photolysis of CH_3CCl_3 are CH_2CCl_2 and CH_2CHCl. The large and fairly constant yield of CH_2CCl_2 and the absence of radical products that would arise from the expulsion of one or more chlorine or hydrogen atoms from CH_3CCl_3 led them to conclude that the major mode of photodecomposition in the 1470 Å photolysis of CH_3CCl_3 is the molecular elimination of HCl from a short lived electronically excited state of trichloroethane ($CH_3CCl_3^{\ddagger}$)

$$CH_3CCl_3 \quad + \quad h\nu \longrightarrow CH_3CCl_3^{\ddagger}$$

$$CH_3CCl_3^{\ddagger} \longrightarrow CH_2CCl_2 \quad + \quad HCl$$

This step is identical to our result (reaction 3a) for the photolysis of CH_3CCl_3 at wavelengths longer than 2000 Å. With reference to the ground electronic states of CH_3CCl_3, CH_2CCl_2 and HCl, the HCl elimination from CH_3CCl_3 is about 13 Kcal/mole endothermic. It is therefore quite clear that molecular elimination of HCl is quite feasible at any wavelength absorbed by the CH_3CCl_3 molecule. It is perhaps surprising that the authors did not observe any evidence for the reaction

$$CH_3CCl_3^{\ddagger} \longrightarrow CH_2CCl_2 + H\cdot + Cl\cdot \qquad 5b$$

Since it might be expected that this reaction which is 100 Kcal more endothermic than the molecular elimination of HCl might become more important with decreasing wavelengths as indeed indicated by our study. Of course, it is possible that reaction 5b may have occurred to some extent but that this was masked by the predominant production of CH_2CCl_2 via reaction 3a.

Tschuikow-Roux and coworkers (21) also observed the production of C_2H_3Cl in the photolysis of CH_3CCl_3 at 1470 Å. The formation of this product was explained by them by the following reaction sequence,

$$\begin{tikzcd} CH_3CCl_3^{\ddagger} \arrow[r] & CH_3CCl: \arrow[dr] & + \; Cl_2 \\ & & C_2H_3Cl \end{tikzcd}$$

From the lack of radical-radical recombination products such as $CH_3CCl_2CCl_2CH_3$ they concluded that chlorine is expelled molecularly and that the Cl_2 thus produced is insufficiently excited to decompose into Cl atoms. The molecular elimination of Cl_2 was observed by us both in the α-α and in the α-β from $CHCl_2CHCl_2$. We did not observe the production of C_2H_3Cl as reported here in the photolysis of CH_3CCl_3. Later we will point out that in general α-α elimination does not occur as readily as α-β elimination. Thus, the observation that α-α elimination of Cl_2 did occur in energetic system (1470 Å) but not at longer wavelengths (~2000 Å) is in agreement with general observations.

Tschuikow-Roux and coworkers (21) also observed a cleavage of the carbon-carbon bond,

$$CH_3CCl_3^{\ddagger} \longrightarrow CH_3\cdot + CCl_3\cdot$$

Carbon-carbon cleavage is a typical high energy process and was indeed observed by the above authors in the photolysis of many haloethanes at 1470 Å (72). This type of process is not common at wavelengths exceeding 2000 Å.

It is perhaps surprising that C-Cl bond rupture was not observed at 1470 Å. This is especially so since our results seem to indicate that this step becomes more important at shorter wavelengths.

The following reactions have been proposed to explain the products observed in the photolysis of 1,1,2,2-tetrachloroethane.

$$1,1,2,2\text{-}CHCl_2CHCl_2 + h\nu \longrightarrow CHCl_2CHCl_2{}^{*} \qquad (11)$$

$$1,1,2,2\text{-}CHCl_2CHCl_2 + h\nu' \longrightarrow CHCl_2CHCl_2{}^{**} \qquad (12)$$

$$1,1,2,2\text{-}CHCl_2CHCl_2 + h\nu'' \longrightarrow CHCl_2CHCl_2{}^{o} \qquad (13)$$

$$CHCl_2CHCl_2{}^{*} \longrightarrow 1,1\text{-}C_2H_2Cl_2 + Cl_2 \qquad (14)$$

$$CHCl_2CHCl_2{}^{*} \longrightarrow \text{cis \& trans } 1,2\text{-}C_2H_2Cl_2 + Cl_2 \qquad (15)$$

$$CHCl_2CHCl_2{}^{*} \longrightarrow C_2HCl_3 + HCl \qquad (16)$$

$$CHCl_2CHCl_2{}^{**} \longrightarrow C_2Cl_4 + H_2 \qquad (17)$$

$$CHCl_2CHCl_2{}^{o} \longrightarrow CHCl_2CHCl\cdot + Cl\cdot \qquad (18)$$

$$CHCl_2CHCl_2{}^{*} + \text{OFCB} \longrightarrow \text{deactivation} \qquad (19)$$

$$CHCl_2CHCl_2{}^{**} + \text{OFCB} \longrightarrow \text{deactivation} \qquad (20)$$

$$CHCl_2CHCl_2{}^{o} + \text{OFCB} \longrightarrow \text{deactivation} \qquad (21)$$

$$CHCl_2CHCl\cdot + I_2 \longrightarrow CHCl_2CHClI + I\cdot \qquad (22)$$

Since, particular in the case of $CHCl_2CHCl_2$, the reaction mechanism is quite complicated, it seems appropriate to discuss each reaction separately.

Both chlorinated ethanes show the formation of HCl and olefins (reactions 3a and 16) via a molecular detachment step.

Molecular detachment reactions of HCl have been observed frequently since Wijnen (22) first reported them in the photolysis of cis and trans 1,2-$C_2H_2Cl_2$. Ausubel and Wijnen (23,24,25) have shown that in the irradiation of cis and/ or trans 1,2-$C_2H_2Cl_2$ and of 1,1-$C_2H_2Cl_2$ with light of 2000 Å to 4000 Å the molecular detachment of HCl is a very important reaction.

$$\text{cis, trans } 1,2\text{-}C_2H_2Cl_2^* \longrightarrow C_2HCl + HCl \qquad A$$

$$1,1\text{-}C_2H_2Cl_2^* \longrightarrow C_2HCl + HCl \qquad B$$

Fujimoto, Rennert and Wijnen (26) have also reported that in the irridiation of vinyl chloride, the excited molecules yield HCl elimination,

$$C_2H_3Cl^* \longrightarrow C_2H_2 + HCl$$

Fujimoto and Wijnen have reported that in the irradiation of CD_3CHCl_2 one of the major reactions is DCl elimination, (27)

$$CD_3CHCl_2^* \longrightarrow CD_2CHCl + DCl$$

Examples of the dehydrohalogenation reaction from halogen-containing compound abound. Using vacuum U.V. photolysis, a group headed by Tshuikow-Roux has investigated most of the fluoro-ethanes as well as C_2H_5Cl (28), CH_3CHCl_2 (29), CH_3CF_2Cl (30) CF_3CH_2Cl (31), CH_2FCH_2Cl (32). In all cases, HX elimination reaction was observed both at 1470 Å and 1236 Å.

Extensive studies on HCl elimination from vibrationally excited chloroethanes have been carried out by Setser and coworkers (16,17,18,33,34). They produced vibrational excited molecules by recombination of two chlorine containing methyl radicals. A typical example of such a reaction may be given:

$$CH_2Cl\bullet \; + \; CH_2Cl\bullet \longrightarrow 1,2\text{-}C_2H_4Cl_2^*$$

The vibrational excited molecule may then decompose to form HCl and an ethylenic molecule as shown in the following reaction:

$$1,2\text{-}C_2H_4Cl_2^* \longrightarrow C_2H_3Cl \; + \; HCl$$

A group headed by Pritchard (35-38) also studied the decomposition of vibrationally excited CD_3CF_2H (35), CF_2DCFH_2 (36,37), CH_3CF_3 (38) molecules. All of the vibrationally excited molecules did show molecular elimination of HCl and/or HF.

In addition to the decomposition of chemically and light activated molecules, cited above, dehydrohalogenation reactions have been observed by Howlett, et al (39,40,41) in their studies of the thermal decomposition of alkyl chlorides using shock tube pyrolysis. Similiar results were obtained in the thermal decomposition of CH_3CHFCl (42) and CH_3CF_2Cl (43)

$$CH_3CHFCl \longrightarrow CH_2CHF + HCl$$
$$\longrightarrow CH_2CHCl + HF$$
$$CH_3CF_2Cl \longrightarrow CH_2CF_2 + HCl$$
$$\longrightarrow CH_2CFCl + HF$$

In both cases, HCl elimination played the predominant role.

It is, thus, quite clear that HCl eliminations are well established processes and the observations by us of these reactions are in complete agreement with current literature data. It is interesting, however, to study this process a bit further since HCl elimination may occur as a α-α or as a α-β process.

The dehydrohalogenation of haloethanes is generally accepted to proceed via a four center transition state (α-β elimination) in both thermal and chemical activated systems. However from time to time, a three center transition state (α-α elimination) of HX may be observed in which both the hydrogen and halogen atom come from the same carbon atom.

It is clear that the elimination of hydrogen halide from substituted methanes must be an α-α process. Such a process has been observed in CH_3I (44), CHF_3 (45), CHF_2Cl (46), $CHFCl_2$ (47) and CHF_2Br (48).

Hydrogen halide elimination observed in the following compounds must be an α-β process: CH_3CF_3 (49), CD_3CF_3 (50), CH_2CCl_2 (21), CH_3CCl_3 (25,51), CH_3CF_3 (52,53) and CH_3CF_2Cl (54,55,56).

More interesting, however, are studies where both α-α and α-β processes may occur simultaneous. Pritchard and coworkers (35) first observed α-α and α-β eliminations from the vibrationally excited CF_2HCD_3 molecule which had been formed by recombination of $CF_2H\cdot$ and $CD_3\cdot$ radicals. $CF_2H\cdot$ and $CD_3\cdot$ radicals were produced by photolysis of a mixture of 1,1,3,3-tetrafluoroacetone and acetone - d_6 at 3130 Å. The following reaction sequence explains the observations;

$$CF_2H\cdot + CD_3\cdot \longrightarrow CF_2HCD_3^*$$

$$CF_2HCD_3^* \xrightarrow{\alpha-\beta} CFH{=}CD_2 + DF$$

$$\xrightarrow{\alpha-\alpha} CDF{=}CD_2 + HF$$

Since then Setser, Pritchard and Holmes (57) observed α-α and α-β elimination of HF from vibrationally excited $CH_2FCDF_2^*$ which was produced by recombination of $CH_2F\cdot$ and $CDF_2\cdot$ radicals.

$CH_2F\cdot$ and $CDF_2\cdot$ radicals were obtained by cophotolysis of mixtures of 1,3-difluoroacetone and 1,1,3,3-tetrafluoroacetone-d_2

$$\begin{aligned}
&CH_2F\cdot + CDF_2\cdot \longrightarrow CH_2FCDF_2{}^*\\
&CH_2FCDF_2{}^* \xrightarrow{\alpha-\beta} CH_2{=}CF_2 + DF\\
&\qquad\qquad\quad \xrightarrow{\alpha-\beta} \text{cis or trans-}CHF{=}CDF + HF\\
&\qquad\qquad\quad \xrightarrow{\alpha-\alpha} DF + CH_2F\ddot{C}F\\
&\qquad\qquad\qquad\qquad\qquad\quad \hookrightarrow \text{cis or trans-}CHF{=}CHF
\end{aligned}$$

Tschulkow-Roux and coworkers in shock tube pyrolysis experiments also observed α-α elimination and α-β elimination of HX from the following compounds: CF_3CH_2Cl (58), CF_3CHCl_2 (59), CH_3CDF_2 (60).

Recently Tschulkow-Roux and coworkers observed α-α and α-β elimination in the photolysis of CF_3CH_2Cl (31) at 1470 Å.

$$\begin{aligned}
CF_3CH_2Cl &\xrightarrow{\alpha-\alpha} CF_2CHF + HCl\\
&\xrightarrow{\alpha-\beta} CF_2CHCl + HF
\end{aligned}$$

Thus, there is no doubt that both α-α and α-β eliminations of hydrogen halides do occur. It seems that the α-α elimination needs a somewhat higher activation energy than the α-β elimination. Thus, both α-α and α-β processes are observed in shock tube experiments, which energetically more moderate systems produce mainly, if not exclusively, α-β eliminations.

For higher energy photolysis experiments in the far U.V. range α-α processes seem to compete with α-β eliminations.

Also the structure of the molecule determines to some extent the importance of either the α-α or the α-β process. As an example it may be mentioned that in compounds containing two halo atoms attached to the same carbon atom the α-α process competes with the α-β process for HX eliminations.

Of course in the compounds under discussion it is clear that CH_3CCl_3 can only yield α-β elimination. In $CHCl_2CHCl_2$ both α-α and α-β processes may occur and probably did occur although we have no way in determining the individual contributions since no isotope experiments were carried out by us.

The 2nd important process which we observed the photolysis of 1,1,1-CH_3CCl_3 and 1,1,2,2-$CHCl_2CHCl_2$is the scission of carbon-chlorine bond (reactions 3b and 18).

The scission of carbon-halogen bonds, except in the case of fluorine, is well known. The literatures on it is vast. Thus, this is not surprising in observing the cleavage of a carbon-chlorine bond in the photolysis of 1,1,1-CH_3CCl_3 and 1,1,2,2-$CHCl_2CHCl_2$.

$$1,1,1\text{-}CH_3CCl_3^{*} \longrightarrow CH_3CCl_2\cdot + Cl\cdot \qquad 3b$$

$$1,1,2,2\text{-}CHCl_2CHCl_2^{*} \longrightarrow CHCl_2CHCl\cdot + Cl\cdot \qquad 18$$

In order to explain the observed results, it was necessary to postulate that the $CH_3CCl_2^{\circ}\cdot$ radical produced at $\lambda < 2200$ Å contained excess energy which caused it to decompose according to reactions 5a and 5b,

$$CH_3CCl_3^{**} \longrightarrow CH_3CCl_2^{\circ}\cdot + Cl\cdot \qquad 5a$$

$$CH_3CCl_2^{\circ}\cdot \longrightarrow CH_2CCl_2 + H\cdot \qquad 5b$$

Such an hypothesis is quite reasonable if it is realized that the rupture of a carbon-chlorine bond requires only 81 Kcal/mole. Thus, in the 2000 Å wavelength region (corresponding 143 Kcal/mole) the molecule has 62 Kcal/mole excess energy distribute over the $CH_3CCl_2\cdot$ radical and chlorine atom.

Also it should be mentioned that the suggestion is completely analogous to the observation made in the photolysis of acetone (61,62,63), biacetyl (64) and CH_3COOCD_3 (65). In these cases, it was reported that some of the acetyl radicals carried excess energy which forced the radical to decompose;

$$CH_3CO^{\circ} \longrightarrow CH_3\cdot + CO$$

The decomposition of double star higher excited 1,1,1-$CH_3CCl_3^{**}$ also parallel the results of Ausloos, Rebbert and Wijnen (66) who observed the following primary step in the photolysis of vinyl chloride at low wavelengths;

$$C_2H_3Cl + hv \longrightarrow C_2H_2 + H\cdot + Cl\cdot$$

The authors stated that this reaction may, but not necessary, occur via an excited vinyl radical.

Ausubel and Wijnen (23,24) also observed that in the wavelength of 2000 Å the photolysis of cis and trans 1,2-$C_2H_2Cl_2$ produced excited $C_2H_2Cl\overset{\circ}{\cdot}$ radical;

$$\text{cis or trans } 1,2\text{-}C_2H_2Cl_2^{**} \longrightarrow C_2H_2Cl\overset{\circ}{\cdot} + Cl\cdot$$

There is, so far, no evidence for the excited 1,1,2-$C_2H_2Cl_3\overset{\circ}{\cdot}$ radical observed. Nevertheless, in the wavelength of 2000 Å, we can not exclude the possibility of such excited radical formed at the photolysis of 1,1,2,2-$CHCl_2CHCl_2$.

One of the major processes in the photolysis of 1,1,2,2-$CHCl_2CHCl_2$ at wavelength range 2000 Å to 4000 Å is Cl_2 molecule detachment and we did not observe any evidence for the Cl_2 detachment for 1,1,1-CH_3CCl_3 in the same wavelength range.

Ausubel and Wijnen (23,24) found that in the photolysis of cis and/or trans 1,2-$C_2H_2Cl_2$, the Cl_2 molecule detachment is the major product and in the photolysis of 1,1-$C_2H_2Cl_2$, the Cl_2 detachment is the minor product.

Fujimoto and Wijnen (27) also observed that molecular elimination of Cl_2 is a minor phenomena at $\lambda < 2200$ Å in the photolysis of CD_3CHCl_2.

All the above facts indicate that α-α elimination of Cl_2 molecule is not a favorable process at the wavelength of this investigation. From the geometry of these two ethanes, we are clearly seeing that the Cl_2 elimination from 1,1,2,2-$CHCl_2CHCl_2$ could be either α-α or α-β elimination and also that there are at least six possibilities for Cl_2 elimination taking place. This is why the Cl_2 elimination is one of the major processes for 1,1,2,2-$CHCl_2CHCl_2$. From the results we obtained, the α-α elimination of Cl_2 is only 5 % of α-β elimination of Cl_2.

It is noteworthy that we did not observe any Cl_2 detachment from 1,1,1-CH_3CCl_3, because if there is a elimination of Cl_2 taking place, the only possible geometric arrangement is α-α elimination which is not a favorable process at this experimental condition.

Finally we also observed the H_2 molecule detachment from 1,1,2,2-$CHCl_2CHCl_2$ but not from 1,1,1-CH_3CCl_3 in the wavelength range 2000 Å to 4000 Å.

Fujimoto and Wijnen (27), when they photolyzed the CD_3CHCl_2 at the same wavelength range, observed the HD elimination.

Tschuikow-Roux and Co-workers (28,32,67), when they photolyzed the C_2H_5Cl (28), CH_2FCH_2Cl (32), C_2H_5Br (67) at the wavelength 1236 Å and 1470 Å, also observed H_2 elimination.

The H_2 molecule elimination only observed on 1,1,2,2-$CHCl_2CHCl_2$ but not on 1,1,1-CH_3CCl_3 is very reasonable, because for 1,1,1-CH_3CCl_3, the H_2 elimination must be a α-α elimination. There is no previous literature reporting α-α elimination of H_2 molecule from halogenated ethanes at wavelength range 2000 Å to 4000 Å.

Another important observation for the photolysis of 1,1,2,2-$CHCl_2CHCl_2$ is the confirmation of the cis-trans 1,2-$C_2H_2Cl_2$ isomerization process.

The mechanism of cis-trans isomerization of 1,2-dichloroethylene was first proposed by Wijnen (68) and Dainton (69) and recently was confirmed by Ausubel and Wijnen (70), when they photolysis the cis 1,2-$C_2H_2Cl_2$ and trans 1,2-$C_2H_2Cl_2$ as follows;

$Cl\cdot + \text{ cis or trans } 1,2\text{-}C_2H_2Cl_2 \longrightarrow C_2H_2Cl_3{*}\cdot$ 23

$C_2H_2Cl_3{*}\cdot \longrightarrow \text{cis } 1,2\text{-}C_2H_2Cl_2 + Cl\cdot$ 24

$C_2H_2Cl\ {*}\cdot \longrightarrow \text{trans } 1,2\text{-}C_2H_2Cl_2 + Cl\cdot$ 25

$C_2H_2Cl_3{*}\cdot + \text{ deactivator } \longrightarrow C_2H_2Cl_3\cdot$ 26

The chlorine atom addition to the double bond of dichloroethylene produces an excited 1,1,2-trichloroethyl radical. Then the hot trichloroethyl radical could have a free rotation on carbon-carbon single bond. This activated radical either is deactivated to a ground state radical or it decomposes. Because there having been free rotation in the intermediate hot radical, the product formed could be either isomer of 1,2-$C_2H_2Cl_2$.

As we mention on page 87 and from the figures 26 and 27, we have observed that at zero time of photolysis of 1,1,2,2-$C_2H_2Cl_4$ the products of cis 1,2-$C_2H_2Cl_2$ and trans 1,2-$C_2H_2Cl_2$ are one to one ratio. With increasing exposure time the ratio increases. At zero time the ratio of cis 1,2-$C_2H_2Cl_2$ to trans 1,2-$C_2H_2Cl_2$ is unity due to the excited 1,1,2,2-$C_2H_2Cl_4$ yields both isomers at equal rate and there is no cis-trans isomerization process occurring at zero time. But as the exposure time increases, the ratio of cis 1,2-$C_2H_2Cl_2$ to trans 1,2-$C_2H_2Cl_2$

increases and approaches 1.6. This fact confirms that cis-trans isomerization do occur and the ratio of cis 1,2-$C_2H_2Cl_2$ to trans 1,2-$C_2H_2Cl_2$ is a excellent agreement with Ausubel and Wijnen (70) observation on the photochemically induced isomerization of the 1,2-dichloroethylenes and they reported $k_{24} / k_{25} = 1.6$.

This cis-trans isomerization processes is also confirmed by carried out the deactivated study of 1,1,2,2-$C_2H_2Cl_4$. As we reported on page 108 and figures 44,45 . The cis 1,2-$C_2H_2Cl_2$ / trans 1,2-$C_2H_2Cl_2$ approaches unity as the OFCB increases. This, without any doubt, indicates that the excited 1,1,2-trichloroethyl radical will more effectively deactivated and go to ground state radical and leads to no cis-trans isomerization process. This is why at zero OFCB pressure the cis 1,2-$C_2H_2Cl_2$ / trans 1,2-$C_2H_2Cl_2$ is equal to 1.6 but when the OFCB pressure increases the cis 1,2-$C_2H_2Cl_2$ / trans 1,2-$C_2H_2Cl_2$ decreases and approaches unity as we reported on figures 44 and 45 regardless of the incident light. Again the ratio of cis 1,2-$C_2H_2Cl_2$ / trans 1,2-$C_2H_2Cl_2$ is equal to 1.6 (at zero OFCB pressure) and this is excellent agreement with Ausubel and Wijnen's observation.

LIFE - TIME CALCULATION FOR THE EXCITED STATE OF CH_3CCl_3

Now, it should be interesting to take a closer look for the excited state yielding the products. From our reaction mechanism on page 47

$CH_3CCl_3 + h\nu \longrightarrow CH_3CCl_3^*$ 1

$CH_3CCl_3^* \longrightarrow CH_2CCl_2 + HCl$ 3a

$CH_3CCl_3^* \longrightarrow CH_3CCl_2\cdot + Cl\cdot$ 3b

$CH_3CCl_3^* + CH_3CCl_3 \longrightarrow \text{deactivation}$ 4a

$CH_3CCl_3^* + \text{OFCB} \longrightarrow \text{deactivation}$ 4b

Reactions 3a and 3b are decomposition reactions. Reactions 4a and 4b are deactivation reactions. From the rate of $k_{deactivation} / k_{decomposition}$ we can calculate the pressure at which the rates of deactivation and decomposition are equal. This value, in terms, is used to calculate the average life time of excited species.

The calculations involve the assumption that each collision between an excited species and a deactivator molecule leads to deactivation. Then if the collisional cross-section is known, from the formula for collisional frequency, the number of collision per second per excited species can be calculated. This is equal to the number of decompositions per second per excited species, the inverse of which is the average life time. (71)

From the average value for k_{4a} / (k_{3a} + k_{3b}) and k_{4b} / (k_{3a} + k_{3b}) is equal to 0.038 X 10^{-17} (molecule/c.c.)$^{-1}$ at λ>2200 Å and accepting as collision diameters for CH_3CCl_3 and OFCB 42 Å and 43 Å respectively, a value of 1 X 10^{-9} sec. was estimated. This is in general order of magnitude expected for vibrationally excited molecules. Ausubel and Wijnen (23) reported the life time of the excited cis 1,2-$C_2H_2Cl_2$ at 2200 Å is 2.4 X 10^{-9} sec. Follmer and Pritchard (36) reported the life time of vibrationally excited CF_2DCFH_2* is 2.3 X 10^{-9} sec. Comparing the life time for lower excited state of 1,1,1-CH_3CCl_3 with the literature results, the agreement is not bad.

Unfortunately at short wavelength (λ>2000 Å) the rate of deactivation / rate of decomposition is not consistent and it was, therefore, not possible to obtain a measurement of the life time of the " two star " excited state of 1,1,1-CH_3CCl_3.

Since we did not obtain the ratio for the rate of deactivation/ rate of decomposition of the excited 1,1,2,2-$CHCl_2CHCl_2$ molecule and the life time of this excited molecule was, therefore, not calculated.

CONCLUSIONS

The study, reported in this thesis, deals with the photolysis of 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane at near ultraviolet light (2000 Å -to 4000 Å.).In each case at least two excited states were found.

For the 1,1,1-CH_3CCl_3, the lower excited state which was produced at $\lambda > 2200$ Å was found to decompose in the following manner;

$$CH_3CCl_3{}^* \longrightarrow CH_2CCl_2 + HCl \qquad 3a$$

$$CH_3CCl_3{}^* \longrightarrow CH_3CCl_2{}^\bullet + Cl^\bullet \qquad 3b$$

The excited $CH_3CCl_3{}^*$ molecule could be deactivated by unactivated CH_3CCl_3 or OFCB in the following manner;

$$CH_3CCl_3{}^* + CH_3CCl_3 \longrightarrow \text{deactivation} \qquad 4a$$

$$CH_3CCl\ {}^* + \text{OFCB} \longrightarrow \text{deactivation} \qquad 4b$$

The average value of $k_{4a} / (k_{3a} + k_{3b})$ is equal to 0.035×10^{-17} (molecule/c.c. $)^{-1}$ and the average value of $k_{4b} / (k_{3a} + k_{3b})$ is equal to 0.036×10^{-17} (molecule/c.c. $)^{-1}$. This indicates that the OFCB and CH_3CCl_3 are equally effective as deactivators for the excited $CH_3CCl_3{}^*$ molecule.

The average life time of this excited state of CH_3CCl_3* was found to be 1 X 10^{-9} seconds.

The higher excited state $CH_3CCl_3^{**}$ molecule which was produced at wavelength greater than 2000 Å decomposes as follows;

$$CH_3CCl_3^{**} \longrightarrow CH_3CCl_2 + Cl\cdot \qquad 5a$$

$$CH_3CCl_3^{**} \longrightarrow CH_2CCl_2 + H\cdot + Cl\cdot \qquad 5b$$

Where reaction 5b may occur directly or via an excited $C_2H_3Cl_2^{\theta}$ radical as intermediate.

There was no evidence of Cl_2 or H_2 molecular elimination from excited CH_3CCl_3 molecule. We also carried out photolysis of CH_3CCl_3 with I_2 and HI as free radical scavengers. The rate of production of CH_3CCl_2H is dependent on the concentration of HI. The concentration of I_2 is independent of the rate of production of the products. It was, therefore, concluded that

I_2 is a better scavenger than HI for the photolysis of CH_3CCl_3.

The photolysis of 1,1,2,2-$CHCl_2CHCl_2$ was carried out in the wavelength range 2000 Å to 4000 Å and with the I_2 as free radical scavenger.

At least three different excited $CHCl_2CHCl_2$ molecules were found and their decomposition was reported as follows;

$$CHCl_2CHCl_2^* \longrightarrow 1,1\text{-}C_2H_2Cl_2 + Cl_2 \qquad 14$$

$$CHCl_2CHCl_2^* \longrightarrow \text{cis \& trans } 1,2\text{-}C_2H_2Cl_2 + Cl_2 \qquad 15$$

$$CHCl_2CHCl_2^* \longrightarrow C_2HCl_3 + HCl \qquad 16$$

$$CHCl_2CHCl_2^{**} \longrightarrow C_2Cl_4 + H_2 \qquad 17$$

$$CHCl_2CHCl_2^{o} \longrightarrow CHCl_2CHCl\bullet + Cl\bullet \qquad 18$$

The one star excited $CHCl_2CHCl_2^*$ is the precursor for the $1,1$-$C_2H_2Cl_2$, cis & trans $1,2$-$C_2H_2Cl_2$ and C_2HCl_3 regardless of the wavelength of the incident light and/or the pressure of the deactivator. $k_{14} : k_{15} : k_{16} = 0.05 : 1.0 : 0.14$ was obtained.

The molecular elimination of H_2 (reaction 17) was observed but in a very small amount.compared to the production ofdichlor ethylenes and trichloroethylene. The C-Cl bond rupture was also found to occur to a small extent.

A very interesting results of studying the photolysis of $1,1,2,2$-$CHCl_2CHCl_2$ is the confirmation of the cis-trans $1,2$-$C_2H_2Cl_2$ isomerization process.

The mechanism of cis-trans isomerization process of $1,2$-$C_2H_2Cl_2$ was reported as,

$Cl\cdot$ + cis or trans 1,2-$C_2H_2Cl_2 \longrightarrow C_2H_2Cl_3^*$ 23

$C_2H_2Cl_3^* \longrightarrow$ cis 1,2-$C_2H_2Cl_2$ + $Cl\cdot$ 24

$C_2H_2Cl_3^* \longrightarrow$ trans 1,2-$C_2H_2Cl_2$ + $Cl\cdot$ 25

$C_2H_2Cl_3^*$ + deactivator $\longrightarrow C_2H_2Cl_3$ 26

At zero time of photolysis the cis 1,2-$C_2H_2Cl_2$ / trans 1,2-$C_2H_2Cl_2$ was found to be unity, since there is no cis-trans isomerization process. With increased exposure time the ratio increases and approaches 1.6 as expected ($k_{24} / k_{25} = 1.6$).

At zero OFCB pressure the cis 1,2-$C_2H_2Cl_2$ / trans 1,2-$C_2H_2Cl_2$ is 1.6 and the ratio approaches unity as the OFCB pressure increases. This, without any doubt, indicates that the excited 1,1,2-trichloroethyl radical will be more effectively deactivated and goes to the ground state radical (reaction 26), and leads to no cis-trans isomerization process.

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