THE PHOTOLYSIS OF THE DICHLOROETHYLENES

by

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Abstract

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The three isomers of dichloroethylene were photolyzed in the presence of a free radical scavenger with near ultraviolet light. In all three cases, two excited states were hypothesized to explain the data. Where possible, the lifetimes of the six excited species were determined.

For the 1,2-dichloroethylenes, the lower excited state produced acetylene and chloroacetylene by molecular elimination and the chlorovinyl radical. From cis-dichloroethylene, the ratio of the rates of production of acetylene : chloroacetylene : chlorovinyl radical was 3.1 : 1.0 : 0.28; from trans-dichloroethylene, this ratio was 2.1 : 1.0 : 0.27. The higher excited state of cis-dichloroethylene produced acetylene by atomic elimination of two chlorine atoms and excited chlorovinyl radicals, in a ratio of 5 : 1. The higher excited state of trans-

dichloroethylene produced only chlorovinyl radicals. The lower excited state of 1,1-dichloroethylene produced acetylene and chloroacetylene by molecular elimination in a ratio of 1.0 : 3.5. The higher excited state produced only chlorovinyl radicals.

In the photolysis of the 1,2-dichloroethylenes, isomerization also occurred. This was found to be catalyzed by chlorine atoms which reversibly added onto the double bond of the starting material. In the adduct, there was free rotation about the resulting carbon - carbon single bond. When the addition was reversed, either isomer could be formed. The data support a value of 1.6 for the branching ratio, 62% cis-dichloroethylene and 38% trans-dichloroethylene.

The data are discussed, where applicable, with regard to previously available results.

FOREWORD

Near ultraviolet photolysis is an excellent method of investigating the reactions of excited molecules. For most molecules, the energy supplied (up to 143 kcal./mole) is sufficient to cause excitations which lead to decomposition reactions. But, in general, there is not enough energy to cause total fragmentation of the molecule. The reactions observed can be more varied than those observed in pyrolyses. Because they can be performed at room temperature, photolyses generally give fewer secondary reactions. Moreover, by manipulating the spectrum of irradiating light, one compound in a mixture can be selectively excited.

Unlike mercury photosensitization and chemical activation, scavengers can be used in conjunction with photolyses. This reduces the occurrence of secondary reactions, which, in turn, simplifies the determination of the mechanism. Also, much higher pressures can be used than in chemical activation studies.

Of course, a compound cannot be subject to photolysis unless it absorbs the irradiating light. For near ultraviolet light, this requires some degree of unsaturation and/or bathochromic substituents. Sometimes, it

is difficult to restrict the initiating light so that only one excitation is observed. The simultaneous occurrence of reactions of more than one excited state can complicate the interpretation of the reactions. But, the benefits of the method far outweigh these drawbacks.

Of the haloethylenes, the only compound whose reactions under the influence of near ultraviolet light have been studied exhaustively is vinyl chloride.[34,91] A cursory investigation of cis-dichloroethylene[130] has been performed. This dissertation is a continuation of that investigation. Its intent is to elucidate the mechanism of the reactions of the dichloroethylenes induced by near ultraviolet light. It has been expanded to enable the comparison of the reactions of the three isomers of dichloroethylene. There has been no work previously reported on the photolysis of either trans-dichloroethylene or 1,1-dichloroethylene.

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R. L. A.

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"Fate does not seeks its victim -- the victim seeks his own fate."

"Every human action can be disguised with a coat of gilt."

-- Alexander Solzhenitsyn

August, 1914

EXPERIMENTAL

Materials

cis-1,2-Dichloroethylene.--was obtained from the Eastman Chemical Company. It was purified by successive distillations, using a column packed with glass helices. The only impurity in the sample used was trans-1,2-dichloroethylene, which comprised less than 0.1% of the sample.

1,1-Dichloroethylene.--also was obtained from Eastman Chemical Company. It, too, was purified by distillation to better than 99.9% purity, the impurity being trans-1,2-dichloroethylene.

trans-1,2-Dichloroethylene.--was obtained from the Aldrich Chemical Company. It was purified by gas chromatography to better than 99.98% purity. The impurities were cis-1,2-dichloroethylene and 1,1-dichloroethylene. The cis-1,2-dichloroethylene was more than ten times more prevalent than the 1,1-dichloroethylene.

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

Hydrogen chloride.--gas was prepared by dehydration of a solution of hydrochloric acid. B & A hydrochloric acid from Allied Chemical's Industrial Chemicals Division was used. Its assay lists it as better than 99.9% hydrogen chloride solution. The acid solution was added, a drop at a time, to anhydrous phosphorous pentoxide. The gas released passed through a trap cooled by a dry ice-acetone mixture and then was collected in an auxilliary reservoir

of the high vacuum system.

Tetrafluoromethane.--was supplied by the Matheson Company. With the exception of up to 1½% air, the tetrafluoromethane was 99.7% pure.

Sulfur Hexafluoride.--also was supplied by the Matheson Company. It was better than 98% pure. The major impurity was air. Tetrafluoromethane was a minor impurity.

Light Source

The ultraviolet source employed in all experiments was a Hanovia Model 16A13 medium pressure mercury arc collimated by an aluminum shade and reflector. The spectrum of the source ranged from about 2000 Å. through the visible region. The 2537 Å. resonance line of the arc was reversed. Mercury photosensitization could not occur in the reaction cell.

In some experiments a filter was used to remove high frequency light. The transmittance spectra of these filters are shown in Figure 1, page 4.

Technique

The photolysis of the dichloroethylenes was studied under varied conditions. To keep the reactions as simple as possible, oxygen, a free radical scavenger, was excluded from the reaction cell. This was accomplished by using a high vacuum system, a simplified version of which is shown in Figure 2, page 5. The iodine and sample

Figure 1. Transmittance Spectra of Selected Corning Filters

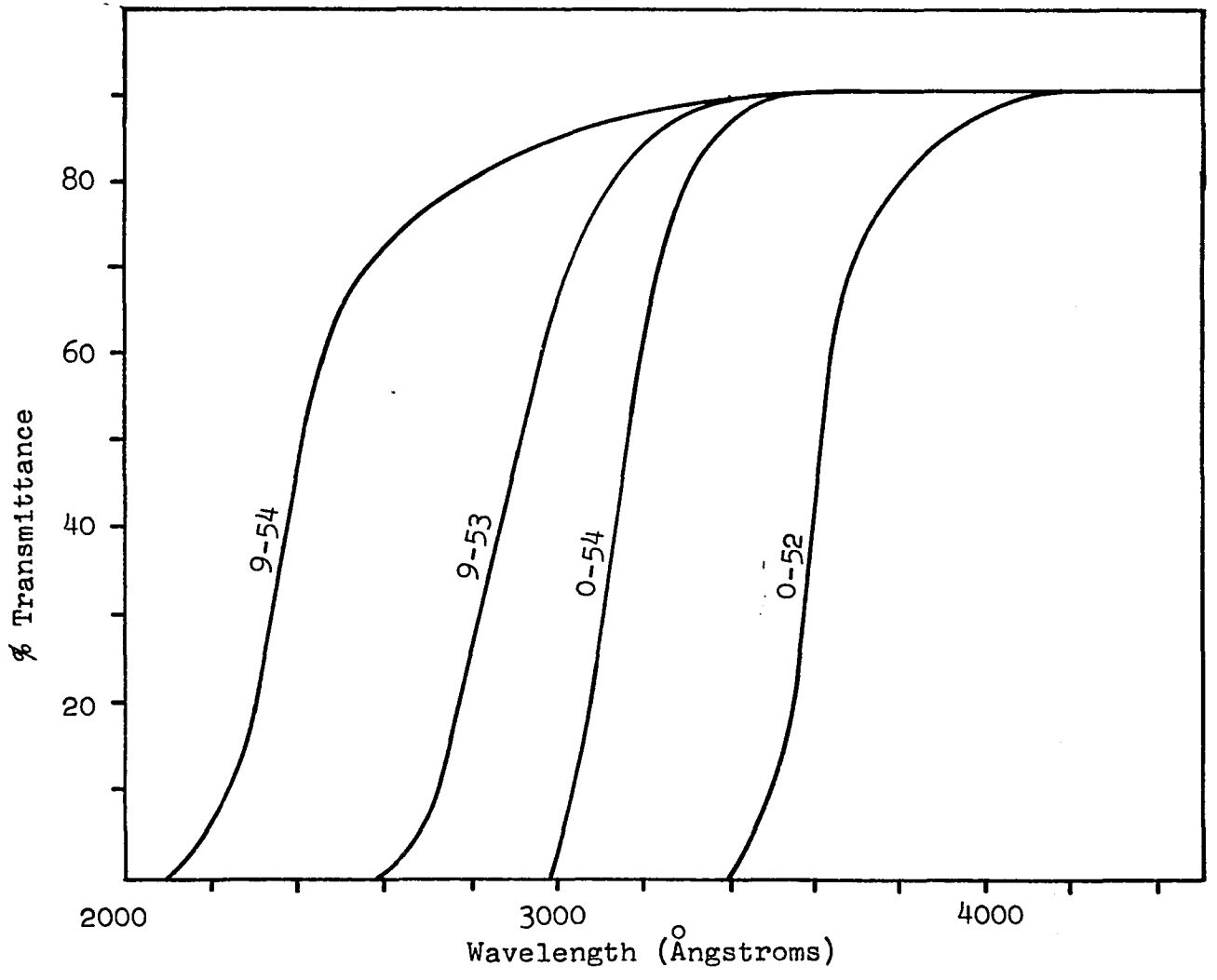
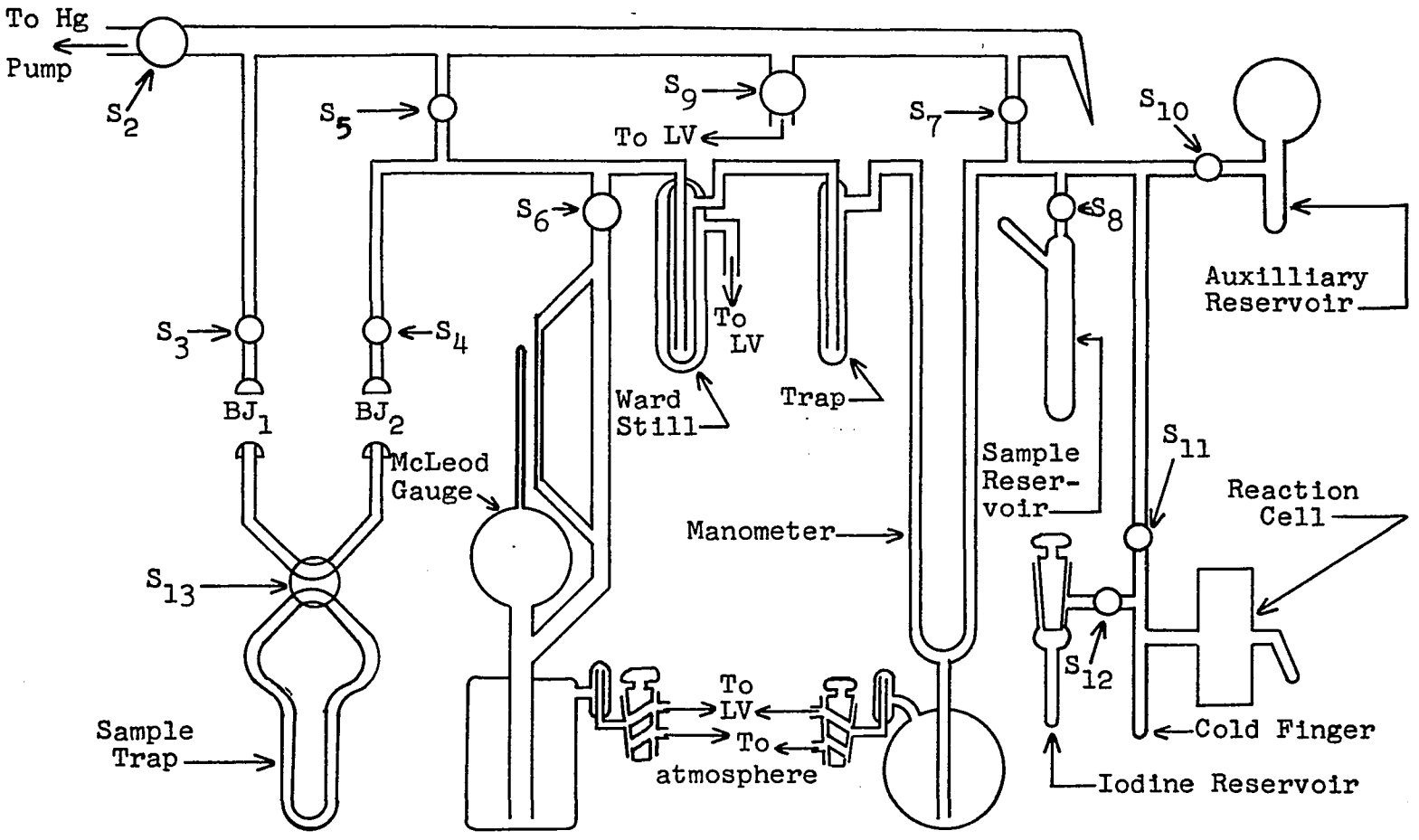


Figure 2. The High Vacuum System



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

reservoirs could be filled directly. Auxilliary reservoirs had to be filled by admitting the compound through one of the ball joint outlets and condensing it into the auxilliary reservoir by cooling the reservoir with liquid nitrogen.

After being introduced into the high vacuum system, the various compounds were degassed thoroughly. This consisted of freezing the compound with liquid nitrogen and pumping on the reservoir with a high vacuum. The process was repeated at least three times. The dichloroethylenes were stored at -78° C.

In a typical experiment, when the vacuum as measured on the McLeod gauge was deemed adequate, the reaction cell was isolated by closing stopcock 11. The cold finger was immersed in liquid nitrogen and iodine condensed into it. After a minute, the iodine stopcock, 12, was closed and the liquid nitrogen removed from the cold finger.

When the cold finger reached room temperature, the dichloroethylene 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 dichloroethylene was allowed to expand into the tubing extending from the manometer to stopcocks 10 and 11. Stopcock 11 then was opened, the dichloroethylene expanding into the 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.

If hydrogen chloride was used as the scavenger instead of iodine, the dichloroethylene was put into the cell first. After the cell stopcock had been closed, the high vacuum manifold stopcock, 7, was opened, pumping away the dichloroethylene remaining in the tubing. After a few minutes, the manifold stopcock was closed again. The hydrogen chloride in its auxilliary reservoir was frozen with liquid nitrogen. The auxilliary reservoir stopcock, 10, was opened and the liquid nitrogen removed. As the hydrogen chloride vaporized, it entered the tubing leading to the reaction cell. The ratio of the tubing volume to the cell volume was known. The pressure of gas in the tubing equivalent to the desired cell pressure had been calculated. When this pressure was reached, stopcock 10 was closed. This procedure insured the exclusion from the reaction cell of any trace of water which may have been in the auxilliary reservoir along with the hydrogen chloride.

With the hydrogen chloride in the tubing and the dichloroethylene in the cell, the cold finger was cooled with liquid nitrogen, condensing the dichloroethylene. Stopcock 11 then was opened, condensing all the hydrogen chloride into the cell. Stopcock 11 was closed again and the cell's contents allowed to reach room temperature.

If another component, a deactivator, was to be added to the cell, the tubing was pumped on, evacuating it. The

deactivator in its auxilliary reservoir was condensed with liquid nitrogen. Then the auxilliary reservoir stopcock was opened. 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 equalize the pressures. Then it was shut and the pressure in the tubing increased again. Stopcock 11 was used in this manner to admit successive small amounts of the deactivator into the cell. When the total pressure wanted in the cell was reached, the auxilliary stopcock was closed and the cell stopcock left open until the pressure was read. Then stopcock 11 was closed. During the experiment, stopcock 7 was opened evacuating the tubing. Then stopcock 7 was closed.

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 board prevented the ultraviolet light from entering the cell. As the board was removed and the ultraviolet light entered the cell, a stopwatch was activated manually. To halt the photolysis, either the light was shut off or the blackened board was replaced.

To collect the sample, a sample trap, also shown in Figure 2, page 5, 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 progress, 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 any of its air into the high vacuum system. It then was cooled with liquid nitrogen. The sample trap was left in this position until the reaction time had elapsed.

After the light had been shut off, the manometer mercury was lowered to a level just below the bottom of the U-tube. This allowed about ten centimeter of pressure to be placed on the mercury without loss of the sample through the mercury and the low vacuum system. The sample was released from the cell by opening stopcock 11. The lowering of the manometer mercury was noted. Stopcock 3 was closed and stopcock 4 was opened.

This exposed the sample to a temperature of -190° C. in the sample trap. The sample condensed, accompanied by a return of the manometer mercury to its previous level. The sample was collected for three minutes. Then stopcock 3 was opened. The sample was frozen into the sample trap. If any air had leaked in through the ball joints, it would be pumped away. After a minute, stopcock 13 was closed, followed by stopcocks 4 and 3.

The sample trap then 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. The experiments with cis-1,2-dichloroethylene and 1,1-dichloroethyl-

ene were analyzed on a Burrell Kromo-Tog using a silicon grease on celite column; those with trans-1,2-dichloroethylene were analyzed on a Burrell Kromo-Tog, Model KD using a silicon grease on firebrick column.

When tetrafluoromethane was used as a deactivator, the procedure for collection of the sample had to modified. Because a high cell pressure of tetrafluoromethane could not be contained in the sample trap, the deactivator had to be pumped off before the sample could be collected.

The sample to be analyzed first was condensed into the Ward still. By applying about five volts to the heating wires of the still, the temperature was elevated to a point where the vapor pressure of tetrafluoromethane was sufficiently high for it to be pumped away. To ascertain whether all the tetrafluoromethane had been removed, the manometer 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 tetrafluoromethane finally had evaporated, the liquid nitrogen was removed from the Ward still. Stopcocks 13 and 4 were closed and the variac raised to 25 volts. Any change in pressure was indicated by the manometer. When, over a considerable period of time, the pressure no longer changed, it reasonably was assumed that all the sample had evaporated. (After a few experiments, the approximate final pressure reading on the manometer could be predicted.)

The sample trap was immersed in liquid nitrogen. Stopcocks 12 and 4 were opened. The variac was shut off. Then, normal sample collection procedures were followed.

In experiments with cis- and trans-dichloroethylene, the cell was surrounded by air. For 1,1-dichloroethylene experiments, the cell was immersed in a constant temperature bath. The transmitted light first passed through a layer of water about five millimeters thick before entering the cell. The use of a constant temperature bath enabled some experiments to be performed at temperatures other than room temperature.

Identification and Analysis of Products

All samples were analyzed by gas chromatography. The retention time of those products which are readily available were confirmed by individually chromatographing each compound and by doping experimental samples with known compounds. These compounds are: acetylene, chloroethene (vinyl chloride), trans-1,2-dichloroethylene, cis-1,2-dichloroethylene, 1,1,2-trichloroethylene, chloroethane, 1,2-dichloroethane, 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane.

To confirm the peaks attributed to trans- and cis-1-chloro-2-iodoethylene, acetylene was allowed to react with iodine monochloride. Two products of this addition reaction had the same retention times as the products which were thought to be trans- and cis-1-chloro-2-iodoethylene.

In a similar experiment, 1,1,2-trichloro-2-iodoethane was confirmed by reacting iodine monochloride with cis-1,2-dichloroethylene. In experiments where hydrogen chloride was used as a scavenger instead of iodine, the peaks attributed to these three iodides disappeared. In their place were peaks easily identified as vinyl chloride and 1,1,2-trichloroethane.

In the photolysis of 1,1-dichloroethylene in the presence of iodine, a peak appeared which was attributed to 1-chloro-1-iodoethylene. In an experiment in which hydrogen bromide was used as a scavenger in place of iodine, a vinyl chloride peak appeared, but not the one attributed to 1-chloro-1-iodoethylene. In fact, this peak was not observed in the absence of iodine. The compound's retention time was slightly less than that of trans-1-chloro-2-iodoethylene (as 1,1-dichloroethylene's retention time is slightly less than that of trans-1,2-dichloroethylene).

The peak which appears between acetylene and chloroethene is attributed to monochloroacetylene. It appears in the photolysis of the three dichloroethylenes and that of 1,1,2-trichloroethylene, but not in the photolysis of vinyl chloride.

Both gas chromatographs used have thermal conductivity detector cells. For similar compounds, this type of detector is more sensitive to more complex, and therefore higher boiling, compounds. Thus, as the retention time in the column increases, so does the sensitivity. The first

peaks observed on a chromatogram correspond to low boiling compounds to which the chromatograph is least sensitive. A plot of sensitivity versus retention time would show an ascending curve with a continuously decreasing slope.

To find the sensitivity of the chromatograph under any set of analysis conditions, a known amount of product was analyzed. This was done at least three times with each compound. The area under the peak was determined by integration with an Ott planimeter. The actual area was not determined, although it is possible to correlate the planimeter units to metric units. 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 the chromatograph to that compound, and dividing the product by the illuminated volume of the reaction cell and by the exposure time. The rate is reported in molecules per milliliter per second.

This determination of sensitivities was performed for acetylene, chloroethene, 1,1-dichloroethylene, trans-1,2-dichloroethylene, cis-1,2-dichloroethylene, 1,2-dichloroethane, 1,1,2-trichloroethylene, 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane, all of which were available for quantitative analysis. With monochloroacetylene and the

iodides, the chemicals were not available. In these cases, an estimate had to be made by interpolating from the sensitivities of compounds with similar retention times. Such estimates are not liable to be wrong by more than 10%.

PRIMARY PROCESSES

INTRODUCTION

In order to get any but the most unstable compounds to react, energy must be supplied to the reaction system. The energy may come in many forms: chemical, electrical, photogenic, physical, radiative, thermal. In this work, the source of energy is photogenic -- light.

The compounds investigated are the three isomers of dichloroethylene. Visible light does not cause these compounds to react. More energetic light is needed. Thus, ultraviolet light is used to irradiate these compounds.

Photolytic Reactions of Ethylene

The parent olefin, ethylene, is the olefin which has been studied most thoroughly, much more so than any of its halogen substituted derivatives. Ethylene does not absorb in the near ultraviolet region, 4000 - 2000 Å.[51] To excite ethylene with energy in this wavelength range, an indirect method of supply must be used. Another species is put into the reaction cell, one which will absorb the light in question. This excited species, then, will transfer its energy on collision with an ethylene molecule. Such a process is known as sensitization. The most commonly used sensitizer is mercury vapor. Cadmium vapor and some aromatic compounds also are used.

Leroy and Steacie[59,60] investigated the mercury photosensitized decomposition of ethylene. Using light of 2537 Å. to excite mercury to its lowest lying triplet, the decomposition product observed was acetylene. They proposed the following mechanism to account for its production:

$$C_2H_4 + Hg\ (^3P_1) \longrightarrow C_2H_4^* + Hg\ (^1S_0)$$

$$C_2H_4^* \longrightarrow C_2H_2 + H_2$$

$$C_2H_4 + C_2H_4^* \longrightarrow 2\ C_2H_4$$

They later reported[60] that with increasing temperature, going as high as 350° C., the production of vinyl radicals becomes an important step.

$$C_2H_4^* \longrightarrow C_2H_3 + H$$

Callear and Cvetanović[30] investigated the mercury photosensitized decomposition of ethylene and deuterated ethylenes. Under the conditions of their experimentation, virtually all the hydrogen formed was produced via molecular elimination. This was evidenced by the inconsequential amounts of HD observed in the decomposition of ethylene - ethylene-d_4 mixtures.

Photosensitization of cis-dideuterioethylene[20] produced D_2, HD and H_2 in a ratio of 1 : 6 : 2. Taking the isotopic effect into account, this suggests that for the formation of molecular hydrogen, all atoms in the ethylene molecule are equally accessible to each other. From the

kinetics of decomposition, the mechanism which best suited their data assumes two excited states of approximately equal lifetimes, both susceptible to collisional deactivation, but only one capable of undergoing decomposition.

$$C_2H_4 + Hg\ (^3P_1) \longrightarrow C_2H_4^* + Hg\ (^1S_0)$$

$$C_2H_4^* \longrightarrow C_2H_4^{**}$$

$$C_2H_4 + C_2H_4^* \longrightarrow 2\ C_2H_4$$

$$C_2H_4^{**} \longrightarrow C_2H_2 + H_2$$

$$C_2H_4 + C_2H_4^{**} \longrightarrow 2\ C_2H_4$$

Ausloos and Gorden[5] found that in mercury photosensitization studies on 1,1-dideuterioethylene the isotopic distribution of hydrogen is "similar, but not exactly the same," as that from 1,2-dideuterioethylene. They suggested that other modes of decomposition may have to be considered.

Rabinovitch, et. al.,[100] studied the kinetics of decomposition and isomerization of trans-dideuterioethylene. They obtained fairly good results using the mechanism proposed by Callear and Cvetanović[20] with only slight modifications. They proposed that the deactivation of the higher excited state of ethylene leads to equal amounts of cis- and trans-dideuterioethylene, while deactivation of the lower excited state (the one which decomposes to give all three isotopic acetylenes and hydrogens) gives the three dideuterioethylenes, each with equal probability.

$$CHD{=}CHD + C_2H_2D_2^{*} \longrightarrow \tfrac{1}{2}\ \underline{cis}\text{-}C_2H_2D_2 + \tfrac{1}{2}\ \underline{tr}\text{-}C_2H_2D_2 + CHD{=}CHD$$

$$CHD{=}CHD + C_2H_2D_2^{**} \longrightarrow 1/3\ \underline{cis}\text{-}C_2H_2D_2 + 1/3\ \underline{tr}\text{-}C_2H_2D_2 + 1/3\ \underline{asym}\text{-}C_2H_2D_2 + CHD{=}CHD$$

The higher excited state was assigned to the lowest lying triplet of ethylene; the lower excited state, the one which decomposes, was thought most probably to be ethylidine, $CH_3CH:$.

Ruland and Pertel[94] used a different mercury line, the one at 1849 Å., to obtain the more energetic $^1P_1$ state of mercury. Again, a mixture of ethylene and ethylene-d_4 was photosensitized. They found that nearly all the hydrogen formed was H_2 or D_2. Here too, the chosen route to acetylene formation is molecular elimination.

A number of organic photosensitizers have been used to excite the dideuterioethylenes.[46,112] No decomposition was observed. However, isomerization, including hydrogen scrambling, occurred. The rates of production of the three dideuterioethylenes were identical. The results were satisfactorily explained by the mechanism modified by Rabinovitch, et al.,[100] where the rate constant for decomposition is zero. There was no decomposition observed because the aromatic compounds used transfer less energy than mercury. Thus, insufficient energy is available for decomposition to occur.

Hunziker[47] and Sato, et al.,[121] have studied the cadmium $^3P_1$ photosensitized isomerization of the dideuterioethylenes. Their results were similar to those for the aromatic sensitizers -- no decomposition but interconversion. However, in both studies it was necessary to modify Rabinovitch's mechanism. Both added another excited state of ethylene which decomposes. But, they chose different ways in which to insert the new excited state into the mechanism. Thus, the definitive mechanism for the photosensitization of ethylene remains uncertain.

In the direct photolysis of ethylene at 1470 Å., Sauer and Dorfman[95] found that there were two primary processes producing acetylene. They are of about equal probability.

$$C_2H_4^* \longrightarrow C_2H_2 + H_2$$

$$C_2H_4^{**} \longrightarrow C_2H_2 + 2\,H$$

Failure to find butadiene or isotopically mixed ethylene from an ethylene - ethylene-d_4 mixture led to the conclusion that the formation of vinyl radicals is not a significant reaction. Hydrogen atoms produced in the second decomposition add onto the starting material and were observed as ethane and butane.

Okabe and McNesby[74] photolyzed ethylene at 1236, 1470 and 1849 Å. No vinyl radicals were observed at 1236 Å. Both molecular and atomic elimination of hydrogen were ob-

served in the production of acetylene. Atomic elimination was more prevalent at lower wavelengths. Working with 1,1- and trans-dideuterioethylene, they found that the distribution of isotopic hydrogen molecules was significantly different in the two isomers. This indicates that the scrambling which occurs in the mercury photosensitized decomposition does not occur in the direct photolysis of ethylene. For both isomers, the isotopic distribution of molecular hydrogen was found to be wavelength independent.

Obi, Ogata and Tanaka[73] compared the relative yields of molecular elimination and atomic elimination of hydrogen from ethylene at various wavelengths. They reported the following results:

	H(eV)	1236	1470	1634	1849
$C_2H_4^* \longrightarrow C_2H_2 + H_2$	1.8	30	46	54	60
$C_2H_4^{**} \longrightarrow C_2H_2 + 2\,H$	6.3	70	54	46	40

This shows that atomic elimination, the process requiring more energy, becomes predominant with increasing energy of light.

Potzinger, Glascow and von Bünau[79] photolyzed ethylene at 147, 163, 185 and 193 nm. They found vinyl radicals at 185 nm. This was deduced by the appearance of 1-butene, formed by the recombination of vinyl and ethyl radicals. The production of vinyl radicals decreases in importance as the energy of light is increased. They found that the

quantum yield of acetylene formed by molecular elimination is independent of the wavelength of light used. The quantum yield of acetylene formed by atomic elimination increases with decreasing wavelength. At least three excited states were needed to explain the results.

Ausloos and Gorden[5] also studied the γ radiolysis of of deuterated ethylenes. In the gas phase, virtually all hydrogen formed was by molecular elimination. The ratio of isotopic hydrogens was different for 1,1- and 1,2-dideuterioethylene. Therefore, decomposition does not occur from a scrambled excited state. Both 1,1- and 1,2-elimination of hydrogen molecules occurs.

Photolytic Reactions of Halogenated Ethylenes

Some work has been performed on some of the haloethylenes. Of these substituted ethylenes, the fluoro derivatives are the ones which have received the most attention. Each fluoroethylene has been the subject of at least one study.

In a sense, fluorine is the atypical halogen. It forms the strongest carbon - halogen bond. So strong is this bond that it is not cleaved by near ultraviolet light, neither in photolysis nor in photosensitization experiments. Some of the reactions observed in the fluoroethylenes are observed in no other haloethylenes. The fluorine atom does not quench excited mercury atoms. This makes the fluoroethylenes good compounds in which to study photosensitiza-

tion reactions at double bonds.

Trobridge and Jennings[114] investigated the mercury photosensitized decomposition of vinyl fluoride. The only reaction observed was the molecular elimination of hydrogen fluoride, forming acetylene. They found that their data was best suited by predicting two excited states, both susceptible to deactivation, but only the lower one decomposing. This is very similar to the mechanism proposed by Callear and Cvetanović[20] for the photosensitization of ethylene.

Strausz, et al.,[110] reinvestigated this reaction. They considered their data, as well as that of Trobridge and Jennings, to be "too scattered for precise mechanistic conclusions."

Strausz and coworkers[110] then went on to investigate the mercury photosensitized decomposition of the three isomers of difluoroethylene. All three produced monofluoroethylene, and the 1,2-difluoroethylenes, their geometric isomer. The quantum yield of fluoroacetylene at a given pressure was identical for all three isomers of difluoroethylene. For the cis- and trans- isomers, the quantum yield of isomerization was identical.

Their kinetic data was applied to a one excited state mechanism (similar to Leroy and Steacie's[59] for ethylene) and a two excited states mechanism (similar to Callear and Cvetanović's[20] for ethylene and Trobridge and Jennings's[114]

for vinyl fluoride). They found that both mechanisms obey linear relations and therefore were unable to determine which one is correct.

In the photosensitized decomposition of trifluoroethylene, Strausz, Norstrom and Gunning[109] found that difluoroacetylene is produced by the 1,1-elimination of hydrogen fluoride, followed by the relatively slow rearrangement of the resulting difluorovinylidene.

$$CF_2{=}CHF \longrightarrow CF_2{=}C: + HF$$

$$CF_2{=}C: \longrightarrow CF{\equiv}CF$$

The mercury photosensitized decomposition of tetrafluoroethylene was studied by Atkinson.[4] The only product observed other than polymer was hexafluorocyclopropane. He concluded that this was formed via a difluorocarbene intermediate. This results was confirmed by Heicklen, Knight and Greene.[44]

In the photolysis of vinyl iodide, Sherwood[102] found That both molecular detachment of hydrogen iodide and iodine cleavage occurred.

$$C_2H_3I + h\nu \longrightarrow C_2H_3I^*$$

$$C_2H_3I^* \longrightarrow C_2H_2 + HI$$

$$C_2H_3I^* \longrightarrow C_2H_3 + I$$

The molecular detachment reaction was included because nitric oxide, a free radical scavenger, completely suppressed the production of ethylene and butadiene, while only reducing production of acetylene.

These findings were reinforced by those of Yamashita, Noguchi and Hayakawa,[131] who used a high intensity light source to increase radical - radical reactions. Again, nitric oxide suppressed free radical products but not acetylene.

Bellas, et al.,[12] studied the mercury photosensitized reactions of vinyl chloride. They found two sites for the transfer of energy to vinyl chloride: the double bond and the chlorine atom. In the mechanism proposed,

$$Hg\ (^3P_1) + C_2H_3Cl \longrightarrow C_2H_3 + Cl + Hg \quad (0.49)$$

$$\longrightarrow C_2H_3 + HgCl \quad (0.06)$$

$$\longrightarrow C_2H_3Cl^* + Hg \quad (0.45)$$

$$C_2H_3Cl^* \longrightarrow C_2H_2 + HCl \quad (0.17)$$

$$\longrightarrow C_2H_3Cl + h\nu \quad (0.28)$$

$$C_2H_3Cl^* + M \longrightarrow C_2H_3Cl + M$$

where the numbers in parentheses give quantum yields at zero pressure, the first two reactions are attributed to quenching at the chlorine atom, while the third reaction is attributed to quenching at the double bond. Good agree-

ment was found between this attribution and the relative collisional cross-sections, σ^2. Because acetylene formation was unaffected by nitric oxide, its production was assigned entirely to the decomposition of excited vinyl chloride molecules.

In a study of the direct photolysis of vinyl chloride, Fujimoto, Rennert and Wijnen[34] found that the excited vinyl chloride molecules had two means of decomposition.

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

$$\longrightarrow C_2H_3 + Cl$$

$$C_2H_3Cl^* + M \longrightarrow C_2H_3Cl + M$$

When vinyl radicals were prevented from reacting further, by the presence of scavengers, the ratio of acetylene to vinyl product was found to be 1 : 1.4. This value was found to be independent of temperature and pressure. Thus, both reaction products come from the same excited state.

The appearance of acetylene accompanied by atomic elimination has been observed in the far ultraviolet photolysis of vinyl chloride.[6]

$$C_2H_3Cl^* \longrightarrow C_2H_2 + H + Cl$$

The quantum yield of vinyl radicals was found to decrease with decreasing wavelength.

Reactions of the Dichloroethylenes

For 1,2-dichloroethylene, the thermal decomposition of either the cis or the trans isomer[39,69] produces hydrogen chloride and acetylene. Chlorine atoms also are produced which, unless inhibited, will lead to a chain reaction dehydrochlorination.

Futrell and Newton[36] irradiated liquid samples of both cis- and trans-dichloroethylene with α, β and γ rays. The major products were acetylene, chloroacetylene and dichloroacetylene. The following mechanism was proposed:

$$CHCl{=}CHCl + \text{radiation} \longrightarrow CHCl{=}CH^{*} + Cl$$

$$\longrightarrow CCl{\equiv}CH + HCl$$

$$\longrightarrow CCl{\equiv}CCl + H_2$$

$$\longrightarrow CHCl{=}CCl + H$$

$$CHCl{=}CH^{*} \longrightarrow CH{\equiv}CH + Cl$$

Wijnen[130] found that the major products in the near ultraviolet photolysis of cis-dichloroethylene were acetylene, chloroacetylene and trans-dichloroethylene. The following mechanism was proposed:

$$\text{cis-}C_2H_2Cl_2 + h\nu \longrightarrow C_2H_2 + 2\,Cl$$

$$\longrightarrow C_2HCl + HCl$$

$$Cl + \text{cis-}C_2H_2Cl_2 \longrightarrow C_2H_2Cl_3^{*}$$

$$C_2H_2Cl_3^* \longrightarrow \underline{cis}\text{-}C_2H_2Cl_2 + Cl$$

$$\longrightarrow \underline{trans}\text{-}C_2H_2Cl_2 + Cl$$

The ratio of acetylene to chloroacetylene was found to be wavelength dependent.

Berry and Pimentel[13] investigated the HCl laser emission caused by the photolysis of the three isomers of dichloroethylene with light in the 2100 - 1700 Å. region. They found that the hydrogen chloride vibrational spectra differed significantly among the three isomers. From 1,1-dichloroethylene, only α,β elimination is possible. For the 1,2-dichloroethylenes, the authors found that it is probable that both α,α and α,β eliminations occur.

From this short review, it is clear that the photolysis of the dichloroethylenes has not received much attention. For this reason, the present study was undertaken.

RESULTS AND INTERPRETATION

The reaction products observed in the photolysis of symmetric dichloroethylenes, either the cis or the trans isomer, are acetylene, chloroacetylene and the chlorovinyl radical. This radical was observed, where iodine was used as a scavenger, as cis- and trans-1-chloro-2-iodoethylene or, where hydrogen chloride was the scavenger, as vinyl chloride. Also observed was the geometric isomer of the starting material, viz. trans-dichloroethylene from cis-dichloroethylene, and vice versa. In some instances, the formation of the 1,1,2-trichloroethyl radical was apparent, as inferred by the isolation of 1,1,2-trichloro-2-iodoethane or 1,1,2-trichloroethane.

Many experiments were carried out to obtain information regarding the mode of formation of these products. All experimental results are tabulated in Appendix I, Tables XIV - XXIII. A systematic study was attempted which tried to minimize the number of varying factors which could influence the formation of products.

For example, Table XIV gives the results of a series of experiments in which information was obtained regarding the effect of various initial pressures of cis-dichloroethylene upon the product formation. The data in Table XIV

were obtained using the full arc of the light source. The light transmitted by this arc starts at about 2000 Å. and is continuous into the visible range. Because dichloroethylene does not absorb above 3850 Å., the effective light used in these experiments listed in Table XIV cover the range 2000 - 3850 Å. In Table XV are experiments in which part of the high energy light was eliminated by insertion of filter 9-54 between the cell and the light source, thus narrowing the effective light to the range 2200 - 3850 Å. Table XVI gives the results obtained at various starting pressures of cis-dichloroethylene using filters 9-53, 0-54 and 0-52 with effective ranges of 2600 - 3850 Å., 3000 - 3850 Å. and 3400 - 3850 Å., respectively.

In almost all the experiments a free radical scavenger was used. Its purpose was to reduce the number of secondary and higher order products. As was mentioned previously, the chlorovinyl radical is a major product of the photolysis. In the absence of a scavenger, the free radical, being unstable, would have to react further. There are a number of reaction paths open to it: abstraction, decomposition, disproportionation, recombination and addition to a multiple bond. The multiplicity of these reactions and their products would make it difficult to trace the production of the radicals. Even worse, some of the products of these radical reactions would be the same as those produced by the initial decomposition of the excited dichloroethylene, e.g. chloroacetylene. In analysis of the

products, it would be impossible to determine what proportion of the product came via which pathway.

However, a free radical preferentially will react with a scavenger. The scavenger is chosen to ensure that the product of this reaction will be unique to the reaction system. Thus, the free radical easily can be observed and its concentration measured.

Time Studies

Before trying to explain the data, one first must ascertain that, in the time spans involved, the rates of production are linear. Beyond the region of linearity with time, complications may interfere with the proper interpretation of the results. Secondary reactions may occur which will reduce the concentrations of some of the products and may increase the concentration of others.

The time study for cis-1,2-dichloroethylene was conducted using an initial pressure of 30 torr of dichloroethylene which had been saturated with iodine. Experiments were performed for 5, 10 and 15 minutes. As is seen in Figure 3, the results were linear throughout the range tested; the rates of production were constant.

A time of five minutes was chosen as the exposure time for further experimentation. This time lies well within the region of linearity. Also, the amounts of products formed during this time could be analyzed without much difficulty. For experiments performed using filters,

Figure 3. Time Study for the Photolysis of cis-$C_2H_2Cl_2$

A) Acetylene and Chloroacetylene

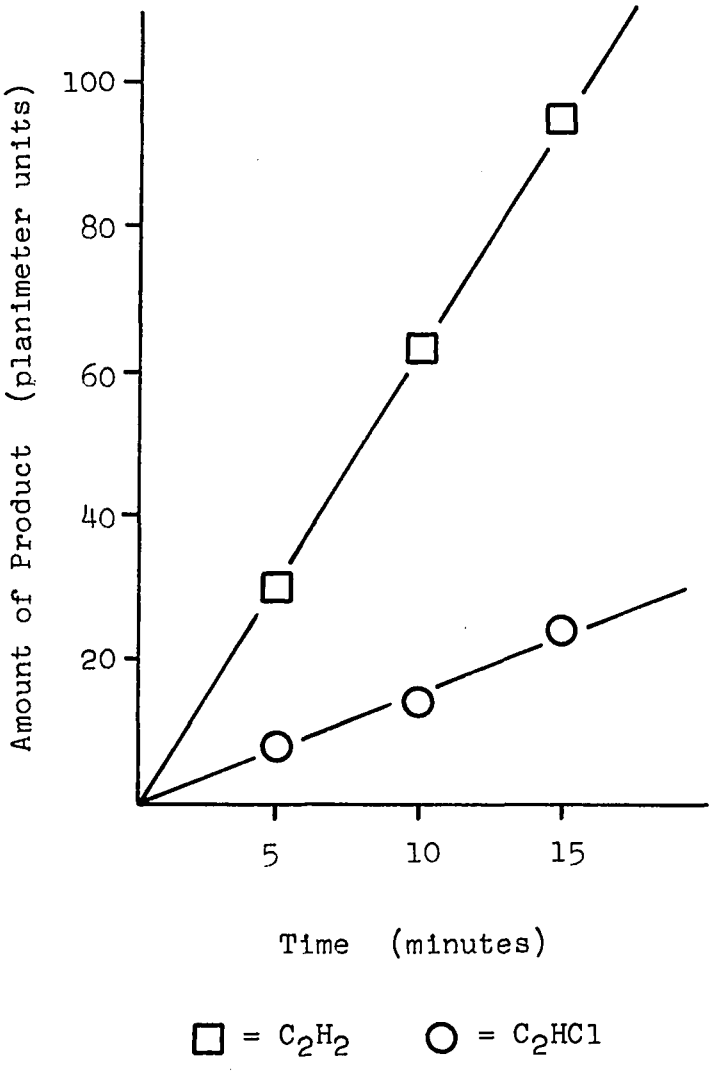


Figure 3. Time Study for the Photolysis of cis-$C_2H_2Cl_2$

B) trans- and cis-1-Chloro-2-iodoethylene

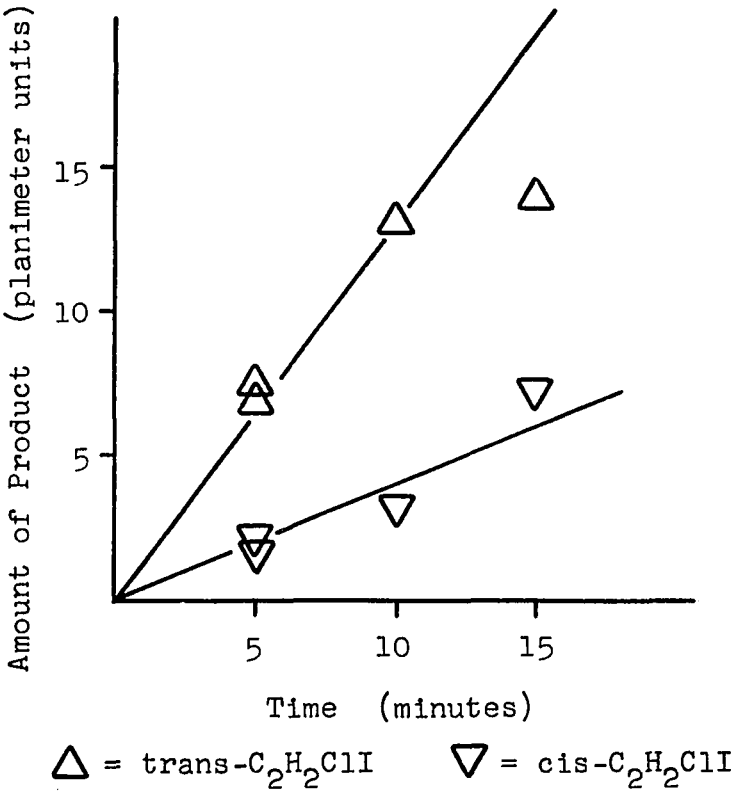
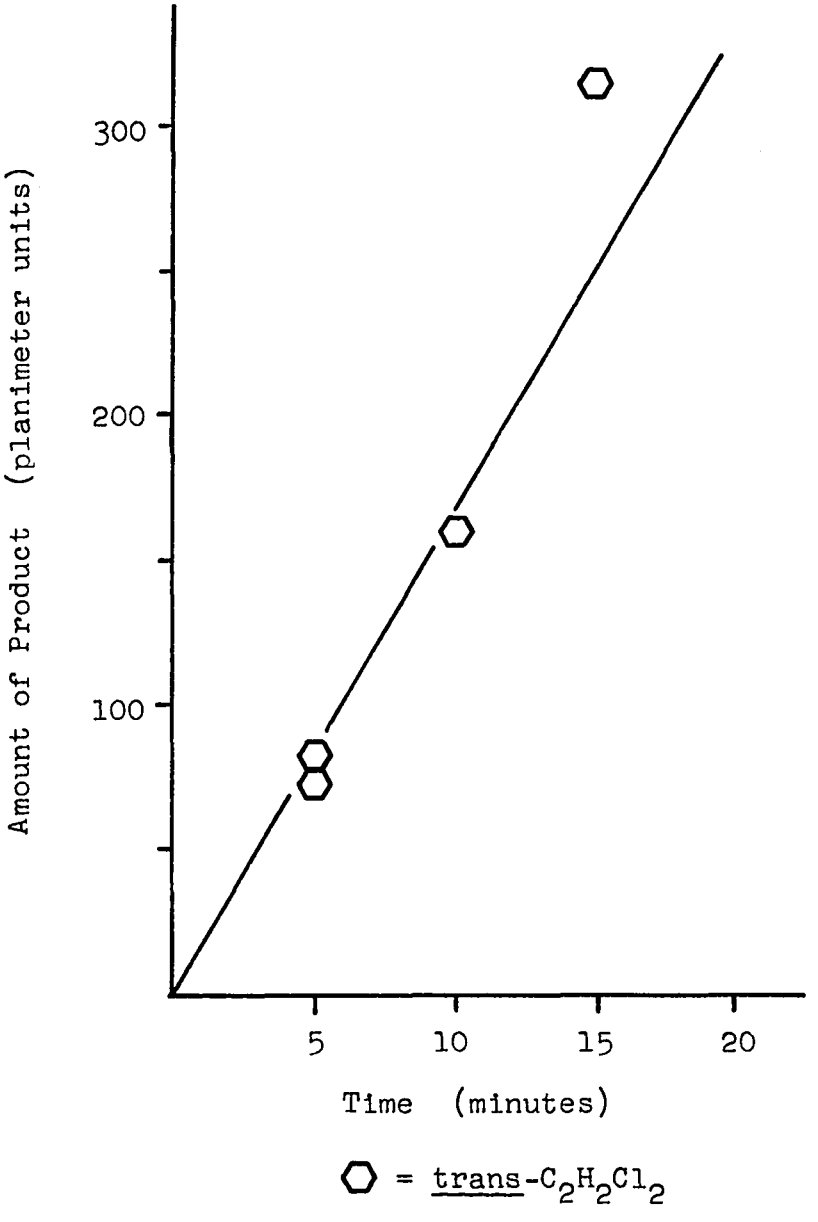


Figure 3. Time Study for the Photolysis of <u>cis</u>-$C_2H_2Cl_2$

C) Isomerization: Production of <u>trans</u>-$C_2H_2Cl_2$



an exposure time was chosen which gave a decomposition comparable to a five minute exposure of unfiltered light.

The time study for trans-1,2-dichloroethylene was also conducted at a pressure of 30 torr. In this study, too, iodine was used as a scavenger. The results are shown in Figure 4. There is considerable scattering for the isomerization reaction. But, it can be seen that for all the products the rates of production are constant throughout the range investigated, up to 17 minutes. The exposure time chosen for further experimentation was ten minutes.

Of particular interest is the fact that the ratio of trans-1-chloro-2-iodoethylene to cis-1-chloro-2-iodoethylene is about 4 : 1, regardless of which isomer of dichloroethylene is photolyzed. This means that the chlorovinyl radicals produced from cis-dichloroethylene are indistinguishable from the chlorovinyl radicals produced from trans-dichloroethylene.

Energetic Considerations Regarding the Decomposition of 1,2-Dichloroethylene

As was mentioned previously, the photolysis of dichloroethylene in the presence of iodine yields acetylene, chloroacetylene and the chlorovinyl radical, which is scavenged by iodine to give cis- and trans-1-chloro-2-iodoethylene.

In the production of acetylene, two chlorine atoms are lost by the dichloroethylene molecule. Either they de-

Figure 4. Time Study for the Photolysis of <u>trans</u>-$C_2H_2Cl_2$

A) Acetylene and Chloroacetylene

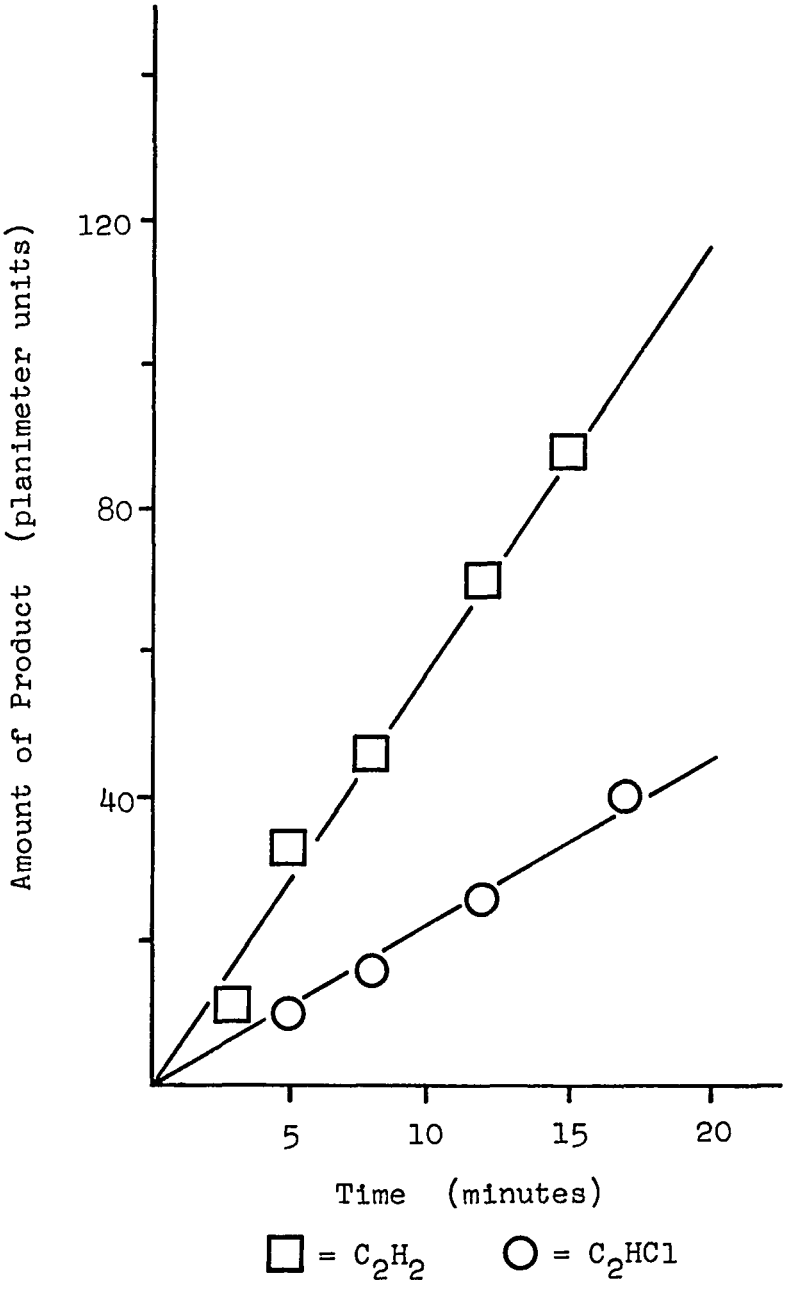


Figure 4. Time Study for the Photolysis of <u>trans</u>-$C_2H_2Cl_2$

B) <u>trans</u>- and <u>cis</u>-1-Chloro-2-iodoethylene

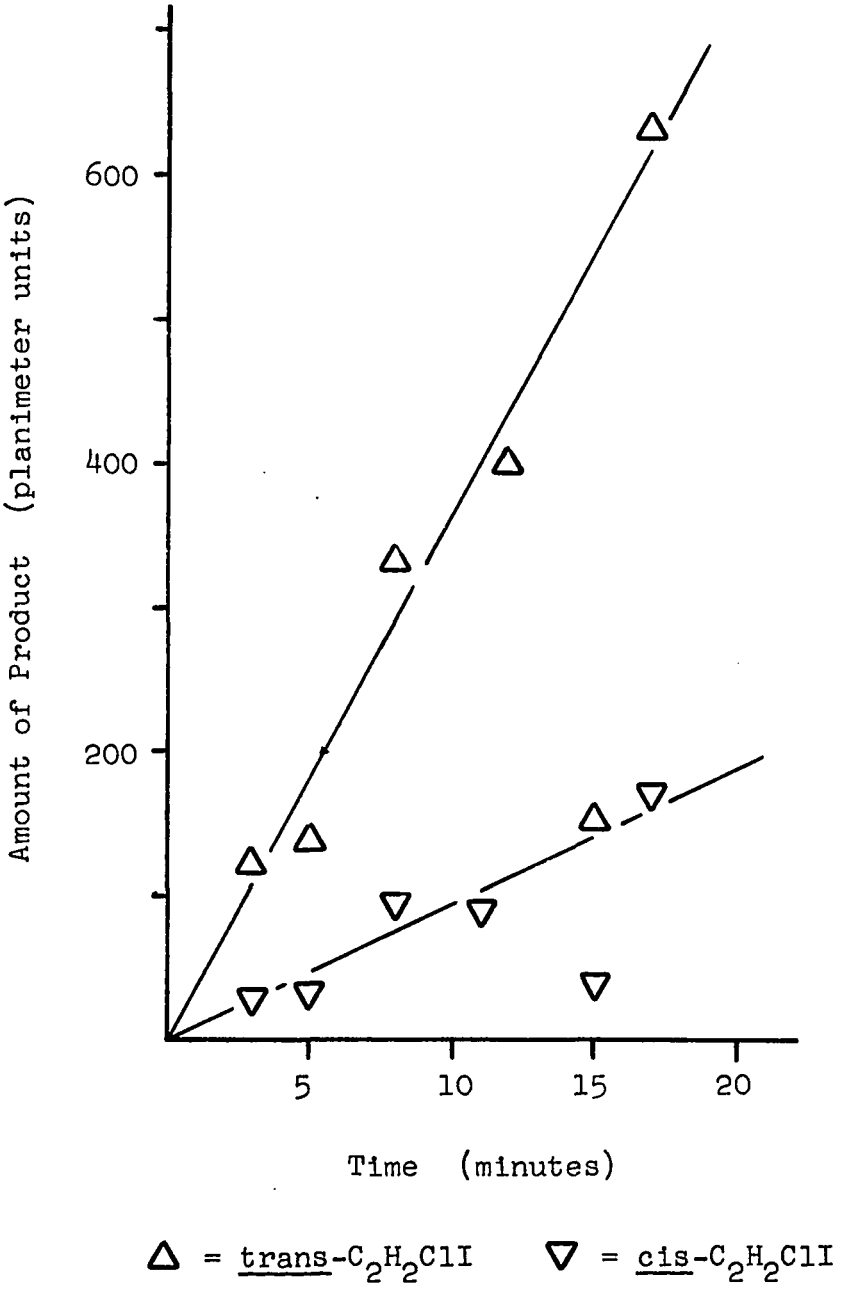
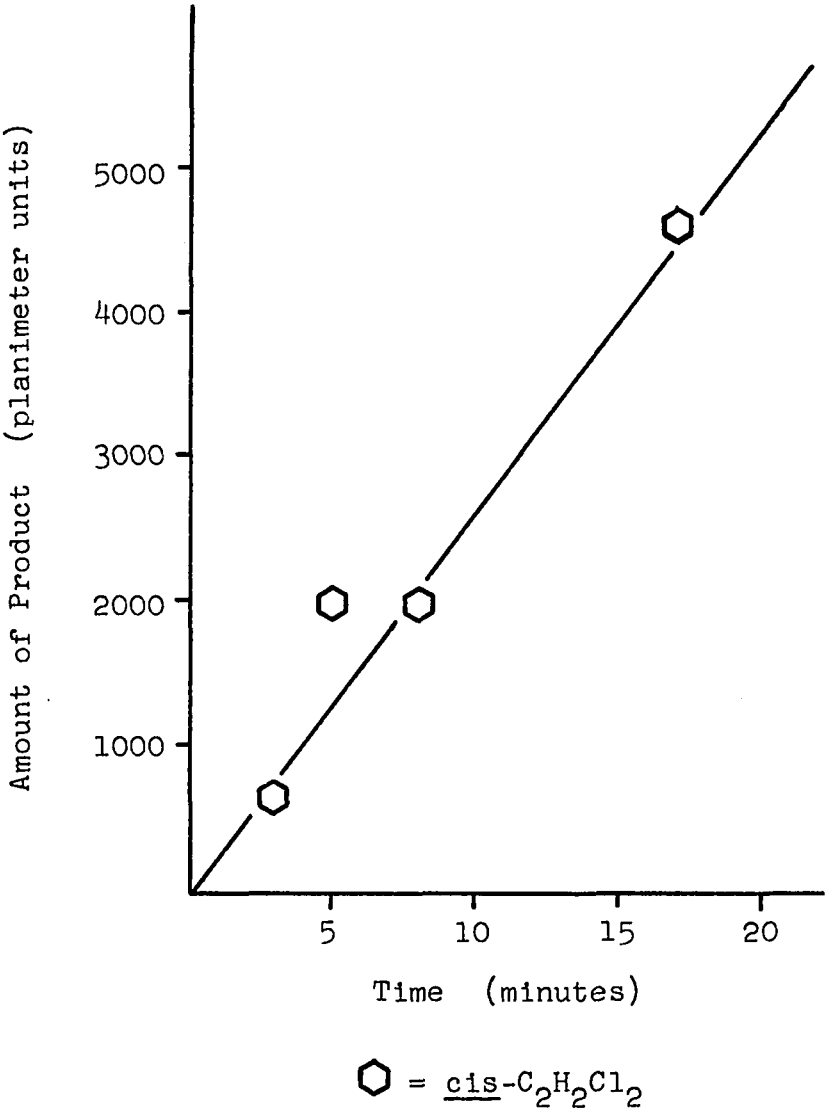


Figure 4. Time Study for the Photolysis of <u>trans</u>-$C_2H_2Cl_2$

C) Isomerization: Production of <u>cis</u>-$C_2H_2Cl_2$



part in unison or individually. If the chlorines are lost in unison, they can leave either as a chlorine molecule or as two chlorine atoms.

The possible reactions which may produce acetylene are:

$$cis\text{-}C_2H_2Cl_2 + h\nu \longrightarrow C_2H_2Cl_2^* \qquad (1)$$

$$C_2H_2Cl_2^* \longrightarrow C_2H_2 + Cl_2 \qquad (2)$$

$$C_2H_2Cl_2^* \longrightarrow C_2H_2 + 2\,Cl \qquad (3)$$

$$C_2H_2Cl_2^* \longrightarrow C_2H_2Cl^{\circ} + Cl \qquad (4a)$$

$$C_2H_2Cl^{\circ} \longrightarrow C_2H_2 + Cl \qquad (4b)$$

Analysis of the energetic requirements for the individual reactions from bond energies will give information regarding the possibility of a reaction's occurring. In Table I, bond energies in kilocalories per mole are given which are of interest to this discussion.

TABLE I

Some Relevant Bond Energies[93] (in kcal./mole)

Cl-Cl	58.0	H-I	71.4	C-C	82.6
I-I	36.1	C-H	98.7	C=C	145.8
H-H	104.2	C-Cl	81.	C≡C	199.6
H-Cl	103.2	C-I	51.		

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

The changes in bonds between the reactant and the products are:

Energy Loss		Energy Gain (Reaction 2)		Energy Gain (Reactions 3 & 4)	
C=C	145.8	C≡C	199.6	C≡C	199.6
C-Cl	81.	Cl-Cl	58.0		
C-Cl	81.				
	307.8		257.6		199.6

Thus, Reaction 2 requires a minimum input of 50 kcal./mole, while Reactions 3 and 4 need a minimum of 108 kcal./mole.

To translate these energy values into wavelengths of light, one uses the equation of quantum chemistry: $E = h\nu$. This can be rearranged into the form:

$$E\lambda = 2.86 \times 10^5$$

where the energy is in kilocalories per mole and the wavelength is in Ångstroms. Applying this equation gives the wavelength of light with the minimum energy which possibly could cause the reaction to occur. It does not mean that that particular wavelength light will cause the reaction to occur; just that it may.

The wavelength calculated for Reaction 2 is 5720 Å.; that for Reactions 3 and 4 is 2650 Å. The experimental data from photolyses with filters 0-54 and 0-52 (see Table XVI) clearly indicate that acetylene is produced at wavelengths longer than 2650 Å. Thus, the first important conclusion is that under these conditions acetylene is pro-

duced exclusively by Reaction 2. At shorter wavelengths, acetylene may be produced by Reactions 2 and/or Reactions 3 and 4.

The production of chlorovinyl radicals, as indicated by Reaction 4a, requires a minimum of 81 kcal./mole, the energy necessary to break the carbon - chlorine bond. This energy corresponds to 3530 Å. Thus, Reaction 4a is a process which could be observed under all conditions of these experiments. It is not surprising that this is the case.

Chloroacetylene can be produced in a similar manner. At this point, no consideration shall be made as to whether the excited state of dichloroethylene from which chloroacetylene comes is the same as that producing acetylene, or even whether the various processes, if they do occur, come from the same excite state. The asterisk is used merely to denote a state with sufficient excess energy to cause a reaction. The possible mechanisms are:

$$C_2H_2Cl_2^* \longrightarrow C_2HCl + HCl \qquad (5)$$

$$C_2H_2Cl_2^* \longrightarrow C_2HCl + H + Cl \qquad (6)$$

$$C_2H_2Cl_2^* \longrightarrow C_2H_2Cl^{\circ} + Cl \qquad (7a)$$

$$C_2H_2Cl^{\circ} \longrightarrow C_2HCl + H \qquad (7b)$$

The following reaction has been omitted as a possibility

$$C_2H_2Cl_2^* \longrightarrow C_2HCl_2^{\circ} + H$$

because in direct photolysis experiments, the rupture of a carbon - hydrogen bond has never been reported in the wavelength region of this investigation.

Energy calculations yield the following information:

Energy Loss		Energy Gain (Reaction 5)		Energy Gain (Reactions 6 & 7)	
C=C	145.8	C≡C	199.6	C≡C	199.6
C-H	98.7	H-Cl	103.2		
C-Cl	81.				
	325.5		302.8		199.6

Reaction 5 requires 23 kcal./mole, a wavelength of 12,400 Å., well into the infrared region. Reactions 6 and 7 require 126 kcal./mole, or a wavelength cutoff of 2270 Å. Thus, the second conclusion is that chloroacetylene produced at wavelengths greater than 2270 Å. is formed exclusively by HCl elimination, as indicated by Reaction 5.

The chlorovinyl radical is produced by the cleavage of a carbon - chlorine bond:

$$C_2H_2Cl_2^* \longrightarrow C_2H_2Cl + Cl \qquad (8a)$$

The chlorovinyl radical produced may be either a thermal radical or an excited radical, the energy exciting the radical being a carry-over of the excess energy from the primary process. As has been mentioned previously, this reaction, requiring 81 kcal./mole or 3530 Å., has been observed at all wavelengths of this investigation.

Iodine was the most frequently used scavenger. Its

TABLE II

Possible Reactions and their Wavelength Thresholds

$\underline{C_2H_2}$

(2) $C_2H_2Cl_2^* \longrightarrow C_2H_2 + Cl_2$ 5720 Å.

(3) $C_2H_2Cl_2^* \longrightarrow C_2H_2 + 2\,Cl$ 2650 Å.

(4) $C_2H_2Cl_2^* \longrightarrow C_2H_2Cl^\circ + Cl \longrightarrow C_2H_2 + 2\,Cl$ 2650 Å.

$\underline{C_2HCl}$

(5) $C_2H_2Cl_2^* \longrightarrow C_2HCl + HCl$ 12400 Å.

(6) $C_2H_2Cl_2^* \longrightarrow C_2HCl + H + Cl$ 2270 Å.

(7) $C_2H_2Cl_2^* \longrightarrow C_2H_2Cl^\circ + Cl \longrightarrow C_2HCl + H + Cl$ 2270 Å.

$\underline{C_2H_2Cl}$

(8) $C_2H_2Cl_2^* \longrightarrow C_2H_2Cl + Cl$ 3530 Å.

reaction with the chlorovinyl radical

$C_2H_2Cl + I_2 \longrightarrow 4/5\ \underline{tr}\text{-}C_2H_2ClI + 1/5\ \underline{cis}\text{-}C_2H_2ClI + I$ (8b)

is exothermic by 15 kcal./mole and requires no carry-over of energy from the initial excitation.

Table II gives a summary of all possible reactions

and the minimum amount of energy (expressed in Ångstroms) required for each reaction. All the processes listed in Table II are possible when the reaction cell is exposed to the full spectrum of the medium pressure mercury lamp. However, if the spectrum is restricted by use of filters, some of these reactions become energetically impossible. Thus, with filter 0-54, which passes light less energetic than 3000 Å., the production of acetylene and chloroacetylene is restricted to one mechanism each. Filter 9-53 still restricts the production of chloroacetylene to one mechanism, although it is just possible that Reactions 3 and 4 may produce acetylene.

The number of reaction products and possible reactions clearly indicates that the reaction mechanism is by no means simple. In order to facilitate its presentation, the primary processes of each dichloroethylene will be analyzed in individual sections. This will be followed by a separate chapter on the cis - trans isomerization of the 1,2-dichloroethylenes.

Primary Processes in the Decomposition of cis-1,2-Dichloroethylene

Comparison of Product Rates as a Function of Pressure

Having discussed the various modes by which acetylene, chloroacetylene and cis- and trans-1-chloro-2-iodoethylene may be produced, it is revealing to compare the

product yields against each other as a function of pressure and of excitation energy. From the data in Tables XIV - XVI, graphs were drawn of the change in rates of production with pressure, Figures 5 - 7. The data from experiments with filters 0-54, 9-53 and 0-52 all fell on the same lines. They therefore were plotted together. From points on these graphs the ratios $R_{C_2H_2}/R_{C_2HCl}$, $R_{C_2H_2}/R_{C_2H_2ClI}$ and $R_{C_2HCl}/R_{C_2H_2ClI}$ were calculated, where $R_{C_2H_2ClI}$ is the sum of $R_{\underline{cis}\text{-}C_2H_2ClI}$ and $R_{\underline{trans}\text{-}C_2H_2ClI}$. At pressures of less than 10 torr, the ratios were taken directly from experimental results because in this region the graphs have the greatest uncertainty. Because relatively small yields of chloroiodoethylene were produced with the more restrictive filters, it was not possible to obtain accurate data for the rates of production of <u>cis</u>- and <u>trans</u>-chloroiodoethylene. Therefore, the only ratio calculated for these filters is $R_{C_2H_2}/R_{C_2HCl}$. These ratios are given in Table III, page 49.

If two products arise directly and solely from the same excited state, the ratio of their rates of production is constant. If the excited state is deactivated, then both rates of production should be reduced to the same extent, leaving the ratio of their rates of production unchanged. If the ratio is not constant, then more than one excited state is involved in the production of the two compounds.

Figure 5. Change in Rates of Primary Production with Pressure of cis-$C_2H_2Cl_2$: Filters 9-53, 0-54 and 0-52

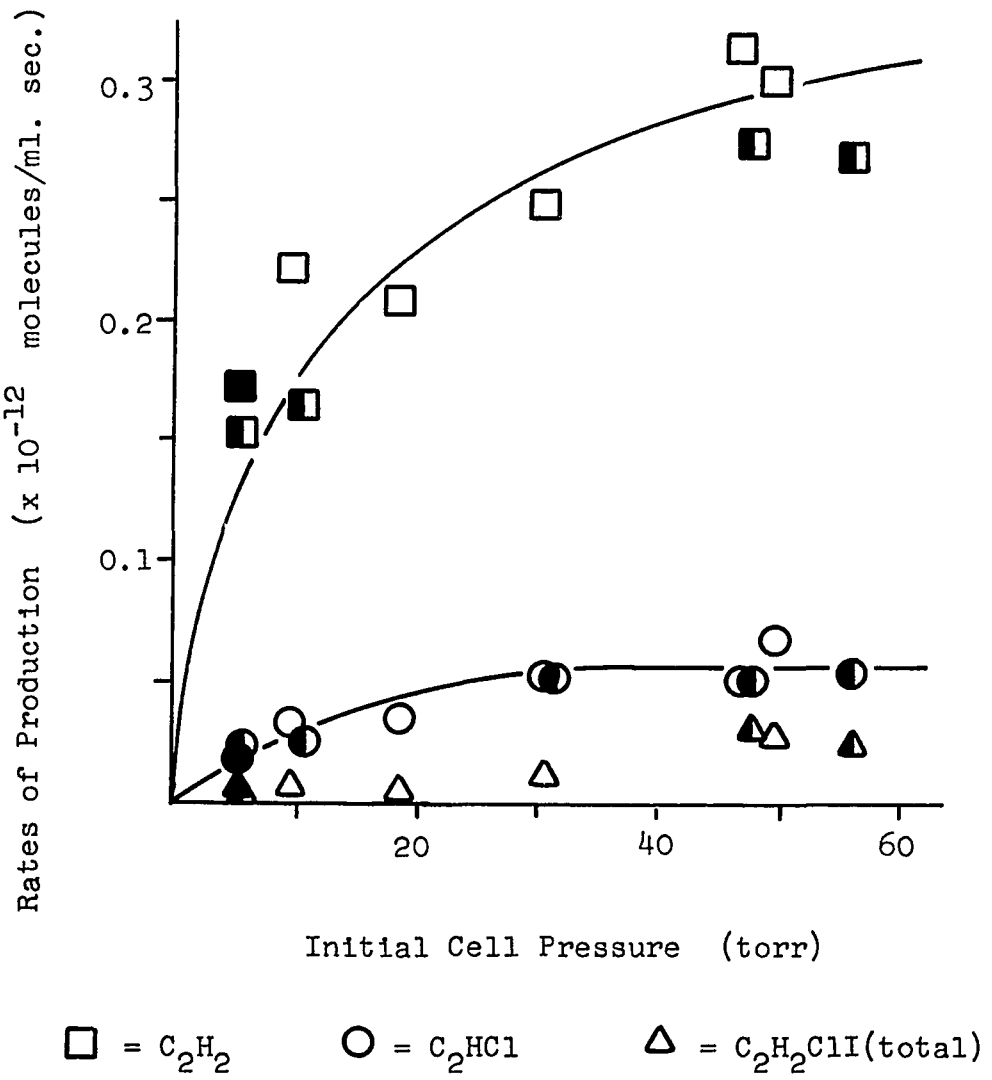


Figure 6. Change in Rates of Primary Production with Pressure of cis-$C_2H_2Cl_2$: Filter 9-54

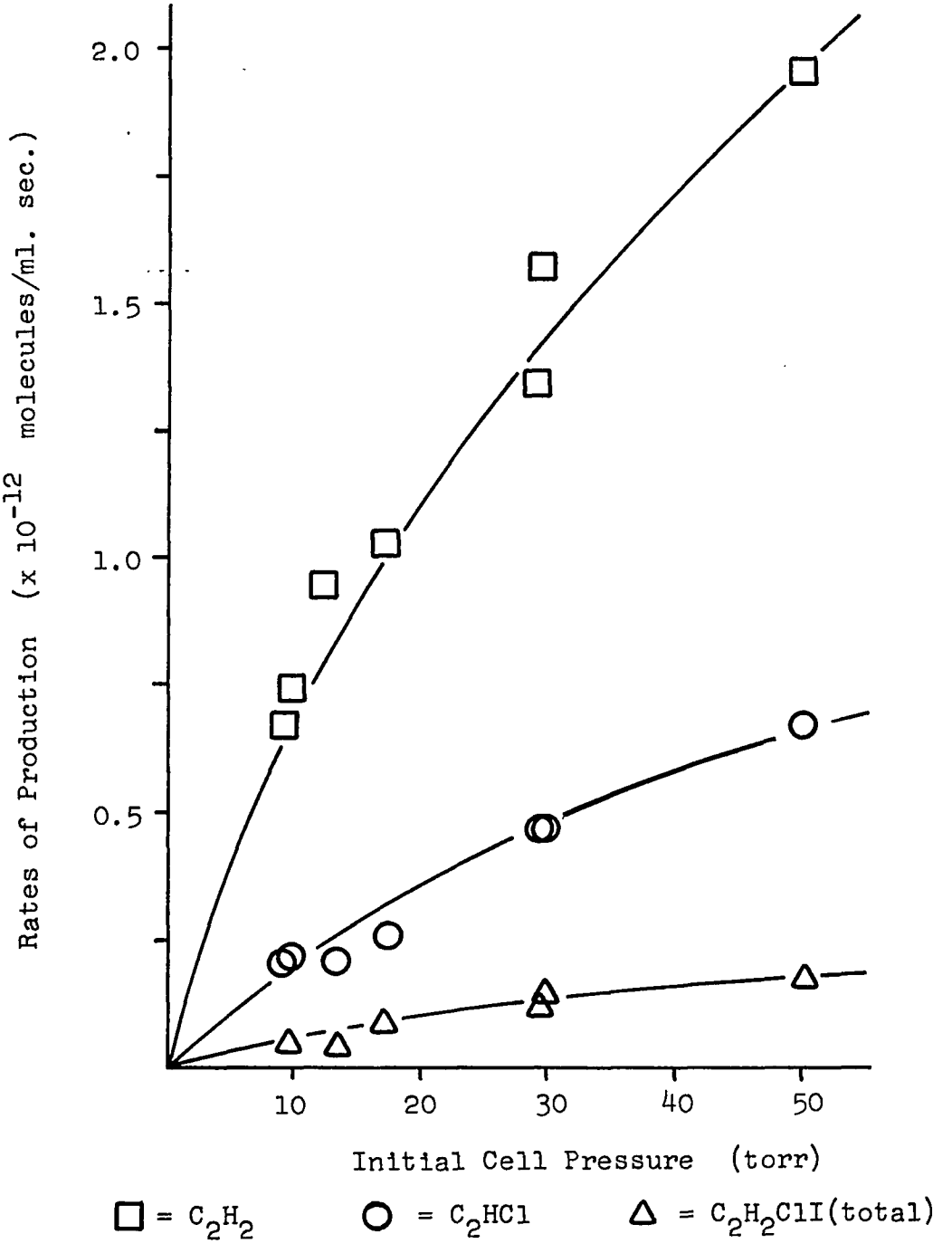


Figure 7. Change in Rates of Primary Production with Pressure of cis-$C_2H_2Cl_2$: No Filter

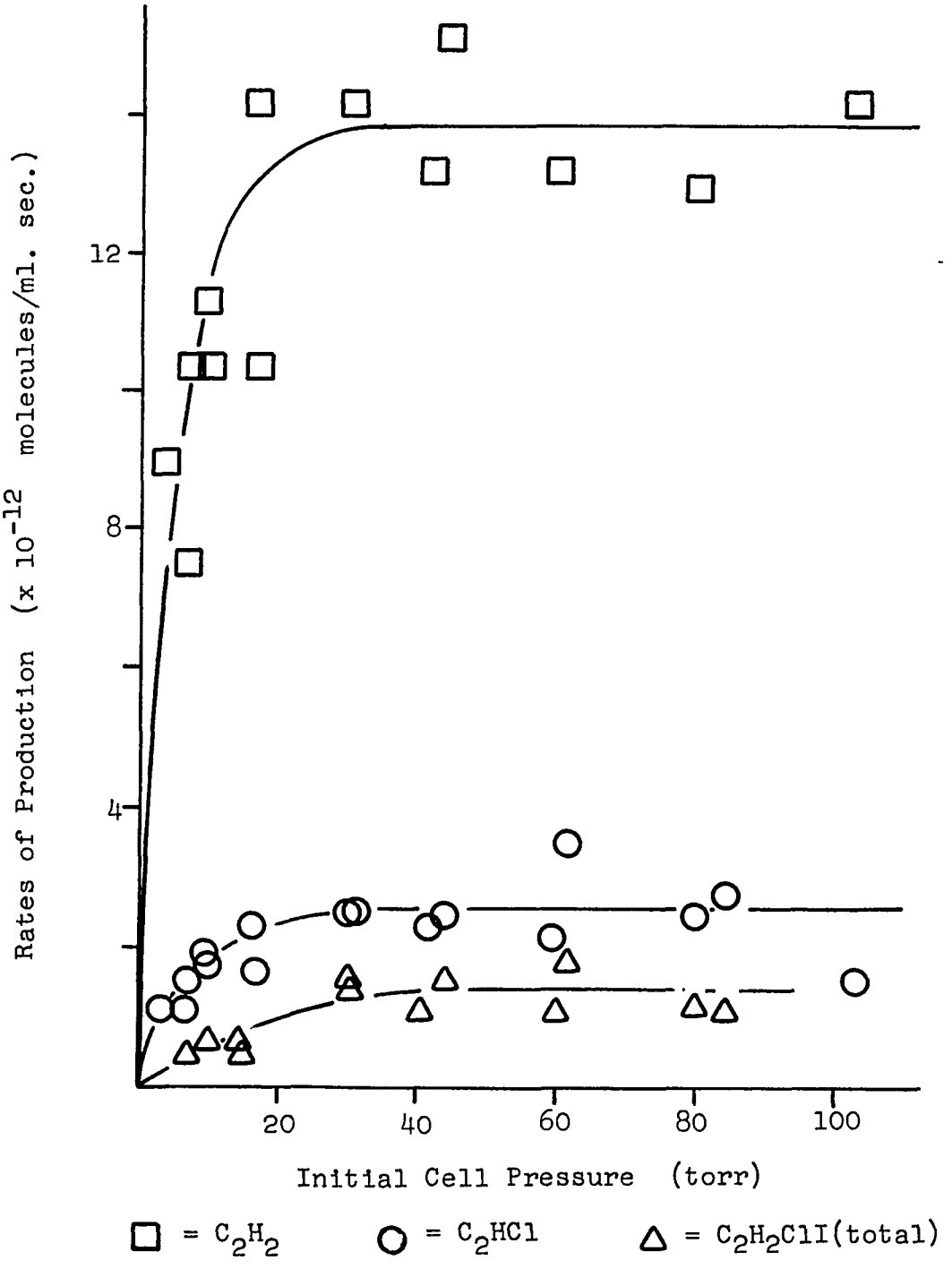


TABLE III

Comparison of Rates of Primary Production in the Photolysis of cis-1,2-Dichloroethylene

Filter Used	Wavelength Range (Å.)	Exposure Time	Pressures in Torrs 3.7	6.7	10*	20*	40*
A)			$R_{C_2H_2}/R_{C_2HCl}$				
none	2000-3850	5 min.	8.2	6.8**	6.1	5.7	5.6
9-54	2200-3850	1 hr.	-	-	3.3	3.0	3.0
9-53	2600-3850	3 hr.	-	-	5.7	5.0	5.3
0-54	3000-3850	10 hr.					
0-52	3400-3850	10 hr.					
B)			$R_{C_2H_2}/R_{C_2H_2ClI}$				
none	2000-3850	5 min.	-	21.3	14.1	11.4	9.9
9-54	2200-3850	1 hr.	-	-	11.7	10.9	10.5
C)			$R_{C_2HCl}/R_{C_2H_2ClI}$				
none	2000-3850	5 min.	-	3.1	2.3	2.0	1.8
9-54	2200-3850	1 hr.	-	-	3.5	3.7	3.6

*These values are taken from graphs, rather than raw data.

**Average value from two experiments.

That the data from experiments with filters 9-53, 0-54 and 0-52 all fall on the same lines indicates that the reaction mechanism is the same under these conditions. Thus, varying the wavelength of light between 2600 Å. and 3400 Å. does not change the mechanism. Previously, it was

demonstrated that Reactions 3 and 4 cannot occur above 2650 Å. Here, it is shown that neither of these reactions does occur to any appreciable extent at 2600 Å.

The product ratios given in Table III, obtained from experiments with filter 9-54 appear constant within experimental error. This suggests that the three primary products all come from the same excited state. Either that, or there is more than one excited state, but the excited states all have approximately equal lifetimes.

The simpler assumption, that with filter 9-54 all three products come from the same excited state, is the better starting point. Thus, in this wavelength region acetylene and chloroacetylene, as well as the chlorovinyl radical, are produced from the same excited state. When the wavelength range of light is increased by removal of the filter and light with energies as high as 2000 Å. enters the cell, the ratio of acetylene to chloroacetylene production increases. And, in experiments with unfiltered light this ratio becomes pressure dependent, decreasing with increasing pressure.

These changes can be explained by the formation of another excited state, one which produces acetylene but not chloroacetylene. This excited state makes no appreciable contribution to acetylene production at wavelengths greater than 2200 Å. It becomes important only in the 2000 - 2200 Å. range. Obviously, it requires more energy to be formed than the excited state which produces all

three primary products. It seems reasonable to associate this new excited state with a method of production of acetylene which also requires more energy, Reactions 3 and/or 4.

$$C_2H_2Cl_2^{**} \longrightarrow C_2H_2 + 2\,Cl \qquad (3)$$

$$C_2H_2Cl_2^{**} \longrightarrow C_2H_2Cl^{\circ} + Cl \qquad (4a)$$

$$C_2H_2Cl^{\circ} \longrightarrow C_2H_2 + Cl \qquad (4b)$$

The acetylene formed by the less energetic excited state would be formed by molecular elimination, Reaction 2.

$$C_2H_2Cl_2^{*} \longrightarrow C_2H_2 + Cl_2 \qquad (2)$$

In the absence of filters, $R_{C_2H_2}/R_{C_2HCl}$ decreases with increasing pressure. Acetylene production is being reduced relative to chloroacetylene production. A change in this ratio must be due to the acetylene production of the more energetic "two star" excited state. This excited state, therefore, is more readily deactivated than the excited state which produces both acetylene and chloroacetylene, the "one star" excited state. This means that the two star excited state has a longer lifetime. It is more susceptible to collisional deactivation because it takes longer to decompose.

The question remains whether this new excited state decomposes via Reaction 3 or Reaction 4. Were it to decompose via Reaction 4, it might be expected that some of the

excited chlorovinyl radicals would be collisionally deactivated.

$$C_2H_2Cl^{o} + C_2H_2Cl_2 \longrightarrow C_2H_2Cl + C_2H_2Cl_2 \quad (9)$$

The thermal chlorovinyl radicals thus formed would be scavenged, forming more chloroiodoethylene. Of course, if Reaction 4b occurs so rapidly that no deactivation is possible, then Reaction 3 and Reaction 4 will be indistinguishable.

The data in Table III indeed show an increase in the amount of chloroiodoethylene found relative to chloroacetylene in the absence of filters. This is a strong indication that Reactions 4 and 9 do occur. However, it does not exclude the possibility of Reaction 3's also occurring. Reactions 4b and 9 predict that $R_{C_2H_2}/R_{C_2H_2ClI}$ will decrease with increasing pressure. This also is observed.

Having found a satisfactory mechanism for the reactions occurring with filter 9-54 and in the absence of filters, the experiments performed at long wavelengths, with filters 9-53, 0-54 and 0-52, can be considered. All three primary products were observed in these experiments. Inconsistencies in the measurements of $R_{C_2H_2ClI}$, though, made it difficult to obtain accurate data.

However, it does seem that the ratio of acetylene to chloroiodoethylene production is the same as that observed with filter 9-54. This suggests that the elimination of

light of 2600 - 2200 Å. had no effect on the mechanism of production of these two compounds. Yet, in the mechanism hypothesized for filter 9-54 experiments, chloroacetylene is produced by the same excited state; why has its rate of production decreased relative to that of acetylene?

Chloroacetylene is known to be unstable.[55] These long wavelength experiments were also, perforce, low intensity experiments. Long exposure times of up to ten hours were needed to produce samples large enough to analyze. During this time, some of the chloroacetylene could have reacted, leaving the resulting product mixture chloroacetylene deficient. Thus, secondary reactions could account for the change observed in $R_{C_2H_2}/R_{C_2HCl}$.

Summary

One excited state of cis-dichloroethylene produces all three primary products:

$$C_2H_2Cl_2^* \longrightarrow C_2H_2 + Cl_2 \qquad (2)$$

$$C_2H_2Cl_2^* \longrightarrow C_2HCl + HCl \qquad (5)$$

$$C_2H_2Cl_2^* \longrightarrow C_2H_2Cl + Cl \qquad (8a)$$

The chlorovinyl radical produced in Reaction 8a is scavenged to form chloroiodoethylene.

$$C_2H_2Cl + I_2 \longrightarrow C_2H_2ClI + I \qquad (8b)$$

This excited state is formed at wavelengths as long as

3400 Å. But it has its absorption maximum at less than 2600 Å.

A second excited state decomposes to form chlorovinyl radicals which still possess excess energy.

$$C_2H_2Cl_2^{**} \longrightarrow C_2H_2Cl^{\circ} + Cl \qquad (4a)$$

The excited chlorovinyl radical can decompose forming acetylene or be deactivated.

$$C_2H_2Cl^{\circ} \longrightarrow C_2H_2 + Cl \qquad (4b)$$

$$C_2H_2Cl^{\circ} + C_2H_2Cl_2 \longrightarrow C_2H_2Cl + C_2H_2Cl_2 \qquad (9)$$

The thermal chlorovinyl radical will be scavenged, as in Reaction 8b. This excited state becomes increasingly important at wavelengths shorter than 2200 Å.

Quantitative Interpretation of Data

The foregoing discussion has shown that the primary processes in the photolysis of cis-dichloroethylene are by no means simple. Nevertheless, it would be extremely interesting if the data and conclusions could be confirmed by somewhat more quantitative considerations than those carried out heretofore. In order to facilitate this quantitative treatment of the data, they will be subdivided into two parts: data obtained in the presence of filters, and data obtained in the absence of a filter.

Results from Experiments with Filters

It seems reasonable to discuss first the data obtained with light of wavelengths greater than 2200 Å. Previous considerations indicated that in this wavelength region all products originate from the same excited state. Thus, the following, relatively simple mechanism is proposed:

$$\underline{cis}\text{-}C_2H_2Cl_2 + h\nu \longrightarrow C_2H_2Cl_2^* \qquad (1b)$$

$$C_2H_2Cl_2^* \longrightarrow C_2H_2 + Cl_2 \qquad (2)$$

$$C_2H_2Cl_2^* \longrightarrow C_2HCl + HCl \qquad (5)$$

$$C_2H_2Cl_2^* \longrightarrow C_2H_2Cl + Cl \qquad (8a)$$

$$C_2H_2Cl_2^* + M \longrightarrow C_2H_2Cl_2 + M \qquad (10)$$

$$C_2H_2Cl + I_2 \longrightarrow C_2H_2ClI + I \qquad (8b)$$

where M is a deactivating species.

According to this mechanism, the rate of production of chloroacetylene is given by

$$R_{C_2HCl} = k_5 \left[C_2H_2Cl_2^*\right] \qquad I$$

To obtain the concentration of these excited molecules, use is made of the steady state approximation. This states that "the very active intermediates . . . build up in concentration quickly to some constant, relatively low value."[21] For any specific set of conditions, once the excited state reaches its steady state concentration, the

rate of production of the excited species is equal to its rate of disappearance, keeping constant the concentration of the excited molecule.* Thus,

$$d\left[C_2H_2Cl_2^*\right] = -d\left[C_2H_2Cl_2^*\right] \qquad \text{II}$$

The rate of formation of excited one star dichloroethylene molecules is directly proportional to the amount of light absorbed per unit time.

$$d\left[C_2H_2Cl_2^*\right] = \alpha I_{abs}$$

where α is the proportion of light absorbed which leads to the one star excited state, and I_{abs} is the intensity of light absorbed.

The disappearance of the excited species is accounted for in Reactions 2, 5 and 8a, decompositions, and Reaction 10, deactivation.

$$-d\left[C_2H_2Cl_2^*\right] = k_2\left[C_2H_2Cl_2^*\right] + k_5\left[C_2H_2Cl_2^*\right] + k_{8a}\left[C_2H_2Cl_2^*\right] + k_{10}\left[C_2H_2Cl_2^*\right]\left[M\right]$$

Substitution of these equations for the rate of appearance and of disappearance of the excited molecule in Equation II

*An example of the acceptability of this approximation is seen in the time studies. The production of chloroacetylene, as well as that of the other products, was linear with time, i.e. the rates of production were approximately constant. Equation I indicates that the rate of production is solely dependent upon the concentration of the excited dichloroethylene molecule. For the rate of production to remain approximately constant, the concentration of the excited species must be approximately constant.

gives the following:

$$\propto I_{abs} = (k_2 + k_5 + k_{8a})\left[C_2H_2Cl_2^*\right] + k_{10}\left[C_2H_2Cl_2^*\right]\left[M\right]$$

The concentration of the excited species is:

$$\left[C_2H_2Cl_2^*\right] = \frac{\propto I_{abs}}{(k_2 + k_5 + k_{8a}) + k_{10}[M]}$$

Thus, $$R_{C_2HCl} = \frac{\propto k_5 I_{abs}}{(k_2 + k_5 + k_{8a}) + k_{10}[M]} \qquad III$$

Intensity of light is related to the concentration of absorbing species by Beer's Law:

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

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

Changing Equation IV so that it may be expressed in terms of light absorbed, I_{abs}, rather than light transmitted, and rearranging, yields

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

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

$$e^x = \sum_{k=0}^{\infty} \frac{x^k}{k!} = 1 + x + \frac{x^2}{2} + \frac{x^3}{6} + \cdots$$

For small values of x, in this case a low absorbance of light, e^x may be approximated by $(1 + x)$. So that

$$I_{abs} = I_o \left[1 - (1 - abc) \right]$$

or

$$I_{abs} = I_o abc$$

This may be written as

$$I_{abs} = \beta I_o \left[\underline{cis}\text{-}C_2H_2Cl_2 \right] \qquad V$$

where β is the absorption coefficient, a b. Equation V is identical to that obtained by the law of mass action.

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

By substitution of Equation V in Equation III, the expression for the rate of chloroacetylene production becomes

$$R_{C_2HCl} = \frac{\alpha \beta I_o k_5 \left[\underline{cis}\text{-}C_2H_2Cl_2 \right]}{(k_2 + k_5 + k_{8a}) + k_{10}[M]}$$

In the experiments reported thus far, the only molecule

available for deactivation is the starting material itself; hence, M = cis-$C_2H_2Cl_2$. Under these conditions

$$R_{C_2HCl} = \frac{\gamma k_5 [\text{cis-}C_2H_2Cl_2]}{(k_2 + k_5 + k_{8a}) + k_{10}[\text{cis-}C_2H_2Cl_2]}$$

where $\gamma = \alpha \beta I_o$, I_o being kept constant. Inverting gives

$$\frac{1}{R_{C_2HCl}} = \frac{(k_2 + k_5 + k_{8a}) + k_{10}[\text{cis-}C_2H_2Cl_2]}{\gamma k_5 [\text{cis-}C_2H_2Cl_2]}$$

Separating the right side of the equation into two terms gives the following equations:

$$\frac{1}{R_{C_2HCl}} = \frac{k_{10}}{\gamma k_5} + \frac{k_2 + k_5 + k_{8a}}{\gamma k_5} \frac{1}{[\text{cis-}C_2H_2Cl_2]}$$

$$\frac{[\text{cis-}C_2H_2Cl_2]}{R_{C_2HCl}} = \frac{k_2 + k_5 + k_{8a}}{\gamma k_5} + \frac{k_{10}}{\gamma k_5}[\text{cis-}C_2H_2Cl_2]$$

Using the data in Table XV, the graphs of these equations, shown in Figure 8, were obtained. From the slopes and intercepts of these graphs the following values were obtained:

$$\frac{\gamma k_5}{k_{10}} = 9.1 \times 10^{-7}$$

$$\frac{k_{10}}{k_2 + k_5 + k_{8a}} = 12 \times 10^{-19}$$

By similar mathematical processes, expressions can

Figure 8A. Application of Rate Equations

for R_{C_2HCl}: Filter 9-54

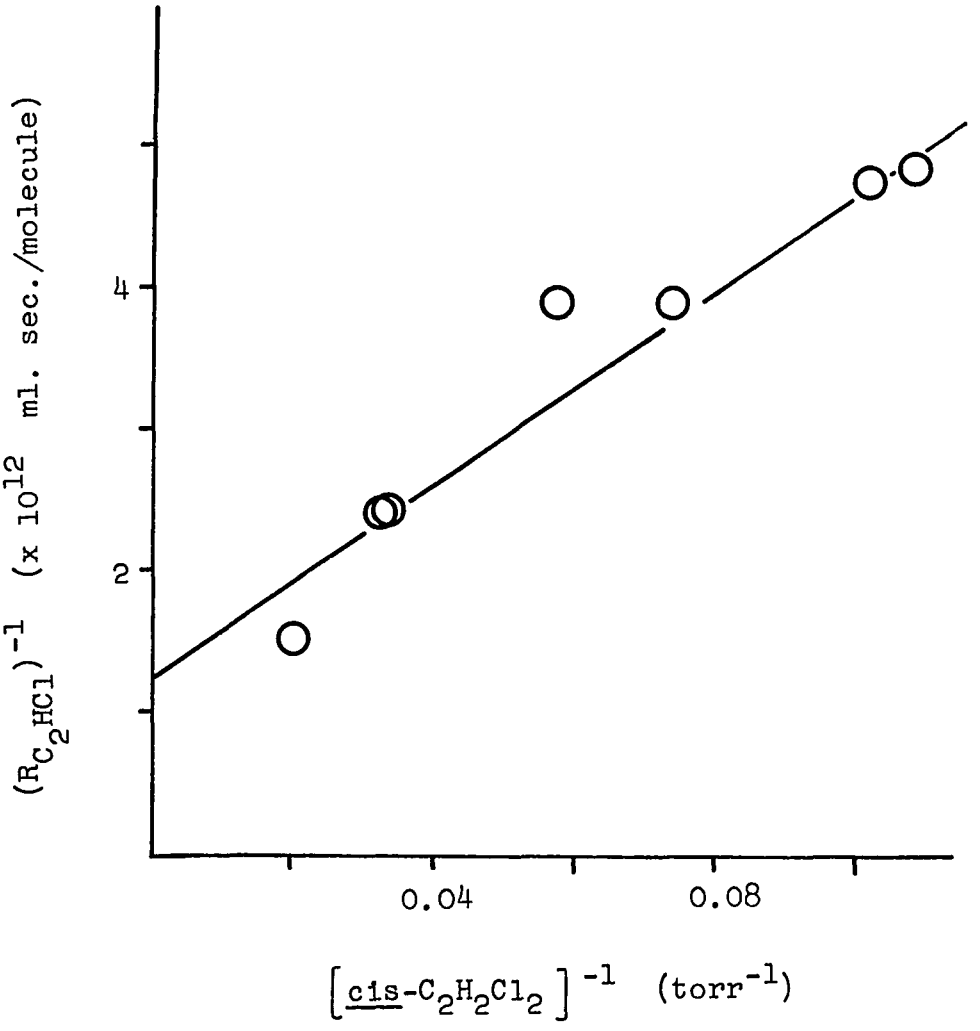
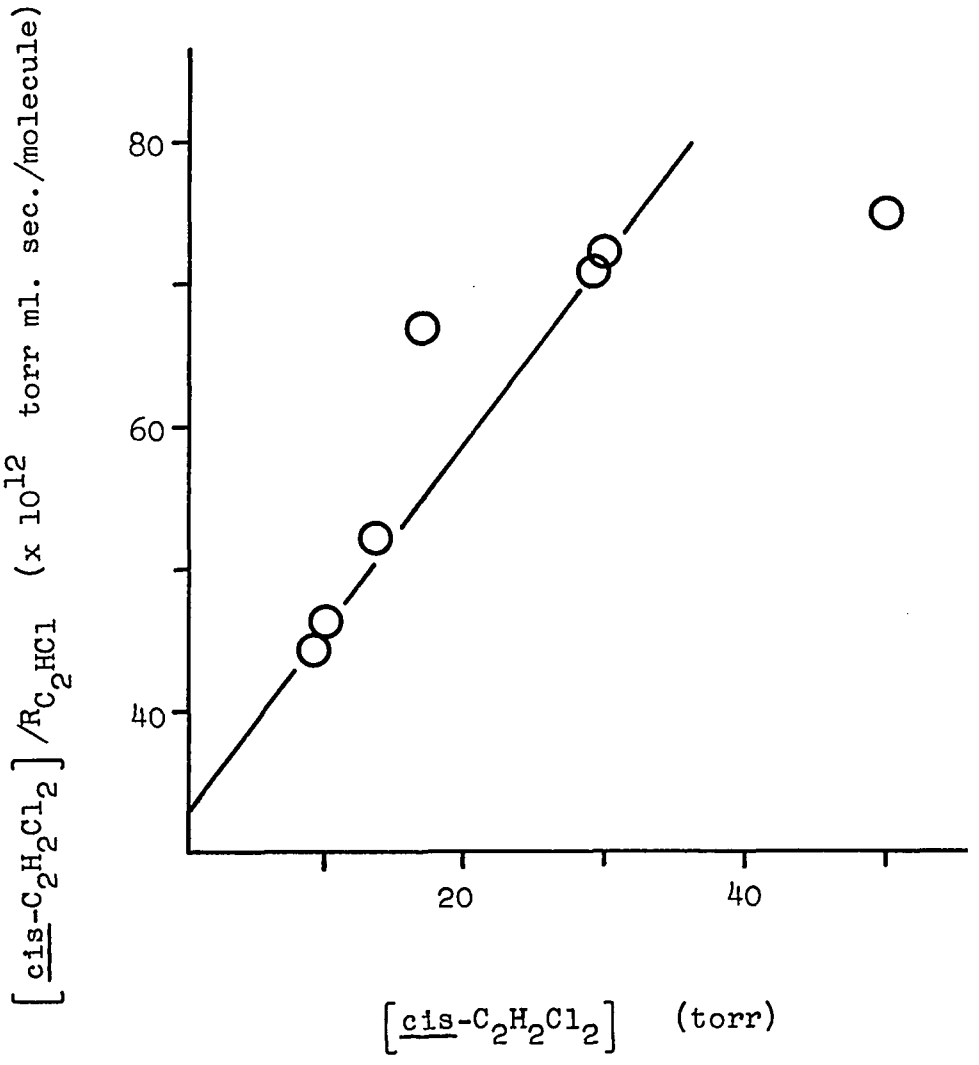


Figure 8B. Application of Rate Equations

for R_{C_2HCl}: Filter 9-54



be derived for the rate of acetylene production. These are exactly analagous to the equations derived for the rate of chloroacetylene production.

$$\frac{1}{R_{C_2H_2(*)}} = \frac{k_{10}}{\gamma k_2} + \frac{k_2 + k_5 + k_{8a}}{\gamma k_2} \frac{1}{[\underline{cis}\text{-}C_2H_2Cl_2]}$$

$$\frac{[\underline{cis}\text{-}C_2H_2Cl_2]}{R_{C_2H_2(*)}} = \frac{k_2 + k_5 + k_{8a}}{\gamma k_2} + \frac{k_{10}}{\gamma k_2} [\underline{cis}\text{-}C_2H_2Cl_2]$$

The asterisk in $R_{C_2H_2(*)}$ emphasizes that the acetylene in question comes from the one star excited state. The graphs of these equations appear in Figure 9. The values obtained from them are:

$$\frac{\gamma k_2}{k_{10}} = 29 \times 10^{-7}$$

$$\frac{k_{10}}{k_2 + k_5 + k_{8a}} = 9.1 \times 10^{-19}$$

Again with chloroiodoethylene, the derivation of rate equations is similar to that shown for chloroacetylene. The only additional step is the application of the steady state approximation to the ground state chlorovinyl radical. The equations derived are:

$$\frac{1}{R_{C_2H_2ClI(*)}} = \frac{k_{10}}{\gamma k_{8a}} + \frac{k_2 + k_5 + k_{8a}}{\gamma k_{8a}} \frac{1}{[\underline{cis}\text{-}C_2H_2Cl_2]}$$

Figure 9A. Application of Rate Equations

for $R_{C_2H_2}$: Filter 9-54

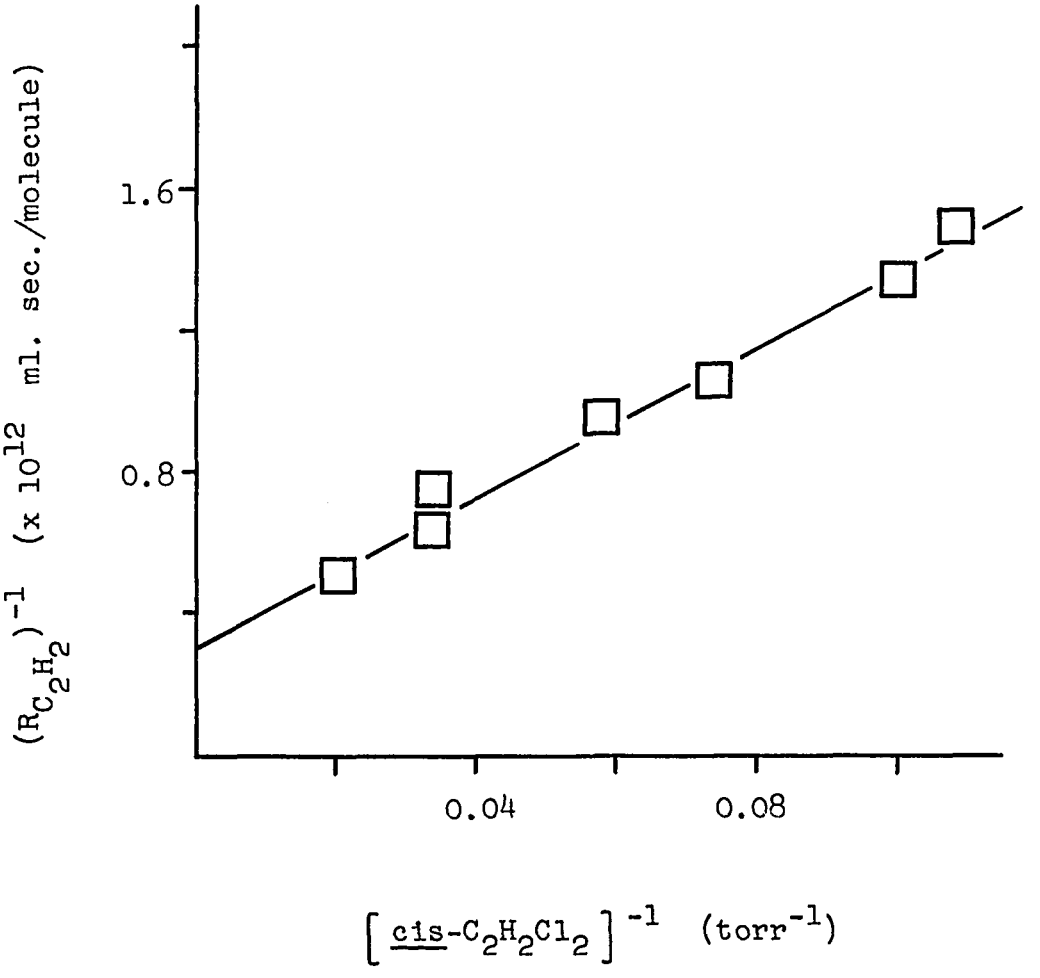
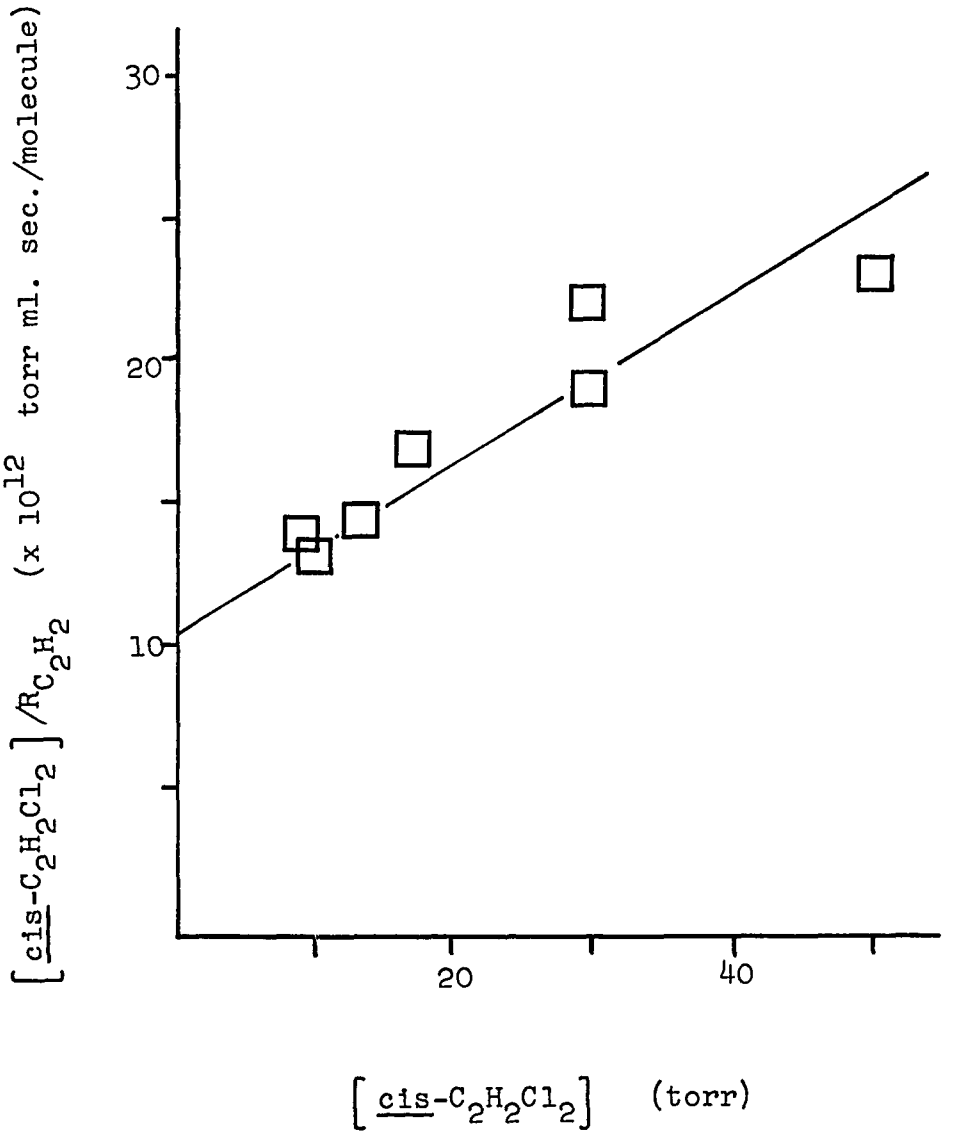


Figure 9B. Application of Rate Equations

for $R_{C_2H_2}$: Filter 9-54



$$\frac{\left[\underline{cis}\text{-}C_2H_2Cl_2\right]}{R_{C_2H_2ClI(*)}} = \frac{k_2 + k_5 + k_{8a}}{\gamma k_{8a}} + \frac{k_{10}}{\gamma k_{8a}}\left[\underline{cis}\text{-}C_2H_2Cl_2\right]$$

where $R_{C_2H_2ClI(*)}$ represents the sum of the rates of cis- and trans-1-chloro-2-iodoethylene produced by the decomposition of the one star excited state. These graphs are shown in Figure 10. The average values obtained from the slopes and intercepts are:

$$\frac{\gamma k_{8a}}{k_{10}} = 2.0 \times 10^{-7}$$

$$\frac{k_{10}}{k_2 + k_5 + k_{8a}} = 5.4 \times 10^{-19}$$

From the graphs of the rate equations for each of the primary products the ratio $k_{10}/(k_2 + k_5 + k_{8a})$ was obtained. These values are:

from $R_{C_2H_2}$	9.1×10^{-19}
from R_{C_2HCl}	12×10^{-19}
from $R_{C_2H_2ClI}$	5.4×10^{-19}

There is excellent agreement between data obtained from acetylene and chloroacetylene, confirming the statement that both products arise from the same excited state. The data obtained from chloroiodoethylene are less accurate. This, however, was expected because the amount of chloro-

Figure 10A. Application of Rate Equations

for $R_{C_2H_2ClI}$: Filter 9-54

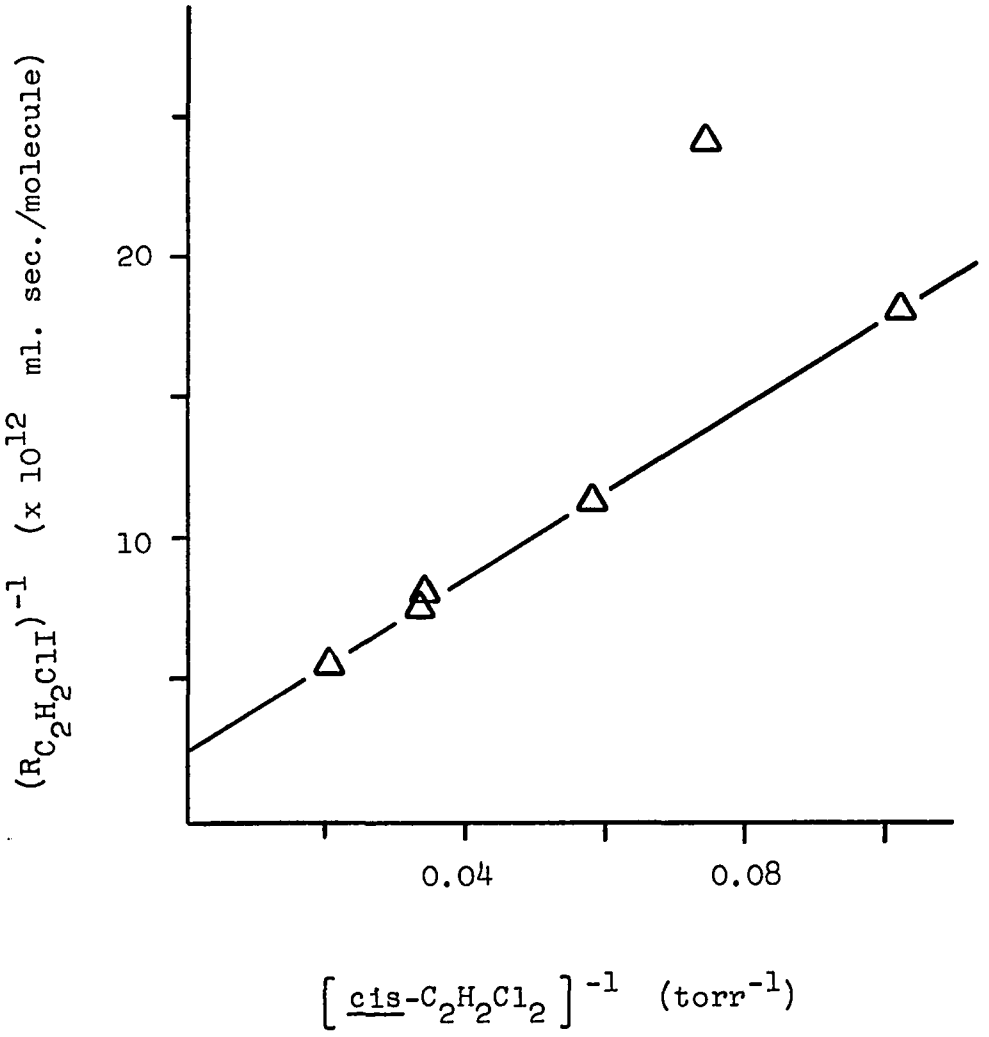
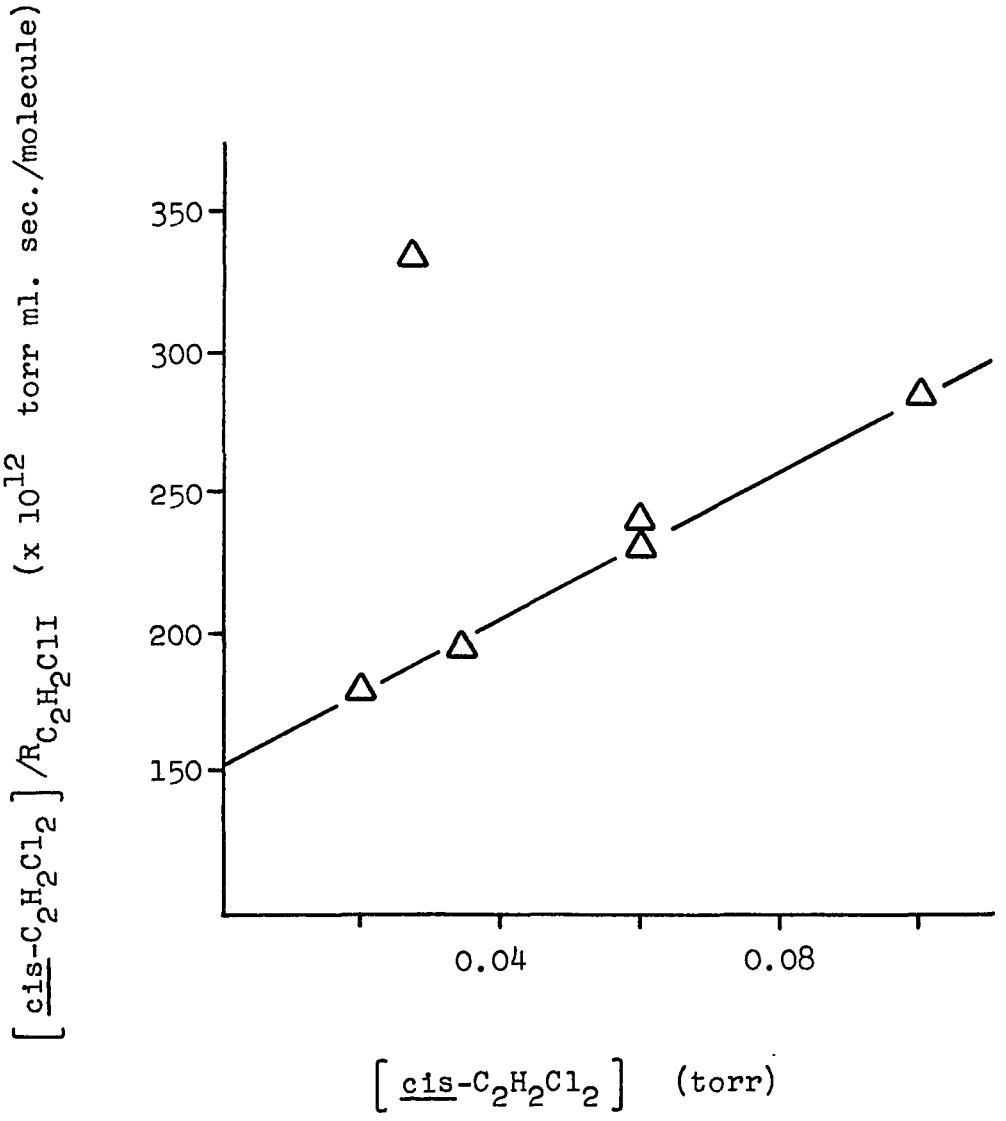


Figure 10B. Application of Rate Equations

for $R_{C_2H_2ClI}$: Filter 9-54



iodoethylene produced was only about 7% of the total primary production and thus was subject to greater experimental error.

Because all three primary products arise directly from the same excited state, the γ's used in the above equations are identical. Thus, the ratio of the rate constants of production of acetylene : chloroacetylene : chloroiodoethylene, $k_2 : k_5 : k_{8a} = 3.2 : 1.0 : 0.22$. These values are in excellent agreement with observations made earlier. In Table III, page 49, the ratio of the rates of production of acetylene : chloroacetylene : chloroiodoethylene was shown to be 3.1 : 1.0 : 0.28.

This same mechanism also should be applicable to the data from experiments using filters 9-53, 0-54 and 0-52. However, as was mentioned earlier (see page 53), due to the products' long residence time in the reaction cell, there is a distinct possibility that some secondary reactions may have occurred. This casts doubt on the accuracy of these data. Consequently, these results cannot be considered suitable for thesting the mechanism.

Results from Experiments without Filters

It is now possible to look at the data obtained in the absence of a filter. Under the full exposure of the mercury arc, another excited state, $C_2H_2Cl_2^{**}$, makes its appearance. The data in Table III, page 49, clearly show that in the absence of a filter the ratio $R_{C_2H_2}/R_{C_2HCl}$ in-

creased and the ratio $R_{C_2HCl}/R_{C_2H_2ClI}$ decreased relative to their values in the presence of filter 9-54. It therefore was suggested that this new excited state will produce additional acetylene and chloroiodoethylene, but <u>not</u> additional chloroacetylene.

The production of an excited state yielding both additional acetylene and chloroiodoethylene is extremely likely if both these products originate via an excited chlorovinyl radical intermediate.

$$C_2H_2Cl_2 + h\nu' \longrightarrow C_2H_2Cl_2^{**} \qquad (1a)$$

$$C_2H_2Cl_2^{**} \longrightarrow C_2H_2Cl^{\circ} + Cl \qquad (4a)$$

$$C_2H_2Cl_2^{**} + M \longrightarrow C_2H_2Cl_2 + M \qquad (11)$$

$$C_2H_2Cl^{\circ} \longrightarrow C_2H_2 + Cl \qquad (4b)$$

$$C_2H_2Cl^{\circ} + M \longrightarrow C_2H_2Cl + M \qquad (9)$$

$$C_2H_2Cl + I_2 \longrightarrow C_2H_2ClI + I \qquad (8b)$$

Finally, there is the possibility that the additional acetylene produced in the absence of filters may be formed exclusively, or in part, by the simultaneous elimination of two chlorine atoms, thus without an intermediate.

$$C_2H_2Cl_2^{**} \longrightarrow C_2H_2 + 2\,Cl \qquad (3)$$

As was mentioned, additional chloroacetylene is not produced by this two star excited state. The graph in

Figure 7, page 48, shows the change in the rate of chloroacetylene production with pressure. It appears that there is total absorption of light at a relatively low pressure, somewhere around 20 torr. This early absorption maximum is, no doubt, caused by the fact that the light intensity in the absence of a filter is much larger than the intensity in the presence of filter 9-54. One assumption which was made in deriving the rate equations is that there must be a low absorbance of light (see page 58). The equations derived, therefore, cannot be applied to the rates of chloroacetylene production in the absence of a filter.

Determination of Rate Equations

The total mechanism for primary product formation in the absence of a filter is complex. Both acetylene and chloroiodoethylene are each produced from two different excited states. To facilitate further discussion, it seems appropriate now to give a summary of all reactions, including deactivations, which lead to the primary products.

$$C_2H_2Cl_2 + h\nu' \longrightarrow C_2H_2Cl_2^{**} \qquad (1a)$$

$$C_2H_2Cl_2 + h\nu \longrightarrow C_2H_2Cl_2^{*} \qquad (1b)$$

$$C_2H_2Cl_2^{**} \longrightarrow C_2H_2 + 2\,Cl \qquad (3)$$

$$C_2H_2Cl_2^{**} \longrightarrow C_2H_2Cl^{\circ} + Cl \qquad (4a)$$

$$C_2H_2Cl_2^{**} + M \longrightarrow C_2H_2Cl_2 + M \qquad (11)$$

$$C_2H_2Cl^{\circ} \longrightarrow C_2H_2 + Cl \qquad (4b)$$

$$C_2H_2Cl^{\circ} + M \longrightarrow C_2H_2Cl + M \qquad (9)$$

$$C_2H_2Cl_2^{*} \longrightarrow C_2H_2 + Cl_2 \qquad (2)$$

$$C_2H_2Cl_2^{*} \longrightarrow C_2HCl + HCl \qquad (5)$$

$$C_2H_2Cl_2^{*} \longrightarrow C_2H_2Cl + Cl \qquad (8a)$$

$$C_2H_2Cl_2^{*} + M \longrightarrow C_2H_2Cl_2 + M \qquad (10)$$

$$C_2H_2Cl + I_2 \longrightarrow C_2H_2ClI + I \qquad (8b)$$

Thus, acetylene is produced by Reaction 2 and by Reactions 3 or 4b, possibly all three. Chloroiodoethylene is produced via Reactions 8a and 9.

Fortunately, because chloroacetylene is produced exclusively from the one star excited state by Reaction 5, simplifications can be made. The data obtained in the presence of filter 9-54 give values for the ratios $R_{C_2H_2(*)}/R_{C_2HCl(*)}$ and $R_{C_2HCl(*)}/R_{C_2H_2ClI(*)}$, where, again, $R_{Product(*)}$ refers to the amount of that product formed exclusively from the one star excited state. The rate of acetylene production from the one star excited state can be calculated by multiplying the known ratio $R_{C_2H_2(*)}/R_{C_2HCl(*)}$ by R_{C_2HCl}. $R_{C_2H_2ClI(*)}$ can be calculated in a similar manner.

By subtracting from the total amount of acetylene produced the amount of acetylene originating from Reaction

2, it is possible to calculate the rate of acetylene production from Reactions 4b and/or 3. Similarly, it is possible to calculate the rate of chloroiodoethylene produced via Reaction 9. Thus, it becomes feasible to compare the rate of acetylene production originating from the two star excited state to the rate of chloroiodoethylene production originating from that same excited state.

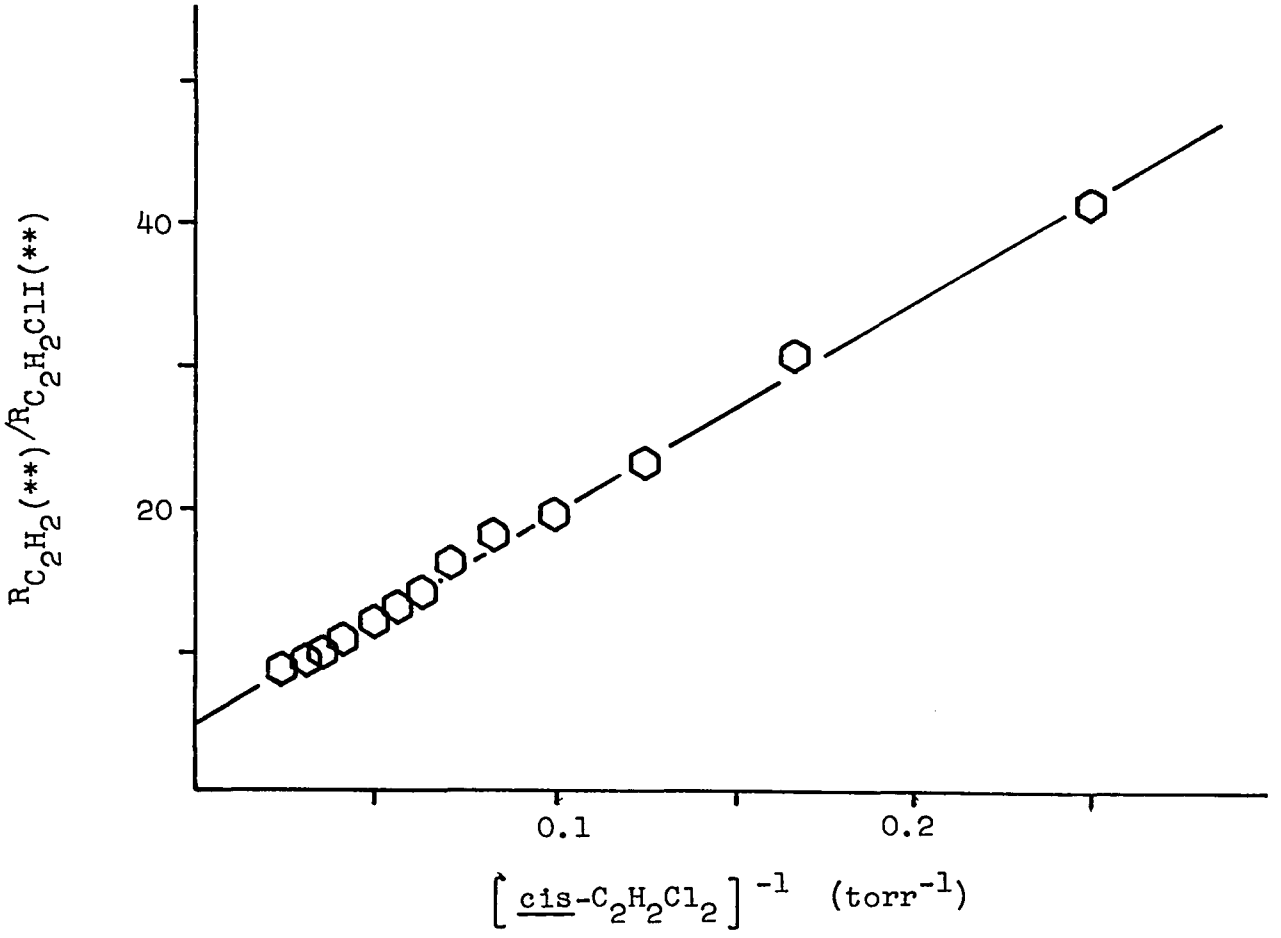
The simplest equation which can be derived in this manner is based upon the assumption that the additional acetylene produced in the absence of a filter is produced exclusively by Reaction 4b. This assumption leads to the following equation:

$$\frac{R_{C_2H_2(**)}}{R_{C_2H_2ClI(**)}} = \frac{k_{4b}}{k_9} \frac{1}{\left[\underline{cis}\text{-}C_2H_2Cl_2\right]}$$

This rate equation predicts a straight line with a positive slope passing thorugh the origin. The graph in Figure 11 shows a straight line with a positive slope equal to 4.7×10^{18}, but also with a positive intercept equal to 5.0.

The appearance of a positive intercept suggests that the mechanism proposed isn't accounting for all the acetylene produced by the two star excited state. As the mechanism already accounts for the acetylene produced via an excited chlorovinyl radical intermediate, the additional acetylene must be produced in a one step reaction, Reaction

Figure 11. Application of the Simple Rate Equation for $C_2H_2Cl_2^{**}$: No Filter



3. Thus, the rate of acetylene production originating from the two star excited state is given by

$$R_{C_2H_2(**)} = k_3\left[C_2H_2Cl_2^{**}\right] + k_{4b}\left[C_2H_2Cl^{\circ}\right]$$

Steady state approximations lead to the following expression:

$$\frac{R_{C_2H_2(**)}}{R_{C_2H_2ClI(**)}} = \frac{k_3}{k_{4a}} + \frac{k_{4b}}{k_9}\left(1 + \frac{k_3}{k_{4a}}\right)\frac{1}{\left[\underline{cis}\text{-}C_2H_2Cl_2\right]}$$

This equation predicts a positive intercept which, indeed, is observed in Figure 11. Therefore,

$$\frac{k_3}{k_{4a}} = 5.0$$

$$\frac{k_{4b}}{k_9}\left(1 + \frac{k_3}{k_{4a}}\right) = 4.7 \times 10^{18}$$

But, k_3/k_{4a} is now known to be 5.0, hence

$$\frac{k_9}{k_{4b}} = 1.3 \times 10^{-18}$$

The results are thus completely in agreement with the mechanism given and indicate that at zero pressure about 17% of the acetylene produced by the two star excited state originates from excited chlorovinyl radicals, while about 83% of these excited molecules directly produce acetylene by the elimination of two chlorine atoms. The ratio k_9/k_{4b}

gives information regarding the lifetime of the excited chlorovinyl radical. This will be discussed later (see page 79).

More Complex Rate Equations

Rate equations also can be derived for $R_{C_2H_2(**)}$ and $R_{C_2H_2ClI(**)}$, individually. However, they are more complex than any equation derived heretofore. In fact, were the values just obtained for k_3/k_{4a} and k_9/k_{4b} not known, these equations could not be written in graphable form. The equations are shown on page 76. Equations VI and VII are for $R_{C_2H_2(**)}$; Equations VIII and IX, for $R_{C_2H_2ClI(**)}$.

Equations VI and VIII, and similarly, VII and IX, even though their left sides are very different, have identical terms on the right side of the equations. Despite the fact that one equation refers to $R_{C_2H_2(**)}$ and the other to $R_{C_2H_2ClI(**)}$, both equations describe the same line.

Points for Equations VI and VIII were plotted on the same graph; the same was done for Equations VII and IX. These graphs are shown in Figures 12A and 12B, respectively, pages 77 and 78. As can be seen, the acetylene and chloroacetylene points do describe the same lines. From these graphs, the following values were derived:

$$\gamma = 1.1 \times 10^{-4}$$

Rate Equations for $R_{C_2H_2}(**)$ and for $R_{C_2H_2ClI}(**)$

$$\frac{1}{R_{C_2H_2}(**)} \frac{\frac{k_3 + k_{4a}}{k_{4a}} + \frac{k_3}{k_{4a}} \frac{k_9}{k_{4b}} \left[\underline{cis}\text{-}C_2H_2Cl_2 \right]}{1 + \frac{k_9}{k_{4b}} \left[\underline{cis}\text{-}C_2H_2Cl_2 \right]} = \frac{k_{11}}{k_{4a}} + \frac{k_3 + k_{4a}}{k_{4a}} \frac{1}{\left[\underline{cis}\text{-}C_2H_2Cl_2 \right]} \qquad \text{VI}$$

$$\frac{\left[\underline{cis}\text{-}C_2H_2Cl_2 \right]}{R_{C_2H_2}(**)} \frac{\frac{k_3 + k_{4a}}{k_{4a}} + \frac{k_3}{k_{4a}} \frac{k_9}{k_{4b}} \left[\underline{cis}\text{-}C_2H_2Cl_2 \right]}{1 + \frac{k_9}{k_{4b}} \left[\underline{cis}\text{-}C_2H_2Cl_2 \right]} = \frac{k_3 + k_{4a}}{k_{4a}} + \frac{k_{11}}{k_{4a}} \left[\underline{cis}\text{-}C_2H_2Cl_2 \right] \qquad \text{VII}$$

$$\frac{1}{R_{C_2H_2ClI}(**)} \frac{\frac{k_9}{k_{4b}} \left[\underline{cis}\text{-}C_2H_2Cl_2 \right]}{1 + \frac{k_9}{k_{4b}} \left[\underline{cis}\text{-}C_2H_2Cl_2 \right]} = \frac{k_{11}}{k_{4a}} + \frac{k_3 + k_{4a}}{k_{4a}} \frac{1}{\left[\underline{cis}\text{-}C_2H_2Cl_2 \right]} \qquad \text{VIII}$$

$$\frac{\left[\underline{cis}\text{-}C_2H_2Cl_2 \right]}{R_{C_2H_2ClI}(**)} \frac{\frac{k_9}{k_{4b}} \left[\underline{cis}\text{-}C_2H_2Cl_2 \right]}{1 + \frac{k_9}{k_{4b}} \left[\underline{cis}\text{-}C_2H_2Cl_2 \right]} = \frac{k_3 + k_{4a}}{k_{4a}} + \frac{k_{11}}{k_{4a}} \left[\underline{cis}\text{-}C_2H_2Cl_2 \right] \qquad \text{IX}$$

Figure 12A. Application of the Complex Equations for $R_{C_2H_2}(**)$ and $R_{C_2H_2ClI}(**)$: No Filter

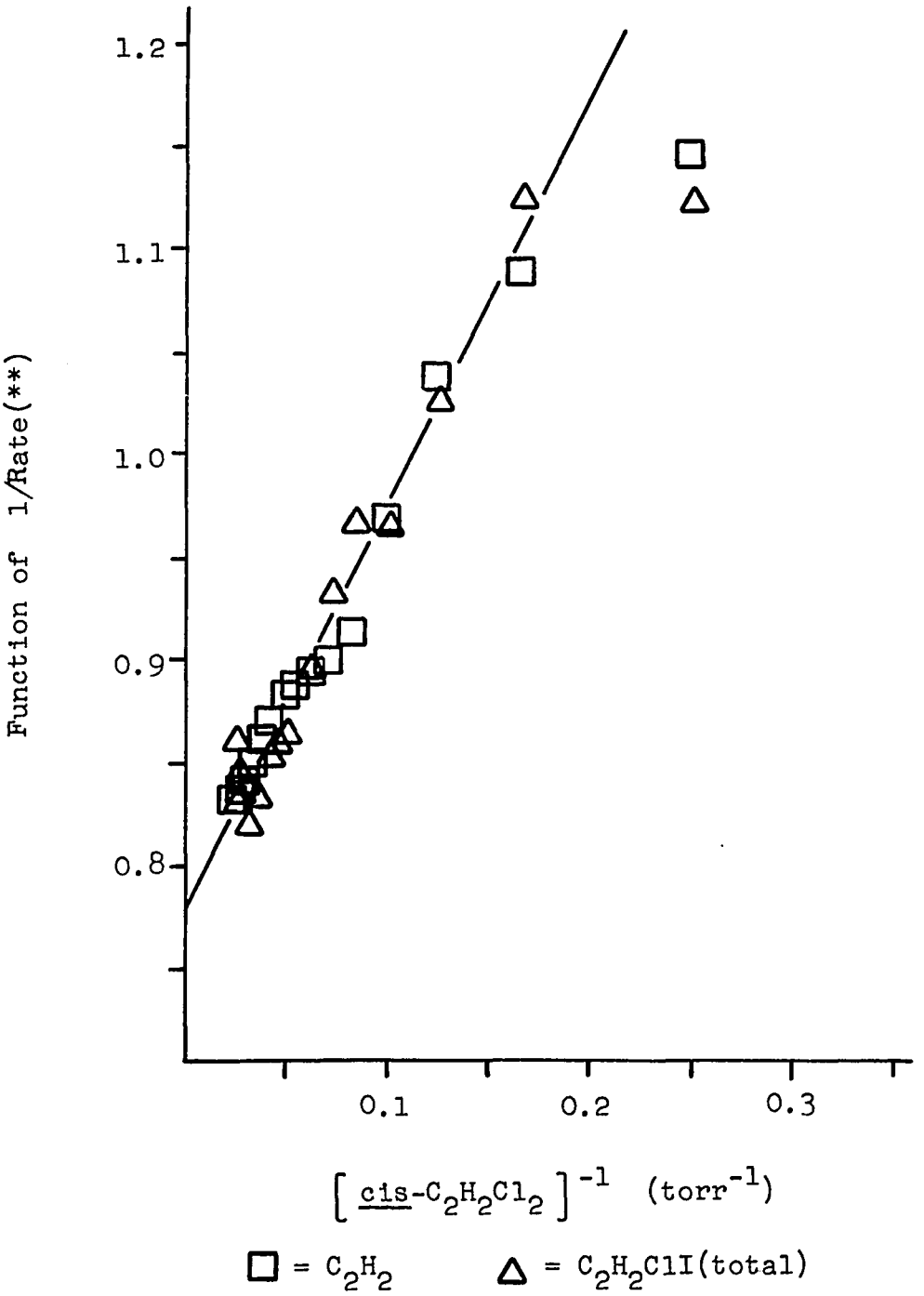
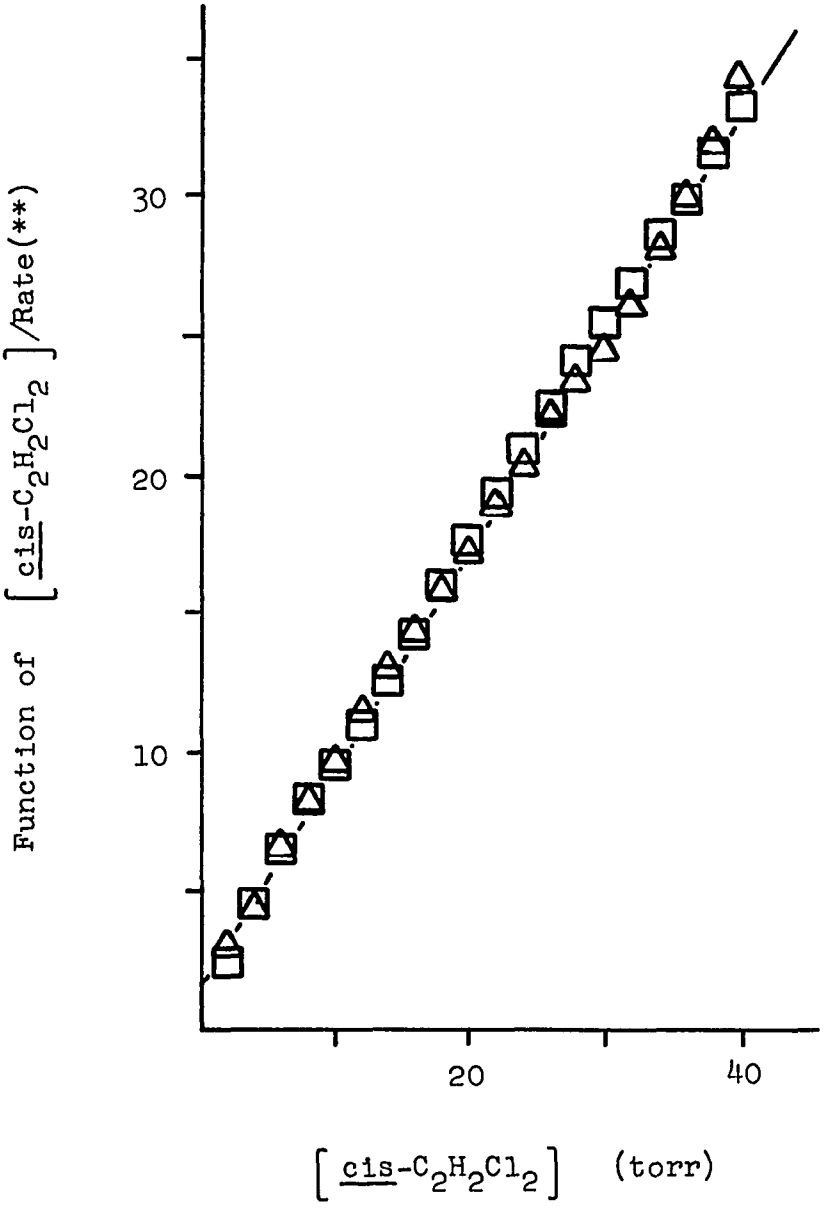


Figure 12B. Application of the Complex Equations for $R_{C_2H_2}(**)$ and $R_{C_2H_2ClI}(**)$: No Filter



$$\frac{k_{11}}{k_3 + k_{4a}} = 8.2 \times 10^{-17}$$

Table IV summarizes the data obtained from the graphs. For the one star excited state, the table contains values for $\gamma k_{decomp}/k_{decomp(total)}$, where k_{decomp} is the rate constant of decomposition into the product named and $k_{decomp(total)}$ is the sum of the rate constants of decomposition, $k_2 + k_5 + k_{8a}$. The sum of the values of this ratio for the three primary products gives the value of γ. Also listed for the one star excited state are the values obtained for $k_{deact}/k_{decomp(total)}$.

Table IV also contains values for $k_{deact}/k_{decomp(total)}$ for the other excited species. For the excited chlorovinyl radical, there is only one mode of decomposition. In this case, $k_{decomp(total)}$ is only k_{4b}. The $k_{decomp(total)}$ of the two star excited state is $k_3 + k_{4a}$. The value of for the two star excited state also is given.

Lifetimes of the Excited Species

For any excited species, from the value of k_{deact}/k_{decomp}, the pressure at which the rates of deactivation and decomposition are equal can be calculated. This value, in turn, is used to calculate the average lifetime of the excited species involved.

The calculations involve the assumption that each collision between an excited species and a ground state

TABLE IV

Relative Rate Constants Derived from the Photolysis of cis-1,2-Dichloroethylene

Filter	Product	Graphs on Pages	Excited State	$\frac{\gamma k_{decomp}}{k_{decomp(total)}}$	$\frac{k_{deact}}{k_{decomp(total)}}$
9-54	C_2H_2	63-64	$C_2H_2Cl_2^*$	$29. \times 10^{-7}$	9.1×10^{-19}
9-54	C_2HCl	60-61	$C_2H_2Cl_2^*$	9.1×10^{-7}	$12. \times 10^{-19}$
9-54	C_2H_2ClI	66-67	$C_2H_2Cl_2^*$	2.0×10^{-7}	5.4×10^{-19}
				$\gamma = 40. \times 10^{-7}$	
none	C_2H_2 C_2H_2ClI	77-78	$C_2H_2Cl_2^{**}$		$82. \times 10^{-18}$
				$\gamma = 1.1 \times 10^{-4}$	
none	C_2H_2 C_2H_2ClI	73	$C_2H_2Cl^o$		1.3×10^{-18}

molecule leads to deactivation. Then, if the collisional cross-section is known, from the formula for collisional frequency, the number of collisions 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 lifetime.

By the metod of Bellas, et al.,[12] the collisional cross-section of cis-dichloroethylene was found to be, $\sigma^2 = 36.5$ Å.^{2}. Bellas's[12] experimental value of $\sigma^2 =$ 29.3 Å.^{2} for the cross-section of vinyl chloride was used as an approximation of the collisional cross-section of the chlorovinyl radical. These calculations and their results for the three excited species referred to in this work are summarized in Table V.

Primary Processes in the Decomposition of trans-1,2-Dichloroethylene

Comparison of Product Rates as a Function of Pressure

Trans-dichloroethylene, being a geometric isomer of cis-dichloroethylene, has the same number and types of bonds. Because of the difference in geometry, however, there will be slight difference in the bond energies for the two isomers. Yet, the bond energies used to calculate the energy needed for the various possible reactions are only average values. They apply equally well to either isomer. Therefore, possible reactions for formation of

TABLE V

Lifetimes of the Excited States

Excited State	Data from Filter Series	$\frac{k_{deact}}{k_{decomp(total)}}$	Pressure (torr) $R_{deact} = R_{decomp}$	Average Lifetime (sec.)
$C_2H_2Cl_2^*$	9-54	1.0×10^{-18}	31.	2.4×10^{-9}
$C_2H_2Cl_2^{**}$	none	$82. \times 10^{-18}$	0.37	2.0×10^{-7}
$C_2H_2Cl^{\circ}$	none	1.3×10^{-18}	24.	3.1×10^{-9}

primary products, which are listed on pages 39-42, are equally probable for trans-dichloroethylene. The corresponding wavelength thresholds for the individual reactions are listed in Table II, page 43.

The work done with trans-dichloroethylene differs from that done with the cis isomer in that no pressure studies were performed using filters. The only pressure studies performed were done under full exposure of the mercury arc. One series used iodine as a scavenger; two other series used hydrogen chloride for that purpose.

Graphs of the rates of formation of the primary products are shown in Figures 13 - 15 for the three pressure studies. The x-axis gives the initial pressure of trans-dichloroethylene. But, there are differences in the concentration of scavenger used.

When hydrogen chloride was used as a scavenger, it was introduced into the cell as a gas. The pressure used was one twentieth of the pressure of trans-dichloroethylene. The ratio of the two was constant.

Iodine vapor was frozen into the cell for a fixed period of time. It then was allowed to warm up to room temperature. The temperature of the room was constant throughout a series of experiments, not varying by more than three centigrade degrees over this time span. Thus, the pressure of iodine, effectively, was kept constant. The greater the pressure of trans-dichloroethylene, the smaller the iodine to dichloroethylene ratio in the cell.

Figure 13. Change in Rates of Primary Production with Pressure of <u>trans</u>-$C_2H_2Cl_2$. Scavenger: I_2

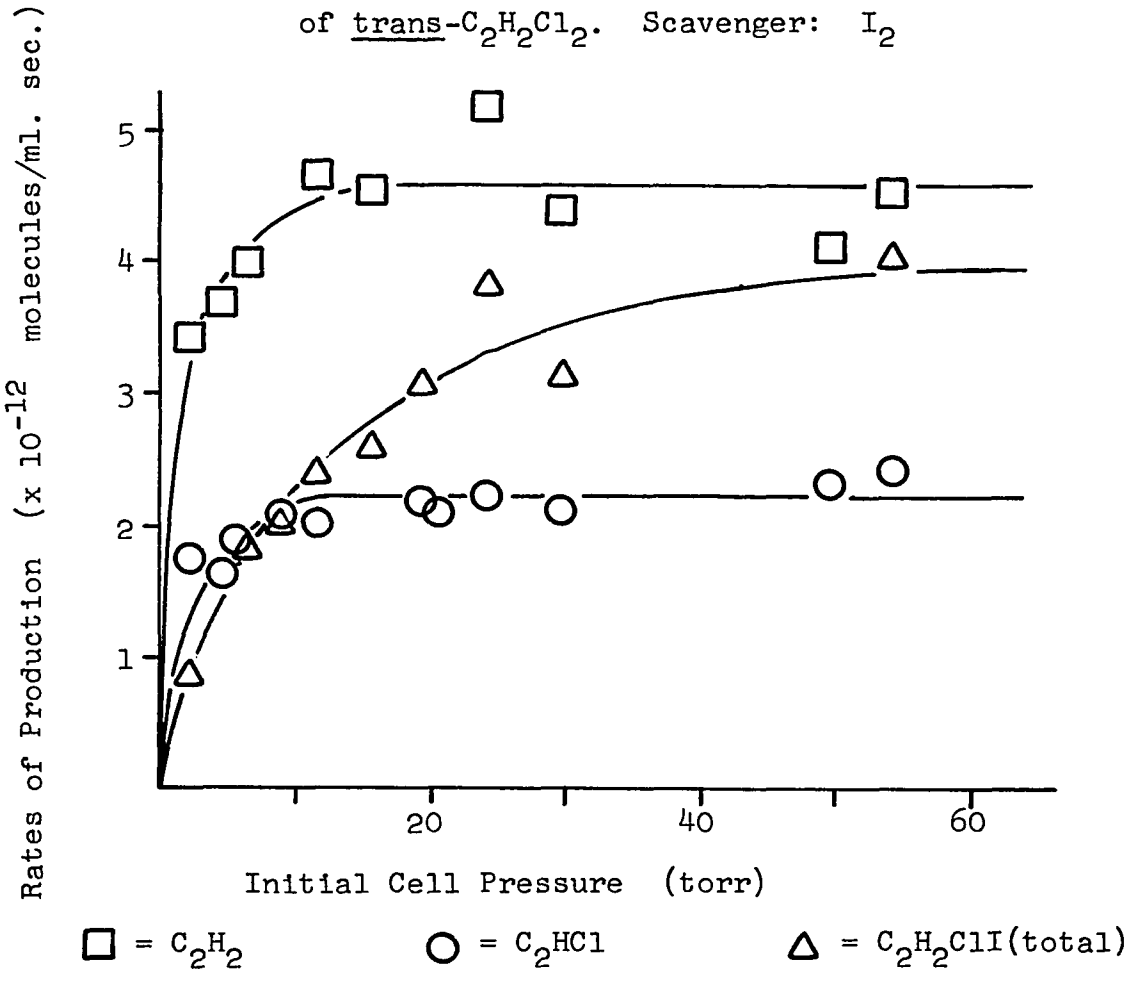


Figure 14. Change in Rates of Primary Production with Pressure of <u>trans</u>-$C_2H_2Cl_2$. Scavenger: HCl (1)

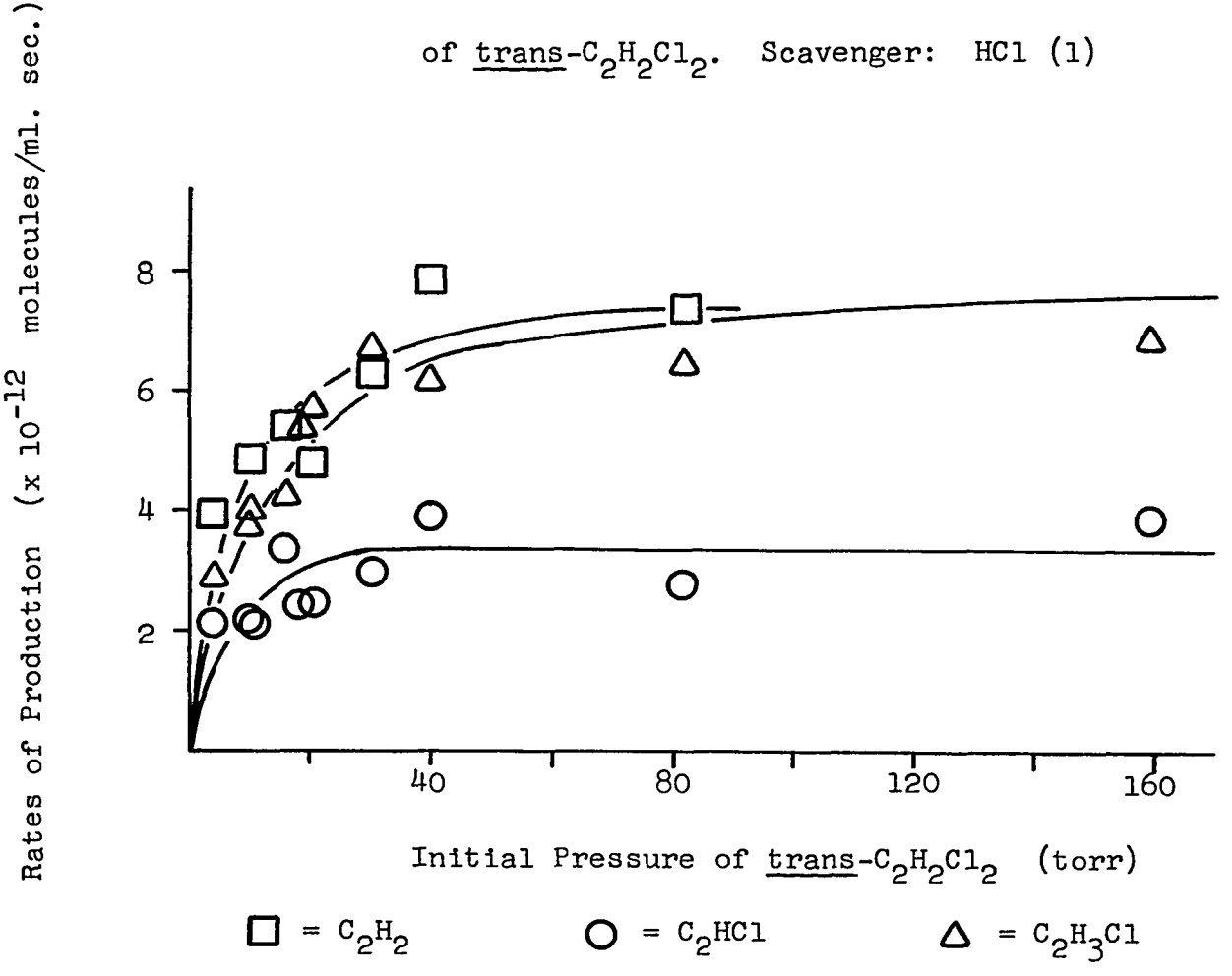
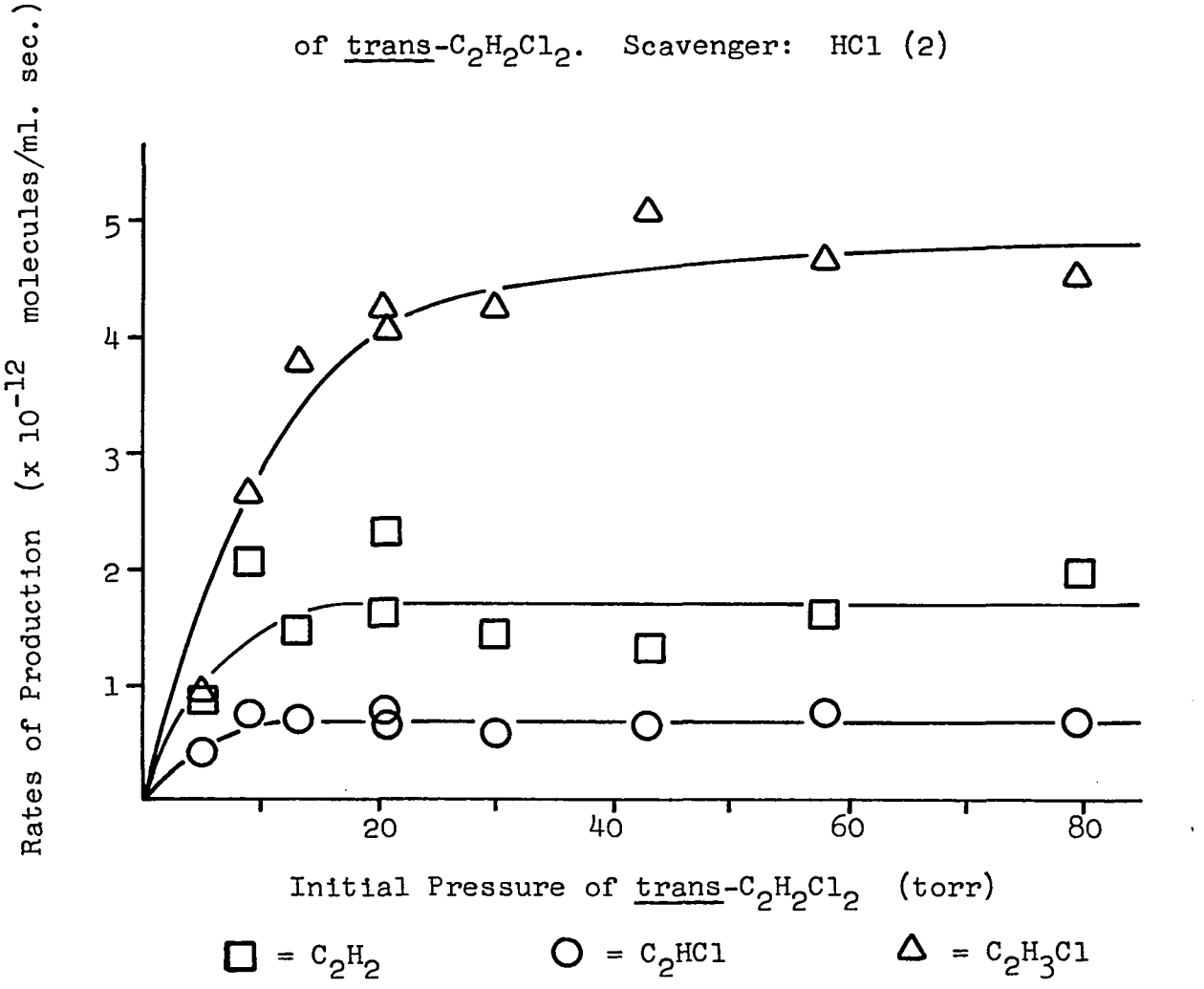


Figure 15. Change in Rates of Primary Production with Pressure of trans-$C_2H_2Cl_2$. Scavenger: HCl (2)



The ratios of the rates of production at various pressures are listed in Table VI. Values at pressures of 10 torr or greater were taken from the graphs of the rates of production, Figures 13 - 15. Those of less than 10 torr were taken from individual experiments.

It has been shown previously that the formation of acetylene and chloroacetylene do not occur through ground state free radical intermediates. Thus, free radical scavengers should not influence the ratio of their rates of production. It is a confirmation of this statement to observe that the acetylene to chloroacetylene ratios are identical, regardless of the scavenger used.

At any particular pressure, it also would be expected that the ratios under the headings $R_{C_2H_2}/R_{C_2H_2Cl}$ be identical, as well as those under the heading $R_{C_2HCl}/R_{C_2H_2Cl}$. Of course, it is clear that in the presence of iodine, the chlorovinyl radical will be converted to cis- and trans-1-chloro-2-iodoethylene, whereas, in the presence of hydrogen chloride, the product is vinyl chloride. The data in Table VI show that these ratios are not identical, not even for the two hydrogen chloride series.

In the course of a series of experiments, a small, but noticeable, build up of deposit on the cell windows was observed. This deposit may have consisted of mercury iodides or chlorides, mercury, and possibly some polymer. It was necessary, therefore, after the termination of a

TABLE VI

Comparison of Rates of Primary Production

in the Photolysis of trans-1,2-dichloroethylene

Scavenger Used	Pressures in Torrs 2.1	4.2	5.2	6.4	10*	15*	30*	50*
				$R_{C_2H_2}/R_{C_2HCl}$				
I_2	1.9	-	-	2.1	2.0	2.0	2.0	2.0
HCl (1)	-	1.9	-	-	2.2	2.0	2.0	2.2
HCl (2)	-	-	2.0	-	2.1	2.2	2.3	2.3
				$R_{C_2HCl}/R_{C_2H_2Cl\cdot}$				
I_2	2.0	-	-	1.0	0.94	0.82	0.65	0.61
HCl (1)	-	0.74	-	-	0.53	0.56	0.55	0.51
HCl (2)	-	-	0.49	-	0.21	0.20	0.16	0.16
				$R_{C_2H_2}/R_{C_2H_2Cl\cdot}$				
I_2	3.9	-	-	2.2	1.9	1.7	1.3	1.2
HCl (1)	-	1.4	-	-	1.2	1.1	1.1	1.1
HCl (2)	-	-	1.0	-	0.45	0.43	0.38	0.37

*These values are taken from graphs, pages 84-86.

series of experiments to remove the cell from the high vacuum system for cleaning. To facilitate the removal of the cell, the light source was taken down. The cell then was filled with aqua regia and left overnight, or until the cell windows again were clean. When the cell and lamp were replaced, their original orientation could not be reproduced.

The greater the distance between the lamp and the cell, the less the amount of illuminating light. This would account for a change in all the rates of primary production, but not for a change in the relative rates, $R_{C_2H_2}/R_{C_2H_2Cl}$ and $R_{C_2HCl}/R_{C_2H_2Cl}$. However, in changing the distance between the light source and the cell, the pathlength of light through air is changed. Oxygen absorbs some of the ultraviolet light; this is evidenced by the odor of ozone detected whenever the mercury arc is on. Because of the absorption of light by oxygen, when the distance between the lamp and the cell is varied, there is a change in the energy distribution of the light transmitted to the cell.

The difficulty in reproducing the conditions of illumination led to a different distribution of excited trans-dichloroethylene states. This, in turn , caused the difference in the relative rates of product formation. But, in all three cases, the ratios follow the same pattern: initially a sharp decrease, followed by a levelling off at higher pressures.

It is notable that with these changes in intensity and energy distribution of light, the ratio $R_{C_2H_2}/R_{C_2HCl}$ remains constant. Moreover, this ratio is invariant throughout the pressure range investigated, having a value of 2.1 ± 10%. With such diverse changes in conditions, the constancy of this ratio can only be ascribed to the fact that both acetylene and chloroacetylene come directly and exclusively from the same excited state of trans-dichloroethylene. At least some significant portion of the chlorovinyl radicals must come from a different excited state.

It should be made clear that the trans-dichloroethylene data are being considered on their own merits. A reaction mechanism is being derived exclusively from these data alone -- not on the basis of opinions formed by the study of cis-dichloroethylene. The similarities and/or differences between the two mechanisms will be considered in detail in the Discussion, to be presented later.

It will be demonstrated later that in the photolyses where iodine is the scavenger, the only source of chlorine atom production is the decomposition of excited trans-dichloroethylene molecules into chlorovinyl radicals (see page 153). The production of chlorine atoms as a coproduct of acetylene (similar to Reactions 3 and 4b), if it occurs at all, is negligible. Therefore, the following mechanism can adequately describe the observed reactions of trans-dichloroethylene:

$$\underline{tr}\text{-}C_2H_2Cl_2 + h\nu \longrightarrow C_2H_2Cl_2^{*} \quad (12a)$$

$$C_2H_2Cl_2^{*} \longrightarrow C_2H_2 + Cl_2 \quad (13)$$

$$C_2H_2Cl_2^{*} \longrightarrow C_2HCl + HCl \quad (14)$$

$$C_2H_2Cl_2^{*} + C_2H_2Cl_2 \longrightarrow 2\ C_2H_2Cl_2 \quad (16)$$

$$\underline{tr}\text{-}C_2H_2Cl_2 + h\nu' \longrightarrow C_2H_2Cl_2^{**} \quad (12b)$$

$$C_2H_2Cl_2^{**} \longrightarrow C_2H_2Cl + Cl \quad (17)$$

$$C_2H_2Cl_2^{**} + C_2H_2Cl_2 \longrightarrow 2\ C_2H_2Cl_2 \quad (18)$$

$$C_2H_2Cl + I_2 \longrightarrow C_2H_2ClI + I \quad (19a)$$

$$C_2H_2Cl + HCl \longrightarrow C_2H_3Cl \quad Cl \quad (19b)$$

with the possible addition of

$$C_2H_2Cl_2^{*} \longrightarrow C_2H_2Cl + Cl \quad (15)$$

it being understood that these one and two star excited states are not necessarily the same as the species referred to in the reactions of <u>cis</u>-dichloroethylene.

Application of Rate Equations

Rate equations can be derived by methods similar to those shown for <u>cis</u>-dichloroethylene. However, as was stated previously, these expressions are valid only at low absorbances of light, where the absorbance is proportional to the pressure of dichloroethylene. The graphs of the

rates of production (Figures 13 - 15, pages 84-86) clearly indicate that at relatively low pressures there is no increase in the rate of production of acetylene and chloroacetylene. There is total absorption of light leading to the excited state which produces these compounds. The equations which would be derived are not applicable to the acetylene and chloroacetylene data.

This leaves the chlorovinyl radical product as the only compounds on which quantitative work may be performed. The question remains whether Reaction 15 plays a significant role in the production of chlorovinyl radicals.

It already has been concluded that because there was no noticeable variation in the ratio $R_{C_2H_2}/R_{C_2HCl}$ with varying experimental conditions, acetylene and chloroacetylene originate from the same excited state. On the other hand, the ratios $R_{C_2H_2}/R_{C_2H_2Cl}$ and $R_{C_2HCl}/R_{C_2H_2Cl}$ (where the rate of chlorovinyl radical formation is measured by the appearance of cis- and trans-chloroiodoethylene in the presence of iodine as scavenger and by the appearance of vinyl chloride, with hydrogen chloride as scavenger) vary considerably with initial pressure of trans-dichloroethylene (see Table VI, page 88). These ratios also vary with the energy of incident light. This is seen from the data in Table VII which summarizes the pertinent results of two filter studies which were performed at different pressures and light intensities.

TABLE VII

Variation in Relative Rates of Production with Light Energy in the Photolysis of trans-$C_2H_2Cl_2$

Filter Used	Wavelength Range (Å.)	$\frac{R_{cis\text{-}\ \&\ tr\text{-}C_2H_2ClI}}{R_{C_2HCl}}$	Number of Experiments
	A) Pressure = 15 torr		
none	2000-4000	4.7	1
9-54	2200-4000	4.4	2
9-53	2600-4000	2.4	1
0-54	3000-4000	2.3	1
0-54	3000-4000	7.2	1
	B) Pressure = 30 torr		
none	2000-4000	12.1	4
9-54	2200-4000	11.0	2
0-54	3000-4000	10.3	1
0-52	3400-4000	8.8	2

Omitting one experiment carried out with filter 0-54, it is clear that there is a decrease in the rate of production of chlorovinyl radicals relative to the rate of chloroacetylene production as the more energetic light is removed. There are two possible explanations for this change in the relative rates of production:

1. Chloroacetylene and the chlorovinyl radical are produced exclusively from different excited states.

2. At least one of the products is produced by more than one excited state. The change in the relative rates of production is caused by a decrease in concentration of one of the excited states as the energy of light is reduced.

Since the ratio $R_{C_2H_2}/R_{C_2HCl}$ is constant, it is the chlorovinyl radical which must, at least in part, be produced from an excited state different from the one producing acetylene and chloroacetylene. This is indicated in the reaction mechanism on page 91 by having acetylene and chloroacetylene produced from the same one star excited molecule, while the chlorovinyl radical is produced by the two star excited molecule. However, the possibility exists that some, but not all, of the chlorovinyl radicals come from the one star excited state.

If some of the chlorovinyl radicals are produced from the excited state which also produces acetylene and chloroacetylene, the ratio of the rate of chlorovinyl radical production from this one star excited state to the rate of acetylene production, $R_{C_2H_2Cl(*)}/R_{C_2H_2}$, must be constant and equal to k_{15}/k_{13}. The total chlorovinyl radical production may then be expressed by

$$R_{C_2H_2Cl(total)} = R_{C_2H_2Cl(*)} + R_{C_2H_2Cl(**)}$$

or $$R_{C_2H_2Cl(total)} - (k_{15}/k_{13})R_{C_2H_2} = R_{C_2H_2Cl(**)} \quad X$$

Were k_{15}/k_{13} known, rate equations could be derived and

applied fairly easily. In a similar situation with cis-dichloroethylene (see page 71), the amount of acetylene formed from its two star excited state was determined by subtracting from the total acetylene production the amount which was produced by the one star excited state.

While the value of k_{15}/k_{13} is not known, its outer limits can be found. This will allow the determination of k_{deact}/k_{decomp} for the two star excited state. A priori, there are two extreme values for k_{15}/k_{13}. One extreme is the value of zero for k_{15}/k_{13}, i.e., no chlorovinyl radicals are produced by the one star excited state. The other extreme value would correspond to a mechanism in which all chlorovinyl radicals are produced from the one star excited state. For the experiments carried out in the presence of iodine, this would lead to

$$\frac{R_{C_2H_2ClI}}{R_{C_2H_2}} = \frac{k_{15}}{k_{13}} = 0.25$$

where 0.25 is the value obtained at the lowest substrate pressure. Since the ratio $R_{C_2H_2ClI}/R_{C_2H_2}$, however, is not constant with pressure, it is clear that at least some, if not all, of the chloroiodoethylene is produced from the two star excited state. Thus, the conclusion is reached that the rate of chlorovinyl radical production from the two star excited state, indeed, is given by Equation X,

$$R_{C_2H_2Cl(**)} = R_{C_2H_2Cl(total)} - (k_{15}/k_{13})R_{C_2H_2} \qquad X$$

and that k_{15}/k_{13} must have as its extreme limits values of zero and 0.25.

The following equations can be derived regarding the rate of chlorovinyl radical production from the two star excited state:

$$\frac{1}{R_{C_2H_2Cl(**)}} = \frac{k_{18}}{\gamma k_{17}} + \frac{1}{\gamma}\frac{1}{[\underline{tr}\text{-}C_2H_2Cl_2]} \qquad XI$$

$$\frac{[\underline{tr}\text{-}C_2H_2Cl_2]}{R_{C_2H_2Cl(**)}} = \frac{1}{\gamma} + \frac{k_{18}}{\gamma k_{17}}[\underline{tr}\text{-}C_2H_2Cl_2] \qquad XII$$

In Figures 16 - 21, Equation XI is plotted for the iodine series using different values for k_{15}/k_{13}. The iodine series is the most sensitive to changes in this ratio. It produced the smallest amounts of chloroiodoethylene relative to acetylene production. Thus, it will have the largest percentage changes in $R_{C_2H_2Cl(**)}$ as k_{15}/k_{13} is varied.

The graph of Equation XI with $k_{15}/k_{13} = 0.25$, Figure 16, page 97, shows a gently convex curve, rather than a straight line. The shape of the curve suggests that the values of the ordinates (y-axis) are too large. This means that the values for $R_{C_2H_2Cl(**)}$ are too small; this is caused by the overlarge value of k_{15}/k_{13}. If, on the other hand, the same treatment is given to the data with

Figure 16. Equation XI. $(k_{15}/k_{13}) = 0.25$

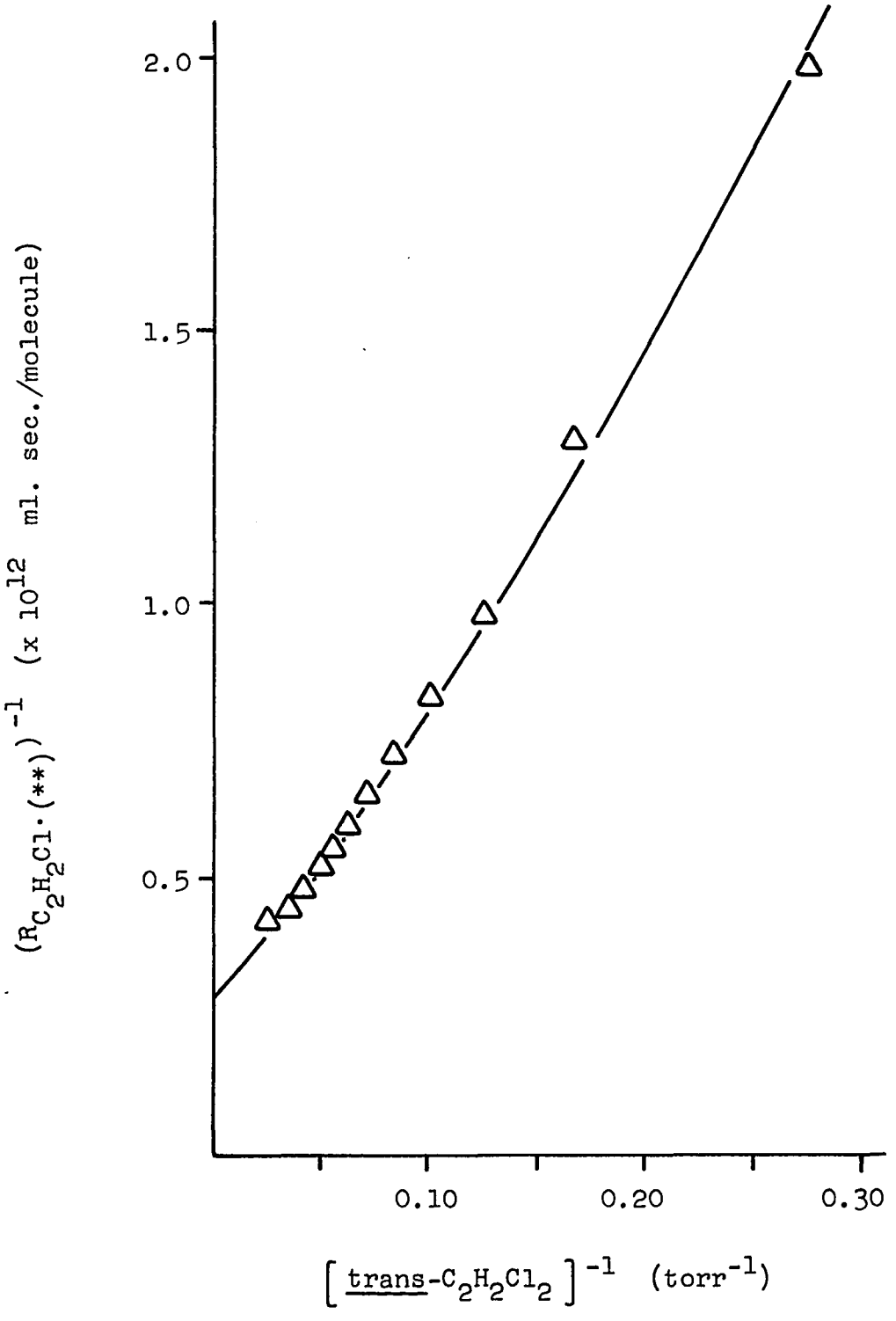


Figure 17. Equation XI. $(k_{15}/k_{13}) = 0$

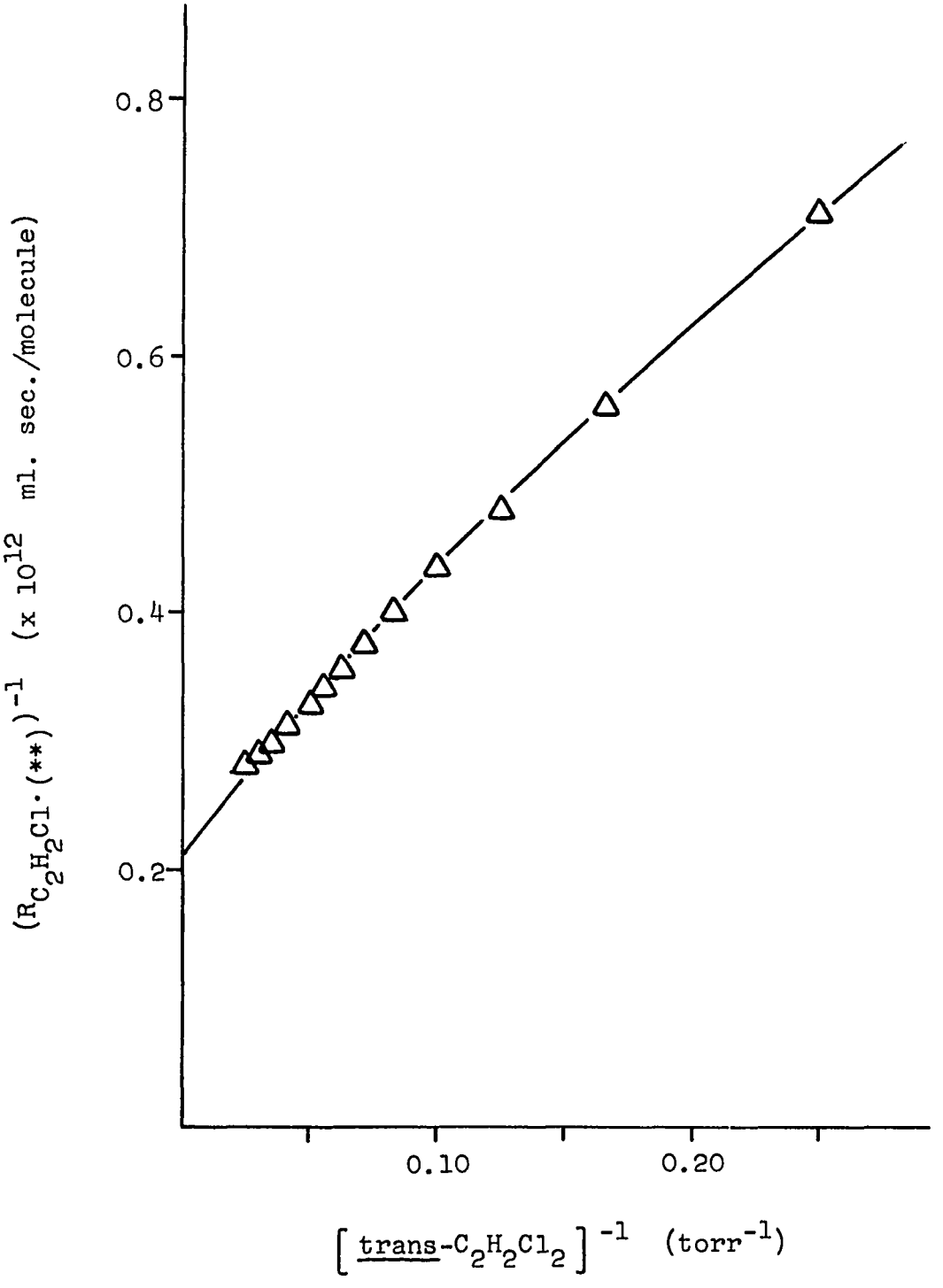


Figure 18. Equation XI. $(k_{15}/k_{13}) = 0.20$

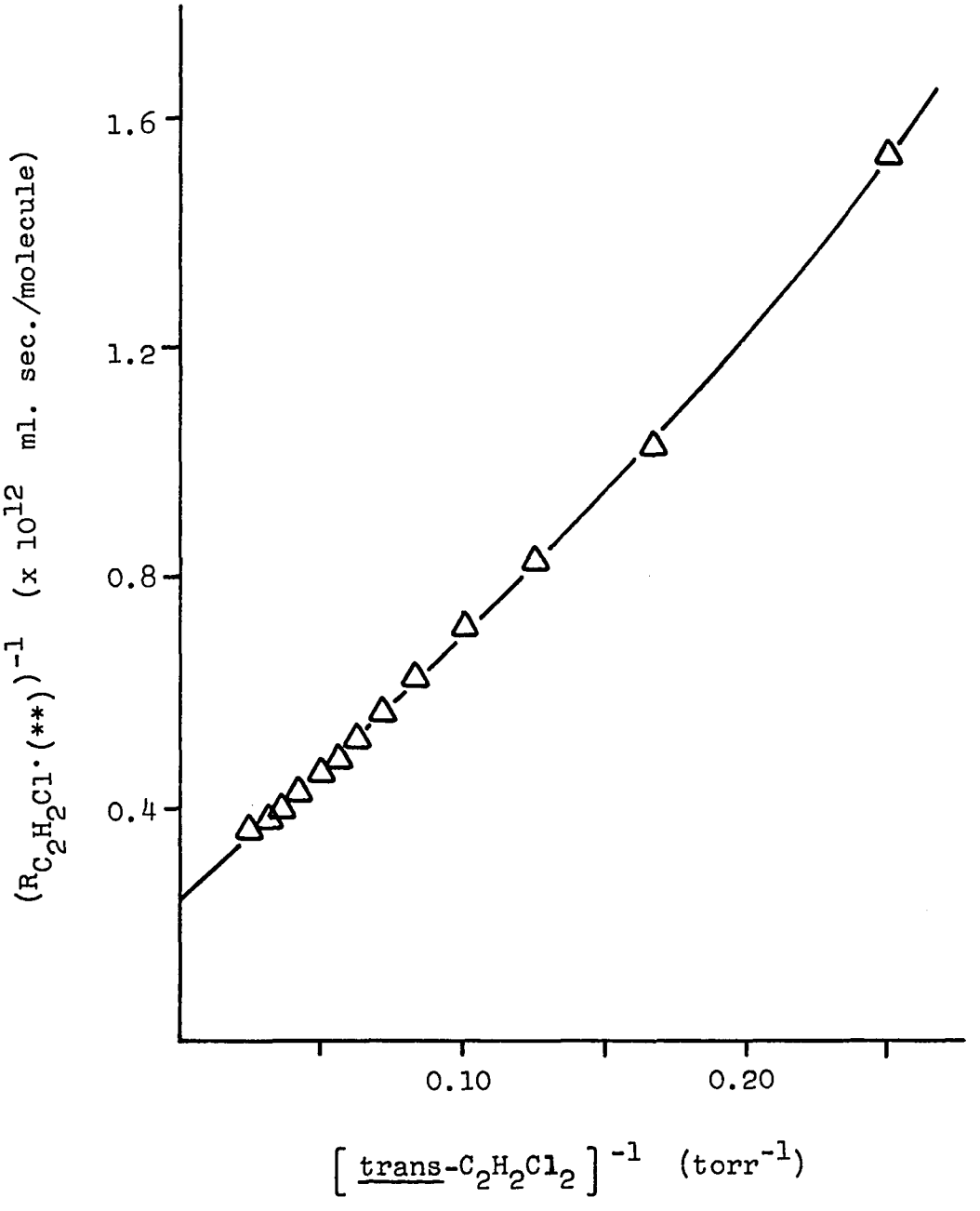


Figure 19. Equation XI. $(k_{15}/k_{13}) = 0.15$

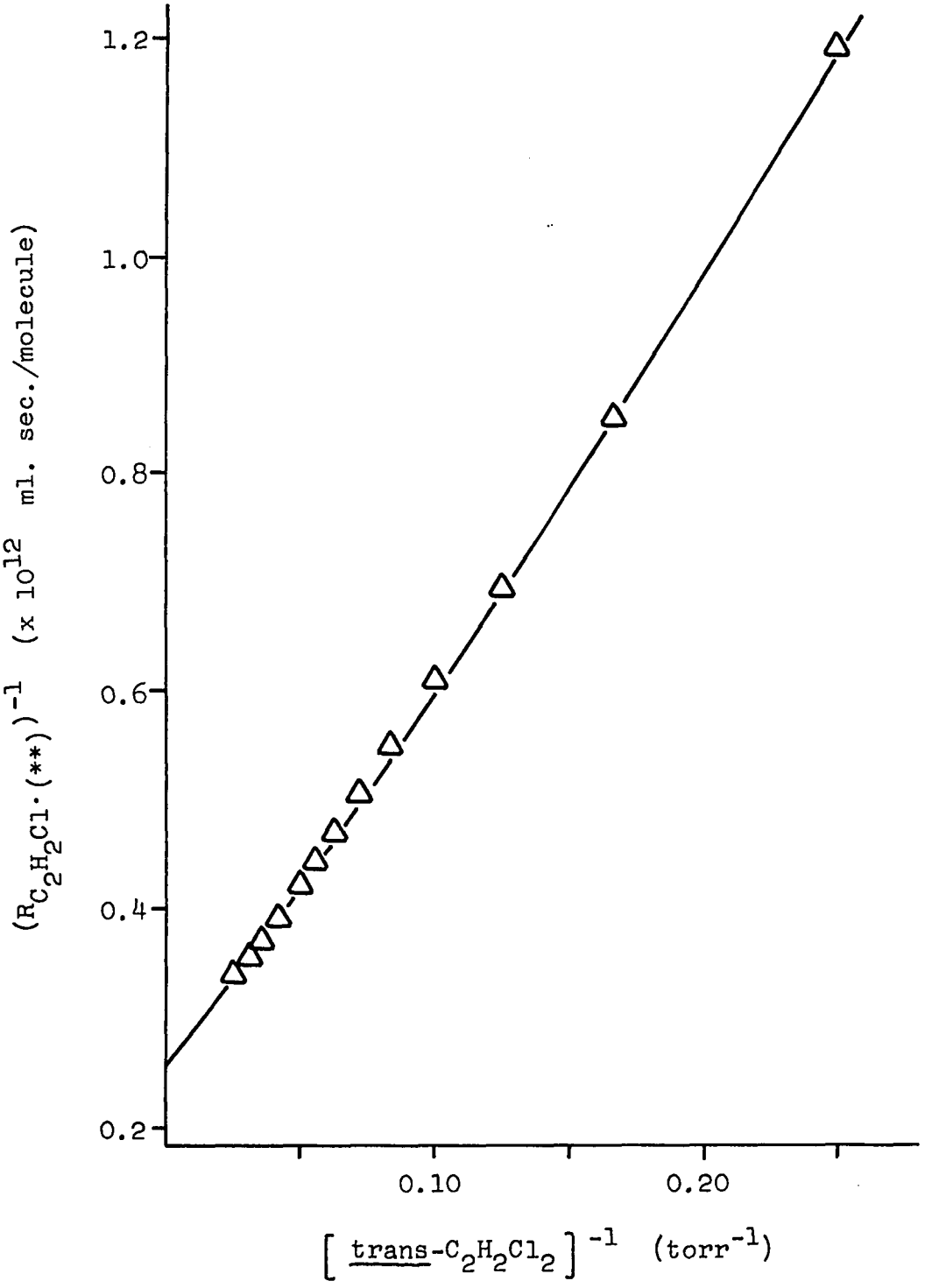


Figure 20. Equation XI. $(k_{15}/k_{13}) = 0.10$

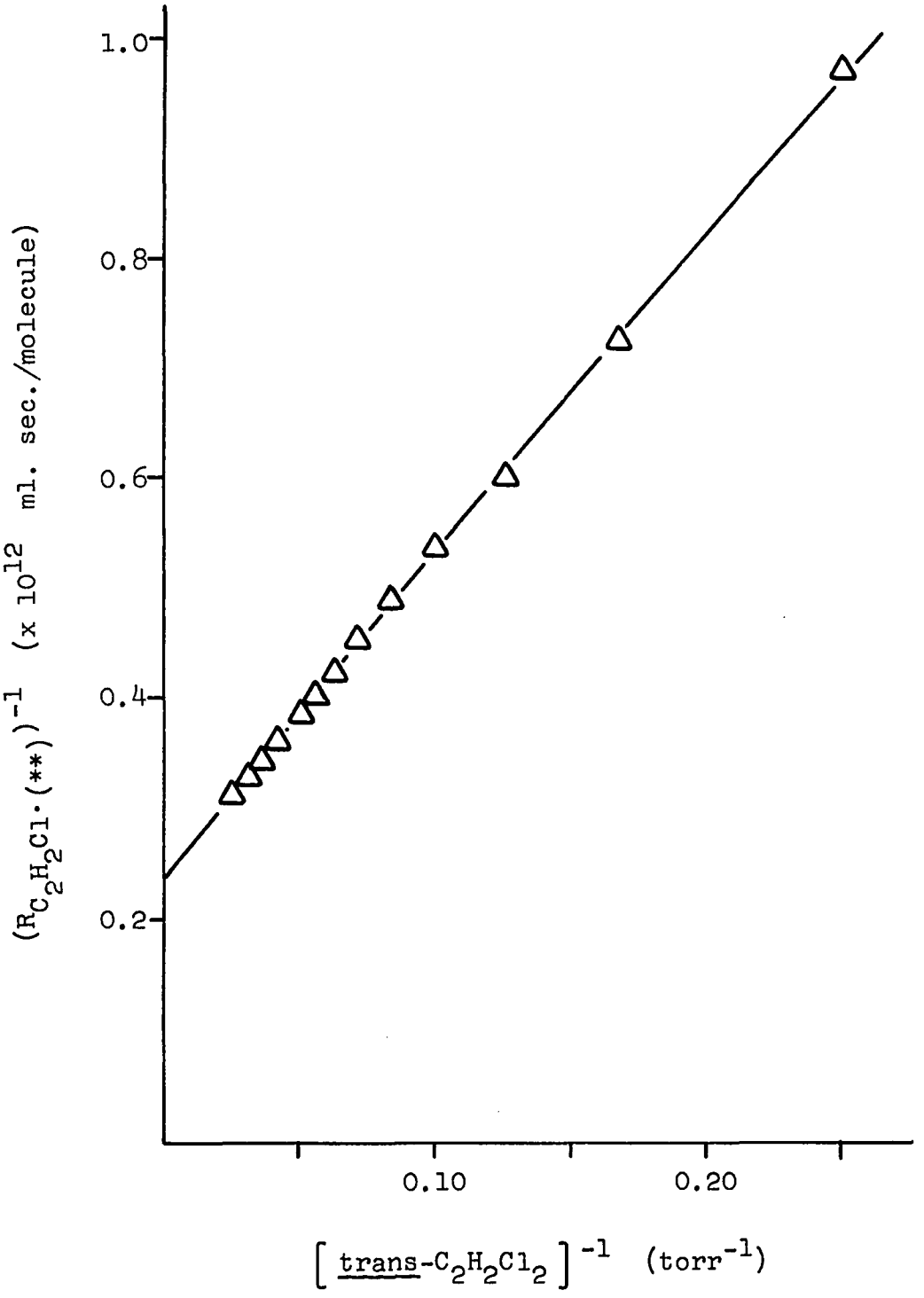
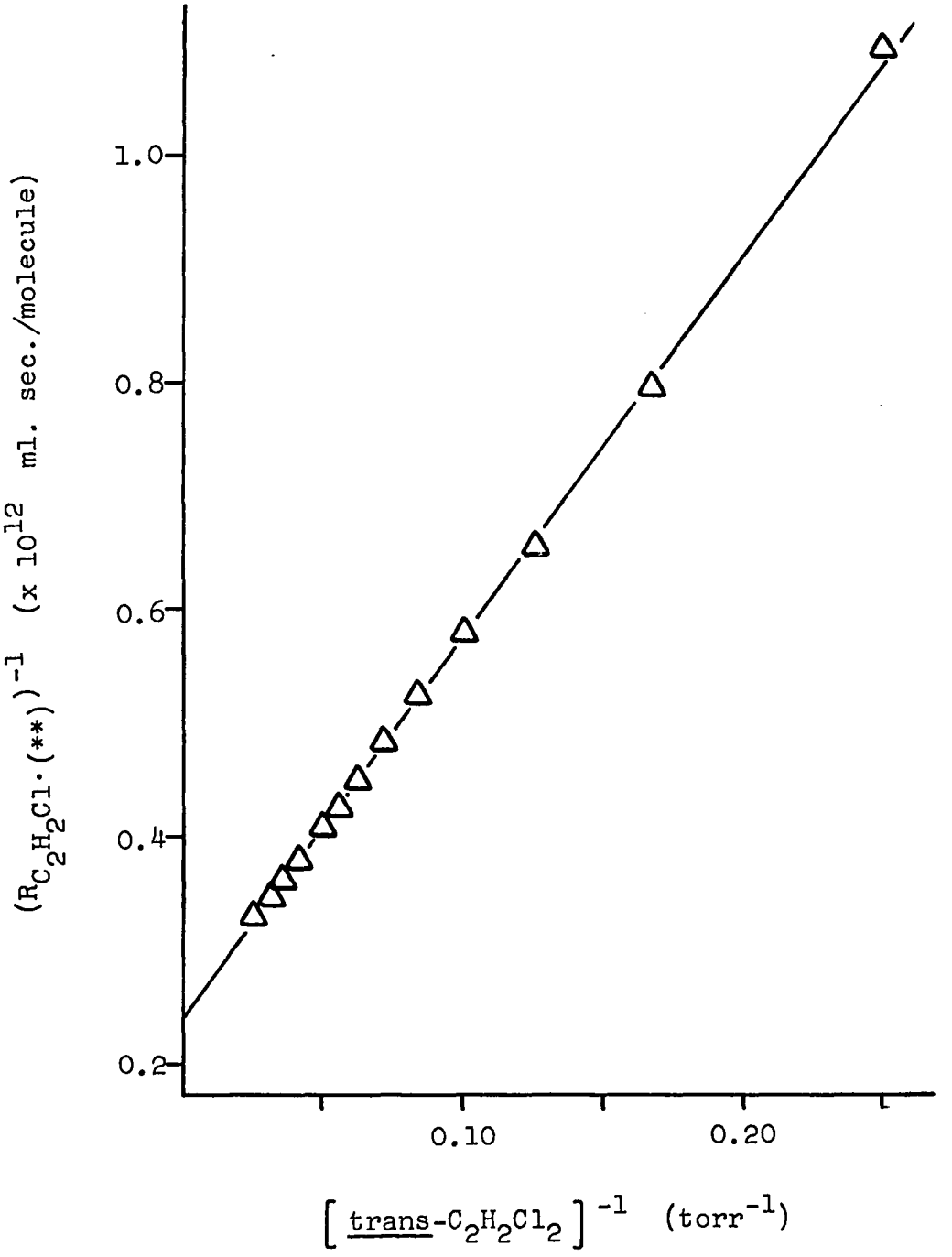


Figure 21. Equation XI. $(k_{15}/k_{13}) = 0.13$



k_{15}/k_{13} equal to zero, a concave curve is obtained (see Figure 17, page 98), indicating that this value of k_{15}/k_{13} is too small.

Repeating these graphs with various allowable values of k_{15}/k_{13} shows that the proper value for this ratio lies between 0.10 and 0.15, with 0.13 a suitable result (Figure 21, page 102).

Having obtained a value for k_{15}/k_{13}, Equations XI and XII can be applied to all the data. In Figures 22 and 23, the plots are given for the data with iodine and the data from the first hydrogen chloride series, respectively. These graphs show excellent agreement with Equations XI and XII. The graphs for the data from the second hydrogen chloride series are given in Figure 24, pages 108-109. While the plots for this series deviate from linearity with increasing pressure, this is not due to the value selected for k_{15}/k_{13}. The large amounts of chlorovinyl radicals produced relative to acetylene make these data so insensitive to the correction for the one star excited state production, that there is virtually no change in the value of k_{deact}/k_{decomp} (k_{18}/k_{17}) as k_{15}/k_{13} is varied from zero to 0.20.

The values obtained from these graphs are given in Table VIII, page 110. Despite the fact that light intensities and distributions were far from similar, the values obtained for k_{deact}/k_{decomp} from the iodine and hydrogen chloride series are in excellent agreement. These values

Figure 22A. Application of Rate Equations

for $R_{C_2H_2Cl\cdot}$ (k_{15}/k_{13}) = 0.13. Scavenger: I_2

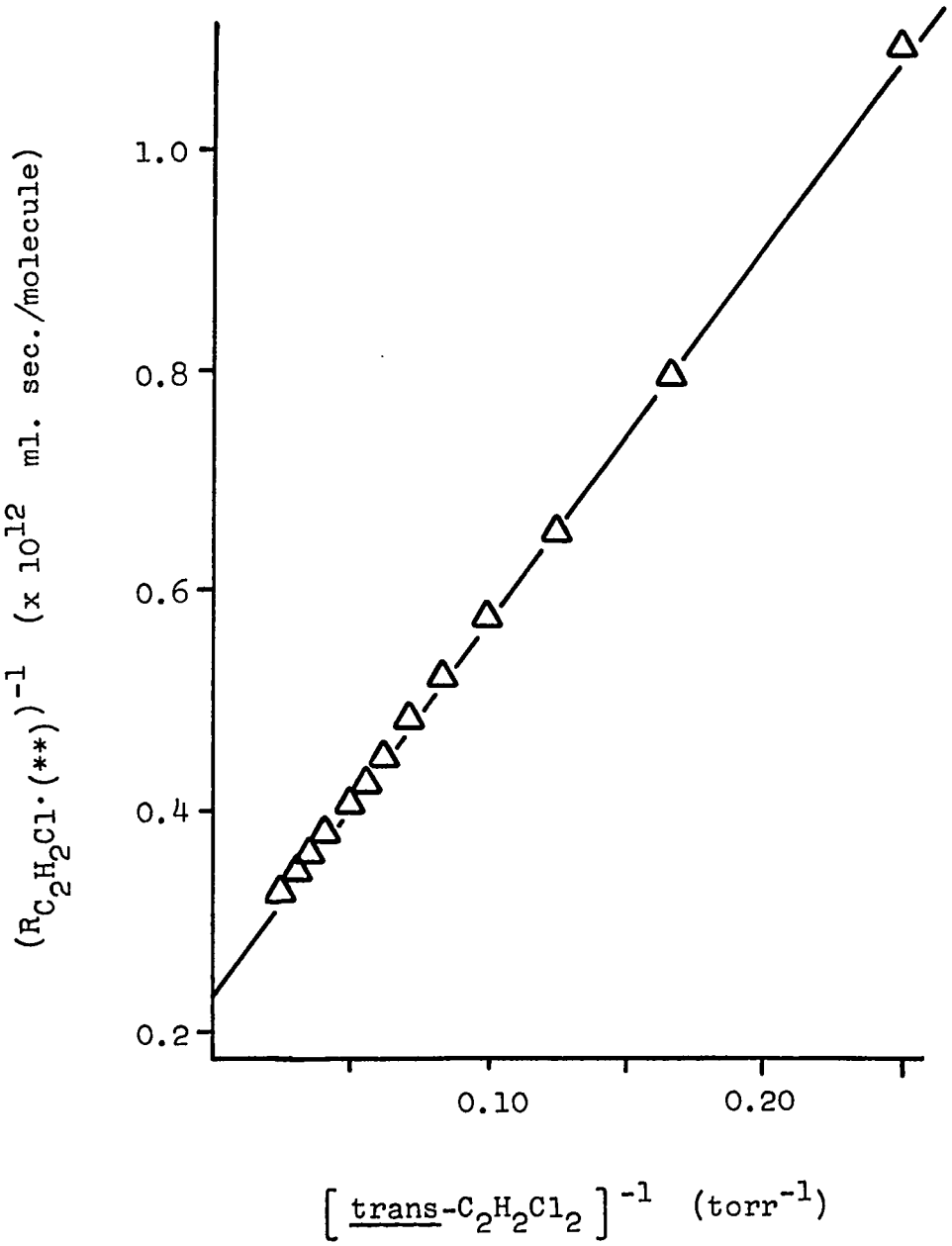


Figure 22B. Application of Rate Equations

for $R_{C_2H_2Cl}$·· $(k_{15}/k_{13}) = 0.13$. Scavenger: I_2

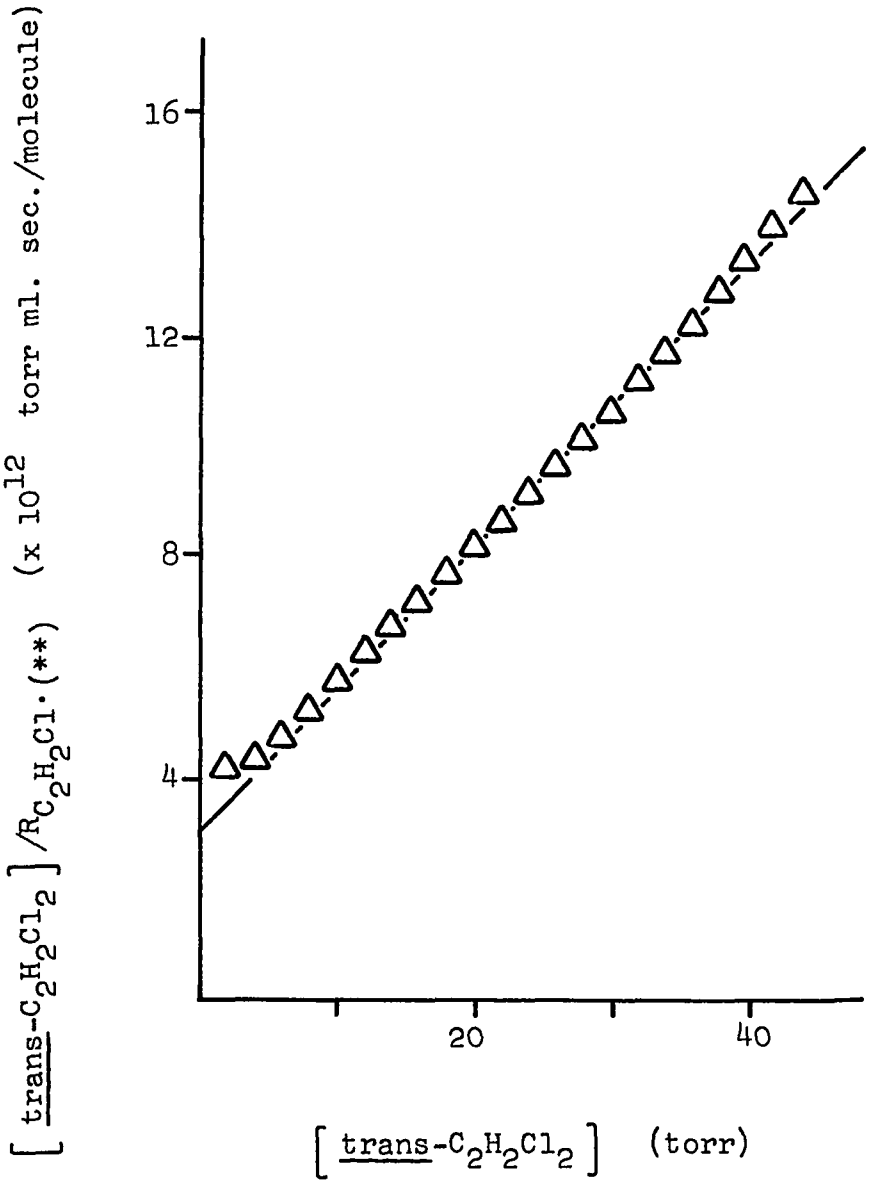


Figure 23A. Application of Rate Equations for $R_{C_2H_2Cl}$..

(k_{15}/k_{13}) = 0.13. Scavenger: HCl (1)

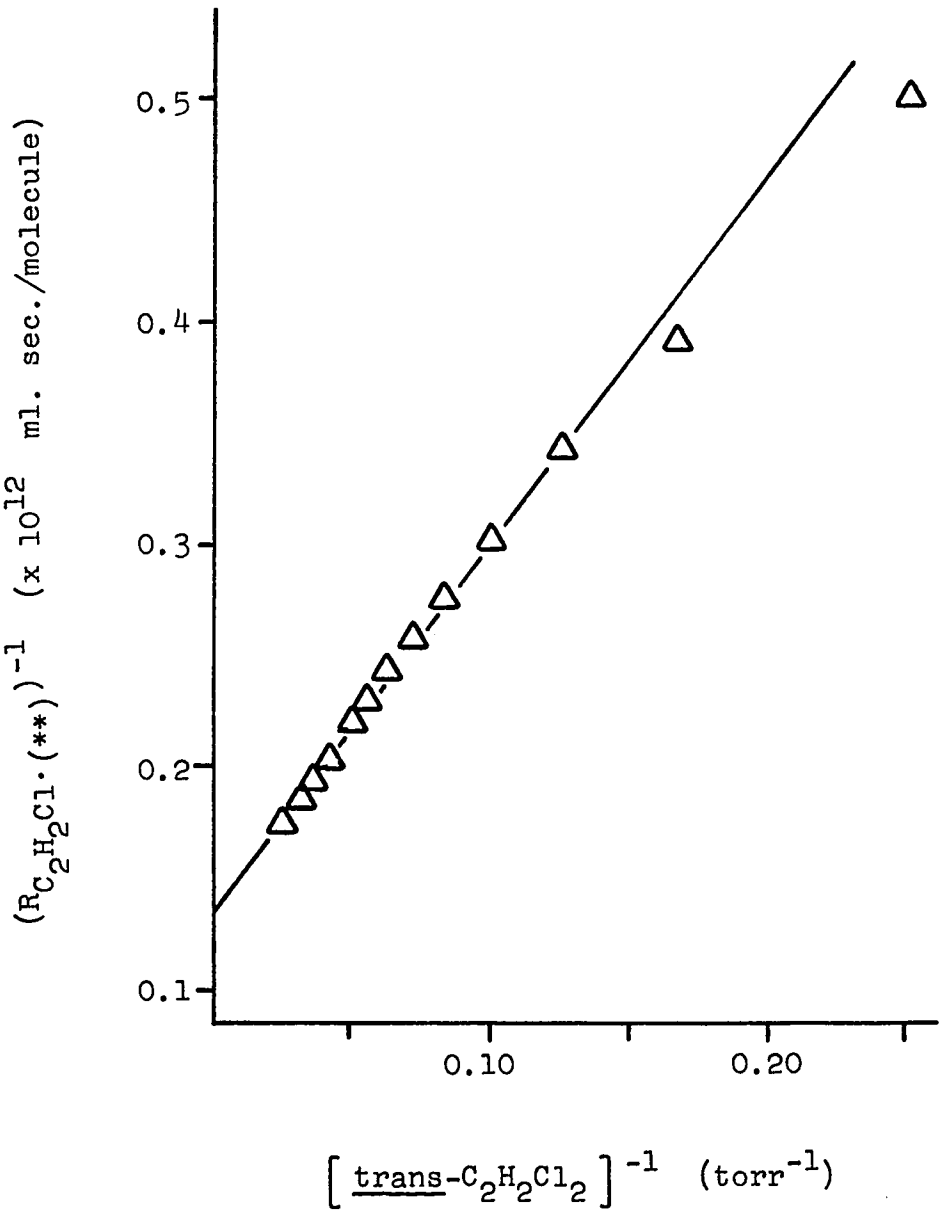


Figure 23B. Application of Rate Equations for $R_{C_2H_2Cl}$..

(k_{15}/k_{13}) = 0.13. Scavenger: HCl (1)

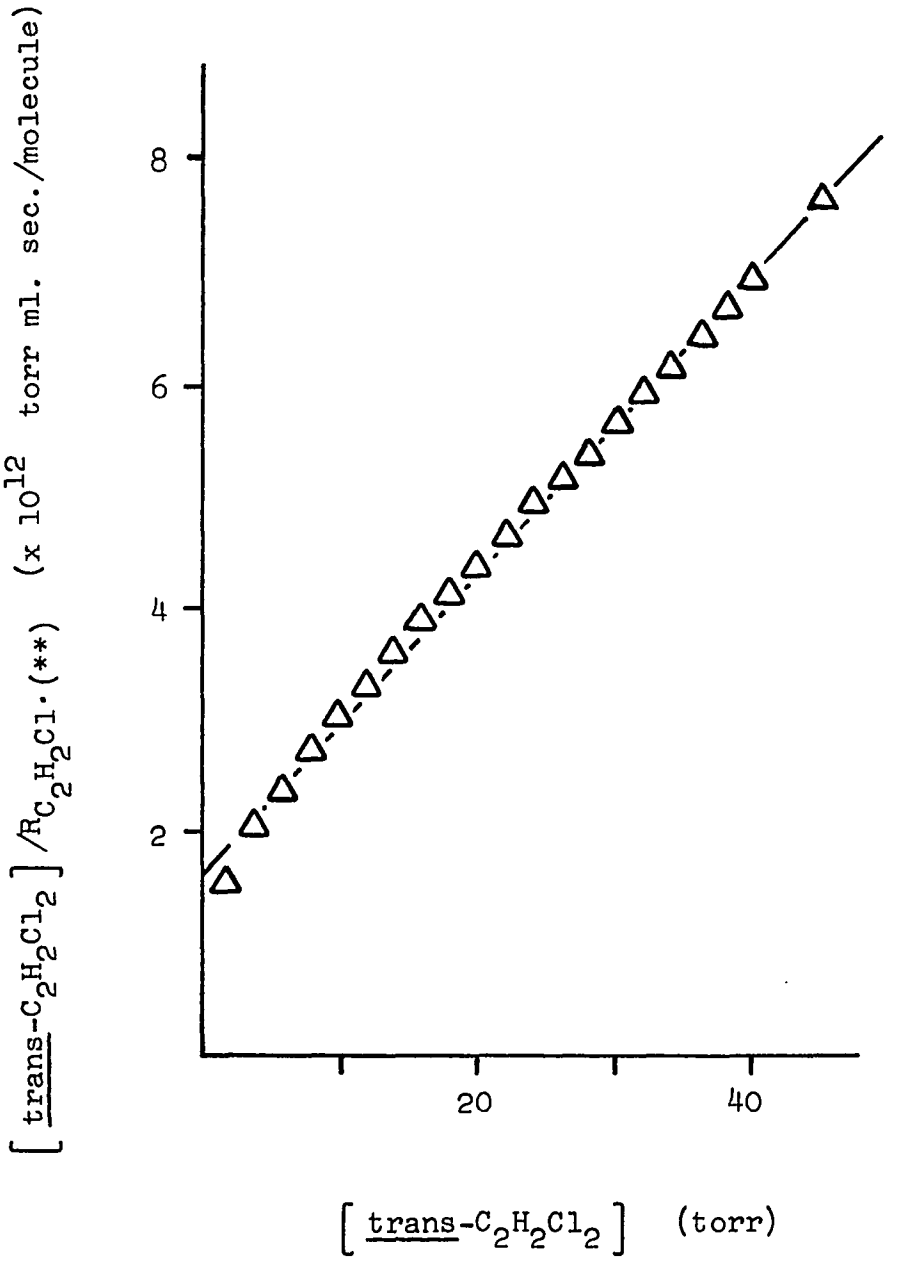


Figure 24A. Application of Rate Equations for $R_{C_2H_2Cl}$..

(k_{15}/k_{13}) = 0.13. Scavenger: HCl (2)

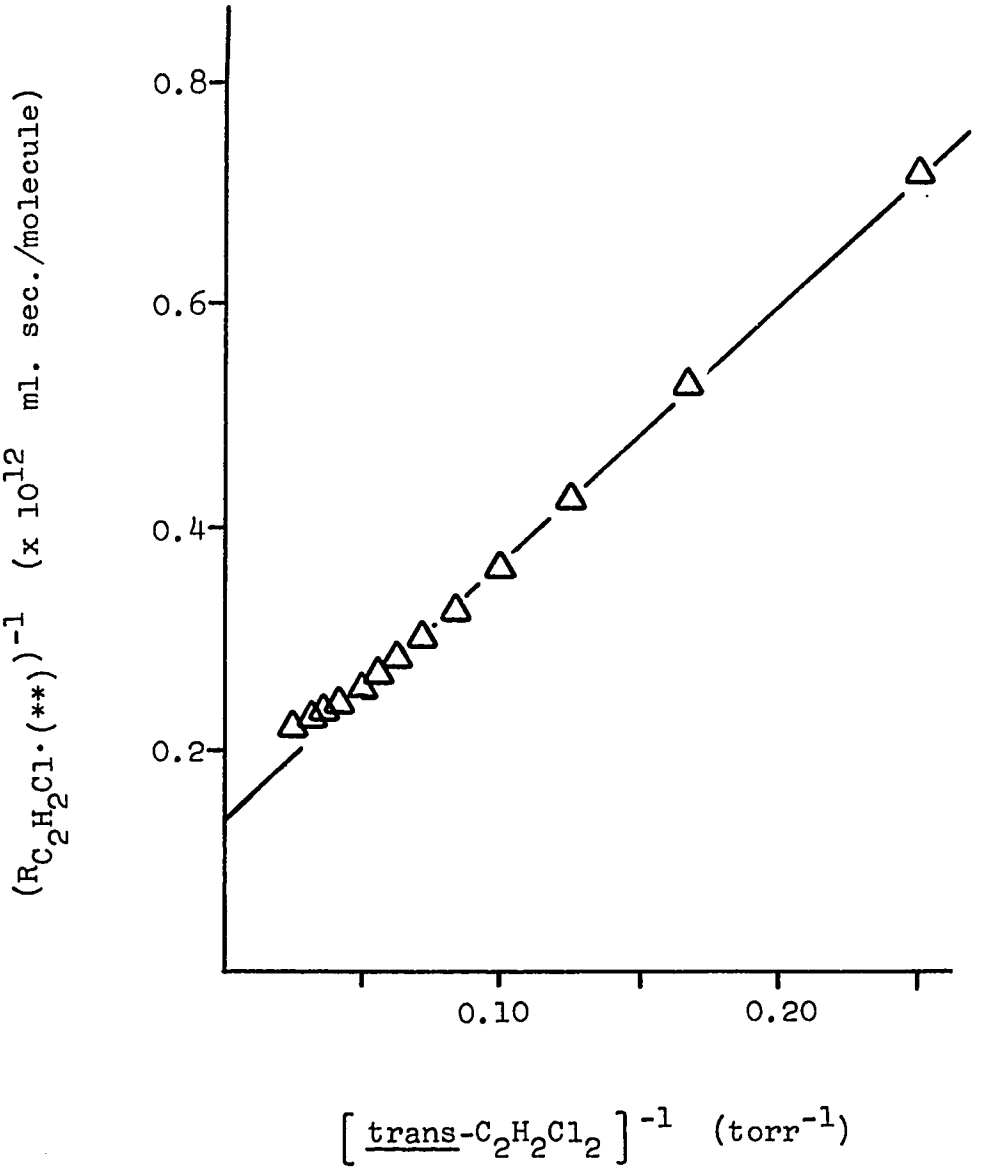


Figure 24B. Application of Rate Equations for $R_{C_2H_2Cl}$..

(k_{15}/k_{13}) = 0.13. Scavenger: HCl (2)

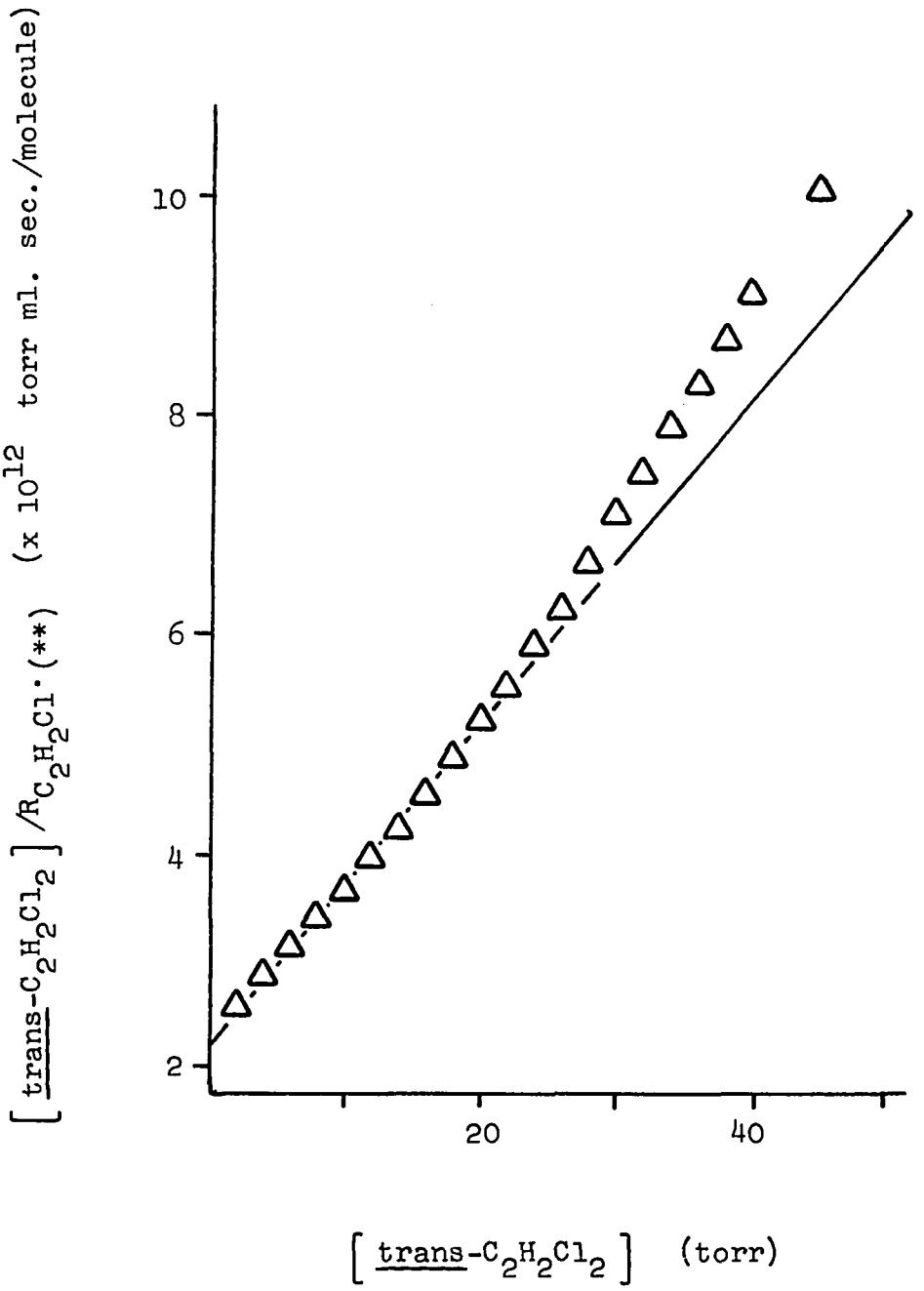


TABLE VIII

Rate Constants for the Production of Chlorovinyl Radicals in the Photolysis of trans-1,2-Dichloroethylene

Scavenger	Graphs on Pages	γ	$\frac{k_{deact(C_2H_2Cl_2)}}{k_{decomp}}$ (k_{18}/k_{17})
I_2	104-105	0.93×10^{-5}	2.3×10^{-18}
HCl (1)	106-107	1.9×10^{-5}	2.5×10^{-18}
HCl (2)	108-109	1.3×10^{-5}	2.0×10^{-18}

Tetrafluoromethane Deactivation Study

Scavenger	Graphs on Pages	γ	$\frac{k_{deact(CF_4)}}{k_{decomp}}$ (k_{20}/k_{17})
I_2	113-114	3.3×10^{-6}	4.0×10^{-19}

should be the same, as they refer to reactions of the two star excited state.

A value of 38.8 $\mathring{A}.^2$ was calculated by the method of Bellas, et al.[12] for the collisional cross-sectional area of trans-dichloroethylene. Using the average value of 2.3×10^{-18} for the ratio of rate constants of deactivation to decomposition, and assuming that each collision with a ground state molecule leads to deactivation of the two star excited state, the average lifetime of that ex-

cited state is calculated to be 5.2×10^{-9} seconds.

Study with an Inert Deactivator

Tetrafluoromethane was added to the reaction system in a series of experiments designed to determine the effects of an inert deactivator on the rates of production. To facilitate the handling of the sample, the tetrafluoromethane was removed before analysis. In pumping off the deactivator, a sizable and indeterminate portion of the acetylene and chloroacetylene was lost. Thus, of the primary products, only chloroiodoethylene presented reliable data (see Table XX in Appendix A).

With this paucity of data on the other primary products and because chlorovinyl radicals are produced by two different excited states, it is impossible to give a full mathematical treatment to this data. The mechanism must be simplified in order to derive an equation which can be graphed. The simplification is the assumption that all chlorovinyl radicals come from the two star excited state. This is not that bad an assumption, for judging by what chloroacetylene data there is, the production of chlorovinyl radicals from the one star excited state accounts for less than 10% of the total production of chlorovinyl radicals.

This simplified mechanism for the production of chlorovinyl radicals, and thus of the chloroiodoethylenes, is:

$$\underline{tr}\text{-}C_2H_2Cl_2 + h\nu' \longrightarrow C_2H_2Cl_2^{**} \qquad (12b)$$

$$C_2H_2Cl_2^{**} \longrightarrow C_2H_2Cl + Cl \qquad (17)$$

$$C_2H_2Cl_2^{**} + C_2H_2Cl_2 \longrightarrow 2\ C_2H_2Cl_2 \qquad (18)$$

$$C_2H_2Cl_2^{**} + CF_4 \longrightarrow C_2H_2Cl_2 + CF_4 \qquad (20)$$

$$C_2H_2Cl + I_2 \longrightarrow C_2H_2ClI + I \qquad (19a)$$

By mathematical processes similar to those shown before, the following equations can be derived:

$$\frac{\left[\underline{tr}\text{-}C_2H_2Cl_2\right]}{\left[CF_4\right]R_{C_2H_2ClI}} = \frac{k_{20}}{\gamma k_{17}} + \frac{1}{\gamma}\left(1 + \frac{k_{18}}{k_{17}}\left[\underline{tr}\text{-}C_2H_2Cl_2\right]\right)\frac{1}{\left[CF_4\right]}$$

$$\frac{\left[\underline{tr}\text{-}C_2H_2Cl_2\right]}{R_{C_2H_2ClI}} = \frac{1}{\gamma}\left(1 + \frac{k_{18}}{k_{17}}\left[\underline{tr}\text{-}C_2H_2Cl_2\right]\right) + \frac{k_{20}}{\gamma k_{17}}\left[CF_4\right]$$

The graphs of these equations appear in Figure 25.

Were the value of k_{18}/k_{17} not known, nothing further could be extracted from these data. However, k_{18}/k_{17} was determined in the pressure studies. Therefore, the value of γ and, consequently, of k_{20}/k_{17} can be calculated. They are:

$$\gamma = 3.3 \times 10^{-6}$$

$$\frac{k_{20}}{k_{17}} = 4.0 \times 10^{-19}$$

These values also are included in Table VIII, page 110.

Figure 25A. Tetrafluoromethane Deactivation Study:

Application of Rate Equations for $R_{C_2H_2ClI}$

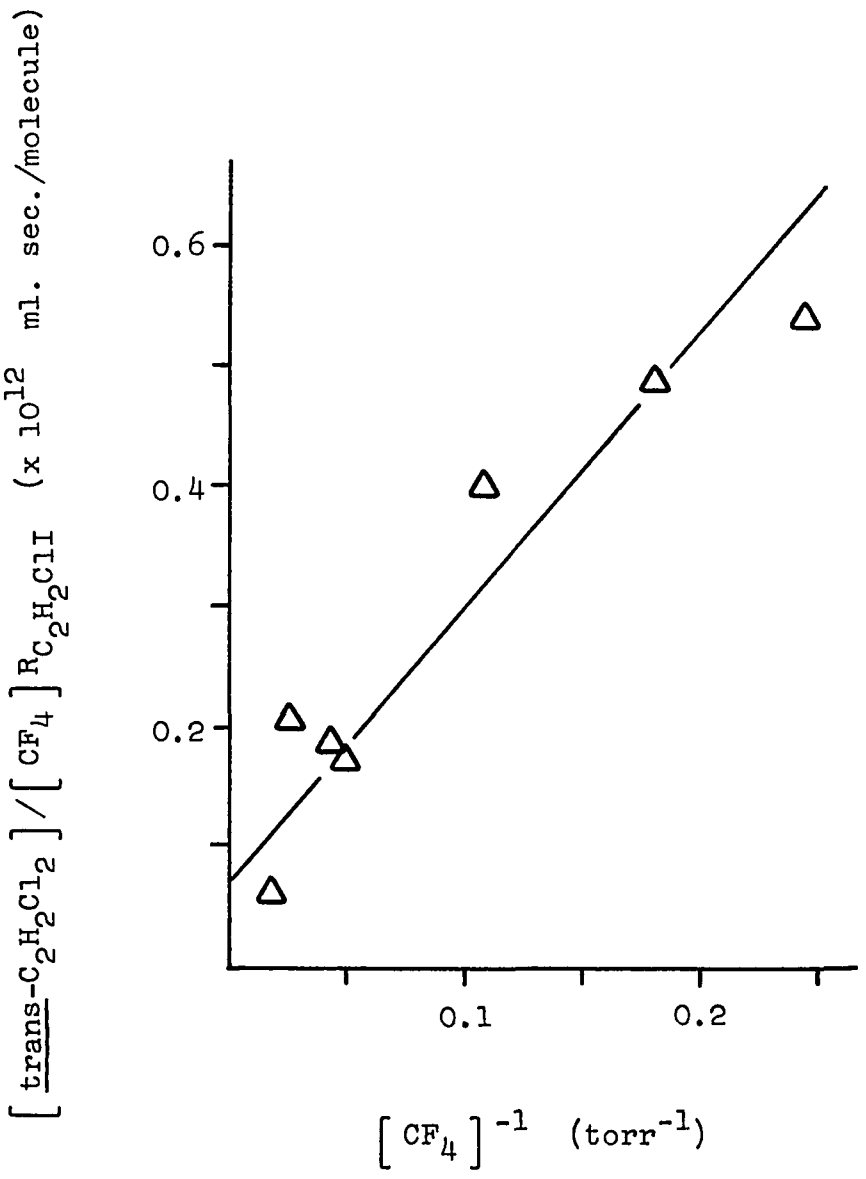
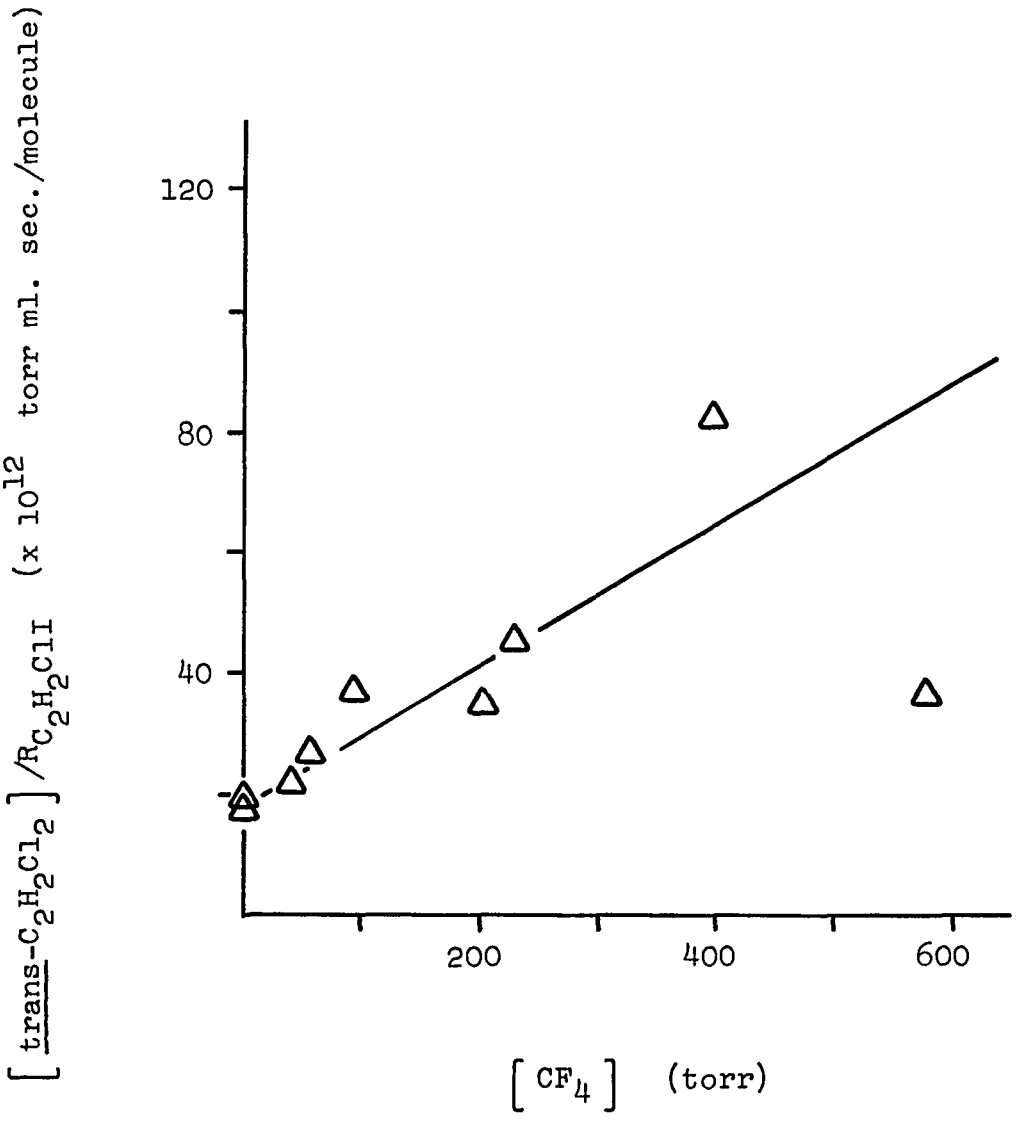


Figure 25B. Tetrafluoromethane Deactivation Study:

Application of Rate Equations for $R_{C_2H_2ClI}$



The value obtained for k_{20}/k_{17} can be used to compare tetrafluoromethane's efficiency relative to trans-dichloroethylene's in the deactivation of the two star excited state. By dividing k_{20}/k_{17} into k_{18}/k_{17}, a value is obtained for k_{18}/k_{20}, the ratio of tetrafluomethane's to trans-dichloroethylene's rate constants, and consequently, rates of deactivation of the two star excited molecule. As can be seen from the values in Table VIII, page 110, trans-dichloroethylene is almost six times as efficient a deactivator as tetrafluoromethane. An error of less than 10% was introduced by neglecting the contribution of the one star excited state to the production of chlorovinyl radicals.

Primary Processes in the Decomposition of 1,1-Dichloroethylene

In conjunction with the investigation of the photodecompositions of the 1,2-dichloroethylenes, a study of how the other isomer, 1,1-dichloroethylene, reacts under similar conditions should be of interest. While this comound was not studied as extensively as the 1,2-dichloroethylenes, the results are of interest.

As can be seen from the data in Tables XXI - XXIII in Appendix A, pressure studies were performed at 28° C., 18° C. and 45° C. In addition, there were short filter and deactivation studies. During the course of these experiments, the relative position of the light source and

the cell was not changed. All photolyses were performed in the presence of the scavenger, iodine. The products observed were acetylene, chloroacetylene, 1-chloro-1-iodoethylene (form the scavenging of the 1-chlorovinyl radical) and 1,1,2-trichloro-1-iodoethane. 1,1,1-Trichloro-2-iodoethane was observed occasionally.

Proposal of a Mechanism

There is considerable scattering in the data. Because of this, in a number of cases it was not possible to draw accurate graphs of the rates of production as initial pressure is increased. Particularly difficult was acetylene, where the possibility exists of the interference of small amounts of air which may have leaked into some samples between their collection and their analysis. This would cause overlarge values for the rates of production. Therefore, the data which will be presented, is that from which conclusions may be drawn.

Of the products, perhaps the least expected is acetylene. For, in the presence of a scavenger, it must be formed by a unimolecular process. This requires the formation of a carbene intermediate and a hydrogen shifting from one carbon to the other.

Table IX gives the values of $R_{C_2HCl}/R_{C_2H_2}$ from the pressure study performed at 18° C. It shows a remarkable consistency. The average value of the ratio is 3.5, with a mean deviation of 0.5. This is not apparent in other

TABLE IX

The Relationship between Acetylene and Chloroacetylene Production

Pressure (torr)	$R_{C_2HCl}/R_{C_2H_2}$	Pressure (torr)	$R_{C_2HCl}/R_{C_2H_2}$
0.36	3.55	4.05	3.74
0.48	2.25	4.23	3.03
0.49	3.55	4.89	4.98
1.17	3.95	6.05	3.04

data. But, it must be recalled that the interference of air will cause a diminution in the value of $R_{C_2HCl}/R_{C_2H_2}$. Yet, even in other series, there are a number of experiments in which the ratio has values of about 3. None is larger than 3.5. That $R_{C_2HCl}/R_{C_2H_2}$ is constant indicates that both acetylene and chloroacetylene arise directly and solely from the same excited state.

This is not the case for the relationship between the chlorovinyl radical and chloroacetylene. The graphs in Figure 26 show that $R_{C_2H_2ClI}/R_{C_2HCl}$ increases with the pressure of 1,1-dichloroethylene. The inconstancy of this relationship is clearly demonstrated in experiments in which sulfur hexafluoride was used as a deactivator. These photolyses were performed at 28° C., with sulfur hexafluoride pressures as high as 73 torr. While there was

Figure 26A. Change in R_{CH_2CClI}/R_{C_2HCl} with Pressure of CH_2CCl_2. Temperature = 28° C.

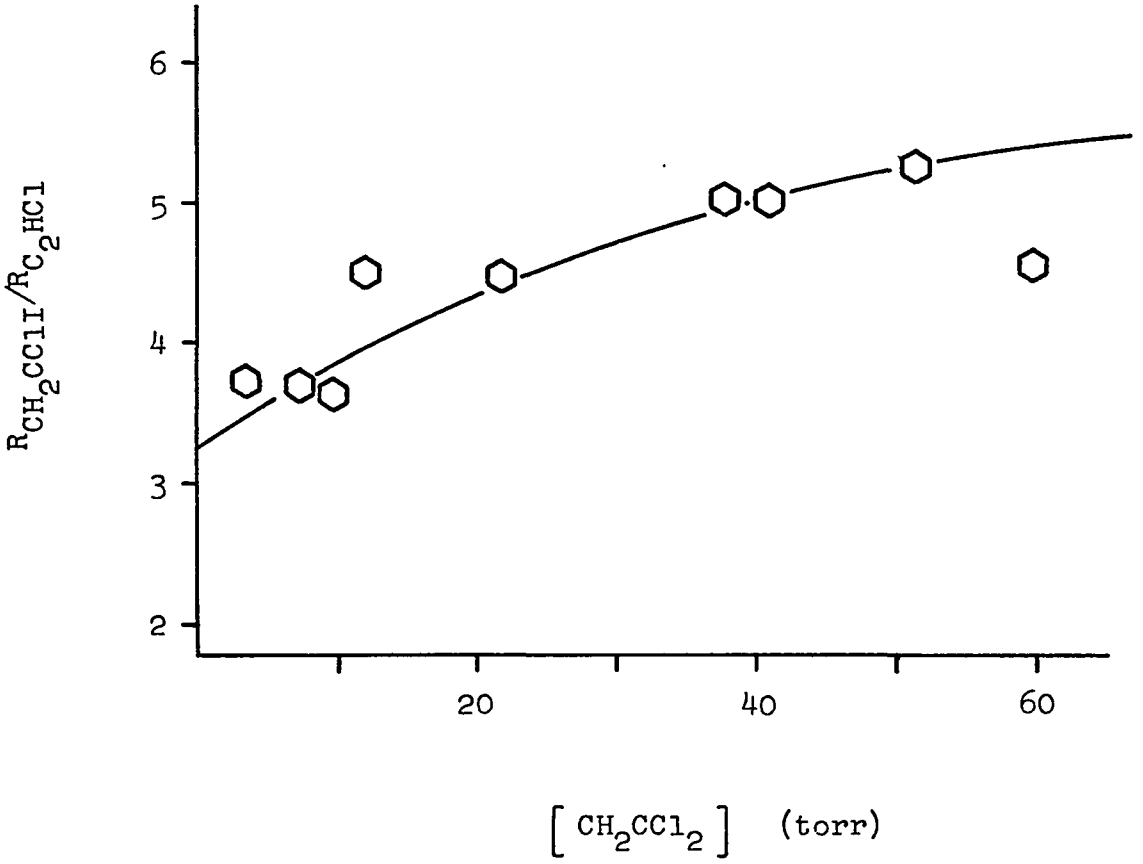
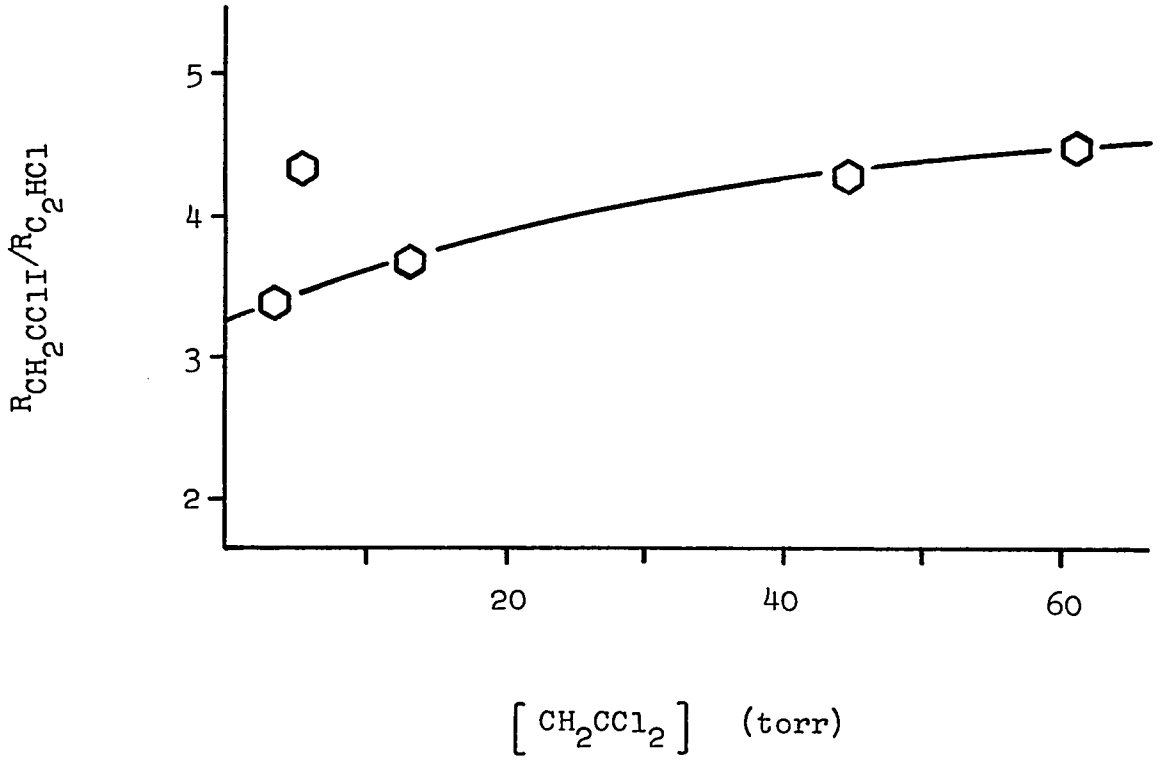


Figure 26B. Change in R_{CH_2CClI}/R_{C_2HCl} with Pressure of CH_2CCl_2. Temperature = 45° C.



a marked decrease in the production of chloroacetylene, there was no apparent reduction on the rate of chloroiodoethylene production.

Further information comes from the filter study. At high pressures, in the absence of filters, $R_{C_2H_2ClI}/R_{C_2HCl}$ is about 5 (see Figure 26). With filter 9-54 (2200 Å. cutoff), this ratio is reduced to 3.5. Filter 0-53 (2600 Å. cutoff) further reduced this ratio to 0.6.

All this demonstrates that more than one excited state leads to the decomposition products. The higher excited state is associated primarily with chloroiodoethylene production. Removal of the higher energy light by filters drastically reduces the production of this compound. It is this excited state which is not deactivated by sulfur hexafluoride. Chloroacetylene production, then, is associated primarily with the lower excited state.

The question remains as to whether any of the products is produced by both excited states. The deactivation study shows no decrease in chloroiodoethylene production. Were there any appreciable chlorovinyl radical production from the lower excited state (which showed deactivation), a reduction in the rate of chloroiodoethylene production would have been observed.

Most of the chloroacetylene must be produced by the lower excited state. This can be seen from the filter study. It cannot, however, be established whether all the chloroacetylene comes from that excited state. Neverthe-

less, Table IX shows that $R_{C_2HCl}/R_{C_2H_2}$ is constant. Were both excited states to produce chloroacetylene, they both would have to produce acetylene as well -- and in the same ratio. This seems unlikely. It is probable that the acetylenes are produced only by the lower excited state.

Before proposing a mechanism, some complications which arose with the 1,2-dichloroethylenes must be considered. With cis-dichloroethylene, the higher excited state produced an excited chlorovinyl radical which could decompose into acetylene. This cannot be the case with 1,1-dichloroethylene in the wavelength region investigated. Were it true, the ratio of acetylene to chloroacetylene would not be constant.

Another question which arose previously is whether the two chlorines which are lost by dichloroethylene are lost as a molecule or as individual atoms. With cis-dichloroethylene both occurred; with trans-dichloroethylene, only molecular elimination was observed. As with trans-dichloroethylene, the solution to this is found in the addition of a chlorine atom to the double bond of the starting material. This was done in trans-dichloroethylene by comparison of the rate of chlorovinyl radical production with the rate of isomerization (see page 153). Here, no isomerization is possible. However, the addition products were observed.

The data at 28° C. show that $R_{C_2H_2ClI}/R_{CH_2ClCCl_2I}$

Figure 27. Relationship Between $R_{CH_2ClCCl_2I}$ and R_{CH_2CClI}

A) Change in Rates of Production with Pressure of CH_2CCl_2

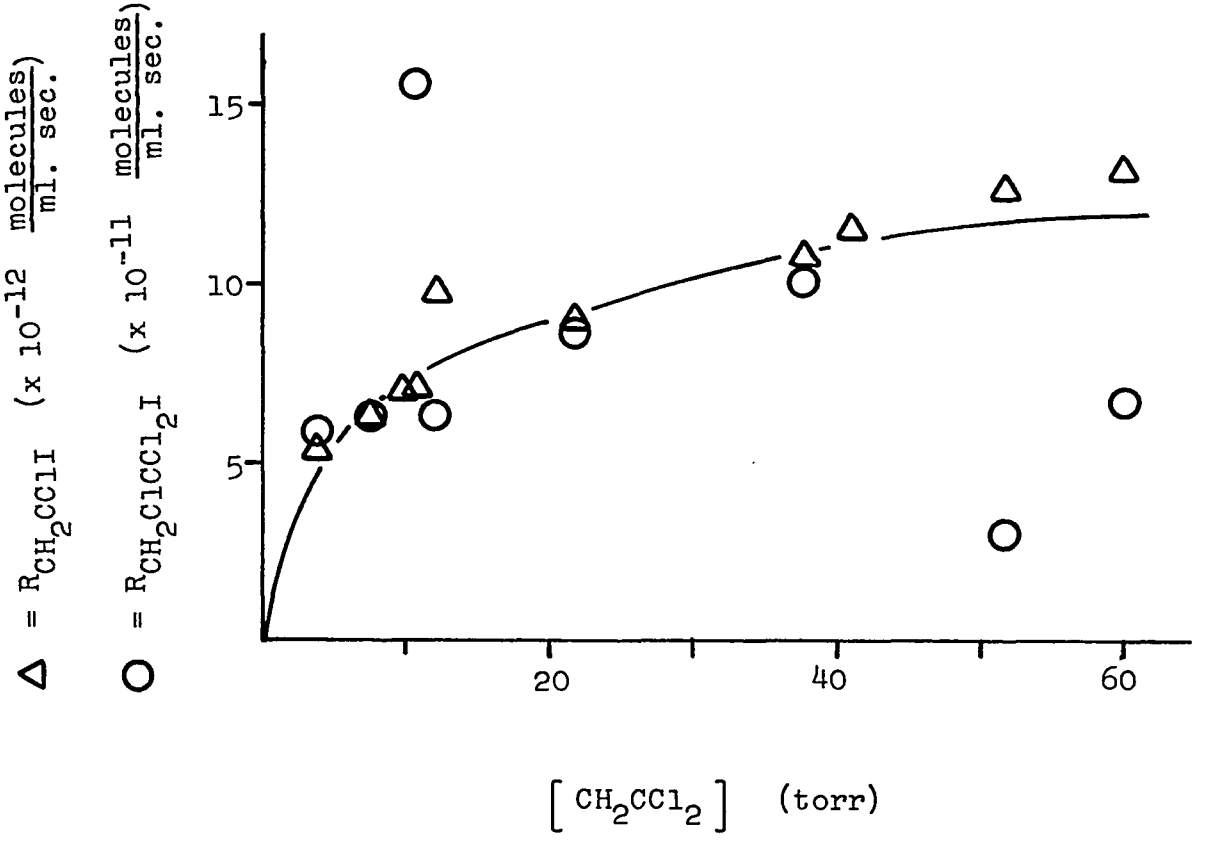
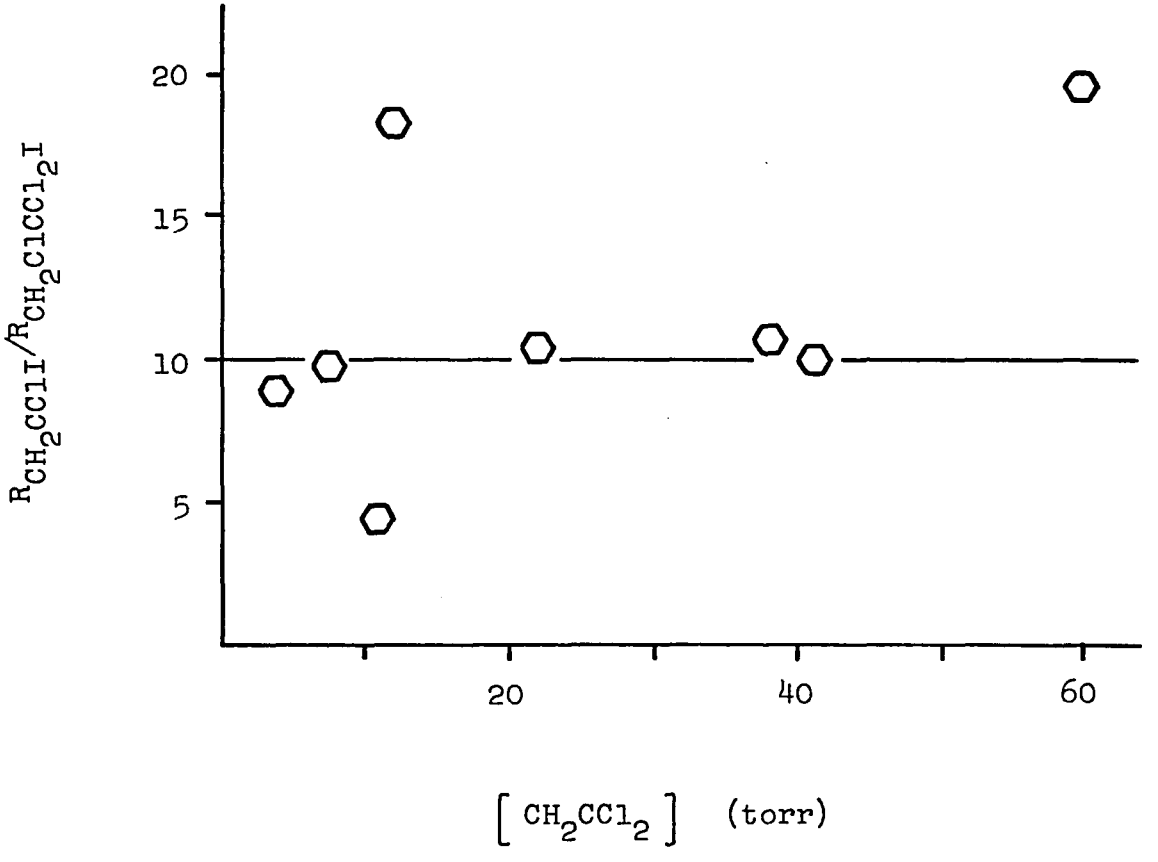


Figure 27. Relationship Between $R_{CH_2ClCCl_2I}$ and R_{CH_2CClI}

B) Change in $R_{CH_2CClI}/R_{CH_2ClCCl_2I}$ with Pressure of CH_2CCl_2



is constant, having a value of 10. This is shown in Figure 27. Thus, there is a relationship between the rate of production of chlorine atoms as the coproduct of the chlorovinyl radical and the rate of addition of chlorine atoms to the starting material. A constant value for this relationship might be expected if the production of chlorovinyl radicals is the only source of all chlorine atoms. Thus, acetylene production must be accompanied by the production of chlorine molecules. It also should be noted that acetylene is observed in the filter study under conditions in which molecular elimination is the only process possible (see page 40).

In the absence of filters, chloroacetylene also may be formed by atomic elimination of a hydrogen and a chlorine atom. Again, the production of chlorine atoms is barred. Moreover, there are no products observed which would suggest that hydrogen atoms are produced in this system.

With these questions answered, a mechanism now can be written which will account for the formation of the primary products.

$$CH_2CCl_2 + h\nu' \longrightarrow CH_2CCl_2^{**} \qquad (21)$$

$$CH_2CCl_2 + h\nu \longrightarrow CH_2CCl_2^{*} \qquad (22)$$

$$CH_2CCl_2^{**} \longrightarrow CH_2CCl + Cl \qquad (23)$$

$$CH_2CCl_2^{**} + CH_2CCl_2 \longrightarrow 2\ CH_2CCl_2 \qquad (24)$$

$$CH_2CCl_2^* \longrightarrow C_2HCl + HCl \quad (25)$$

$$CH_2CCl_2^* \longrightarrow C_2H_2 + Cl_2 \quad (26)$$

$$CH_2CCl_2^* + CH_2CCl_2 \longrightarrow 2\ CH_2CCl_2 \quad (27)$$

$$CH_2CCl + I_2 \longrightarrow CH_2CClI + I \quad (28)$$

Application of Rate Equations

From this mechanism, rate equations now may be derived. The methods involved are the same as those shown for the 1,2-dichloroethylenes. In the following equations, γ_* and γ_{**} are the absorption coefficients of the excited states $CH_2CCl_2^*$ and $CH_2CCl_2^{**}$, respectively.

For the production of 1-chloro-1-iodoethylene, the following equations can be derived:

$$\frac{1}{R_{CH_2CClI}} = \frac{k_{24}}{\gamma_{**}k_{23}} + \frac{1}{\gamma_{**}} \frac{1}{[CH_2CCl_2]}$$

$$\frac{[CH_2CCl_2]}{R_{CH_2CClI}} = \frac{1}{\gamma_{**}} + \frac{k_{24}}{\gamma_{**}k_{23}} [CH_2CCl_2]$$

In general, the data from the series at 18° C. are too scattered to be suitable for graphing. However, the data from 28° C. and 45° C. were used. The graphs are shown in Figures 28 and 29, respectively. The values obtained from the experiments at 28° C. are:

$$\gamma_{**} = 4.7 \times 10^{-5}$$

Figure 28A. Application of Rate Equations

for R_{CH_2CClI} at 28° C.

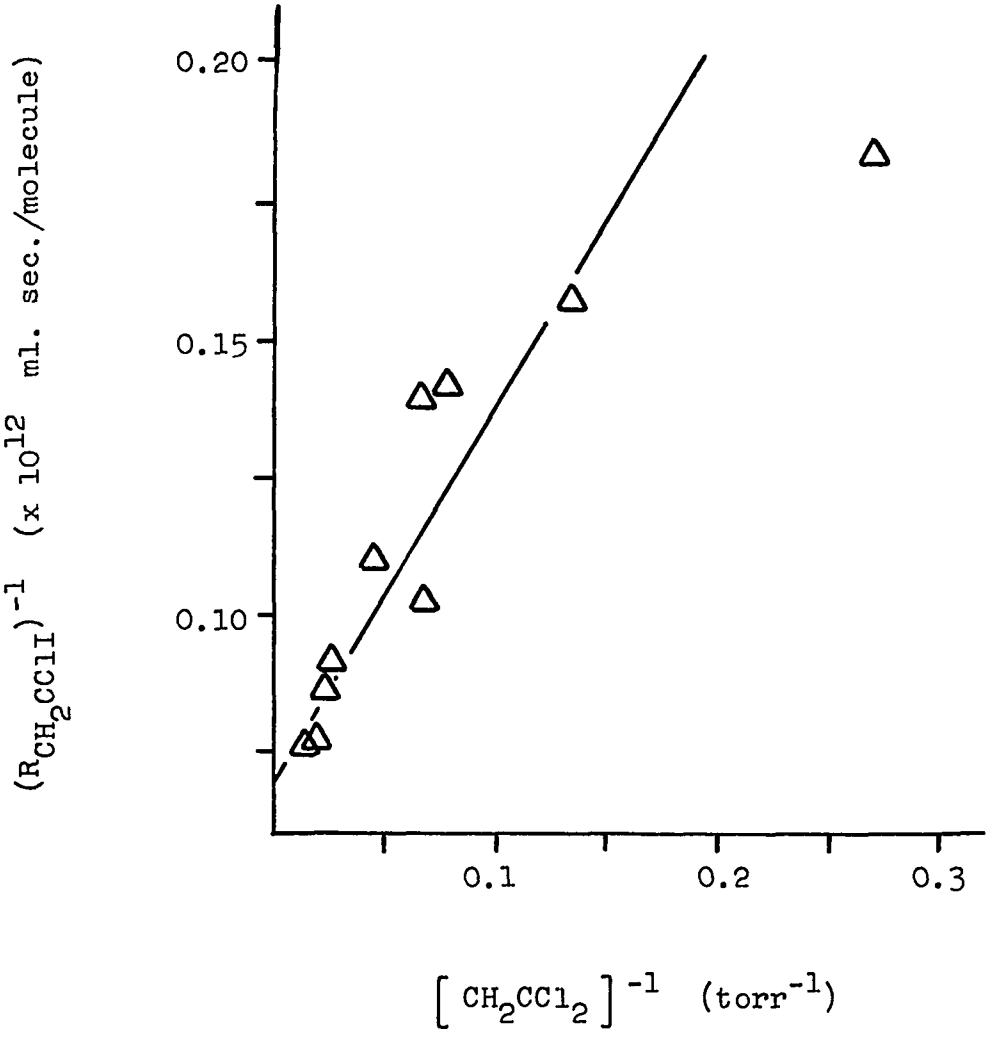


Figure 28B. Application of Rate Equations for R_{CH_2CClI} at 28° C.

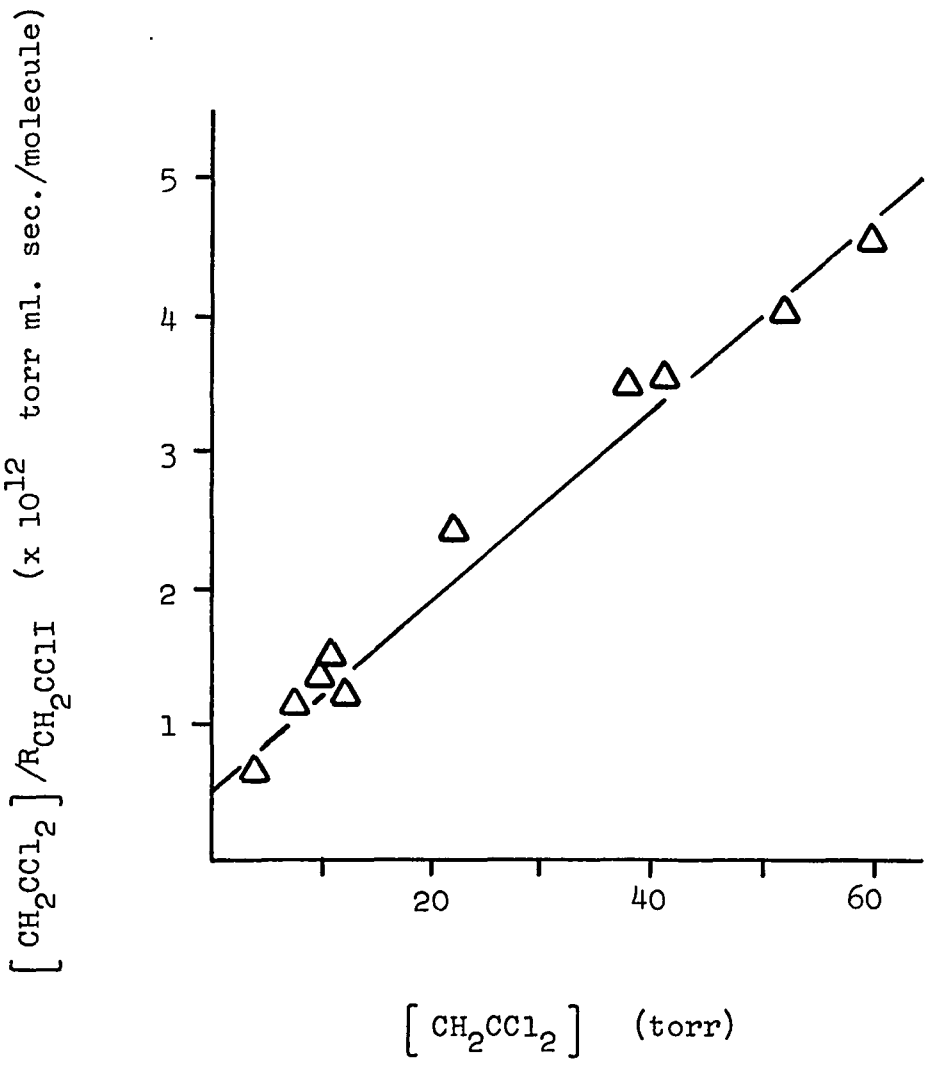


Figure 29A. Application of Rate Equations

for R_{CH_2CClI} at 45° C.

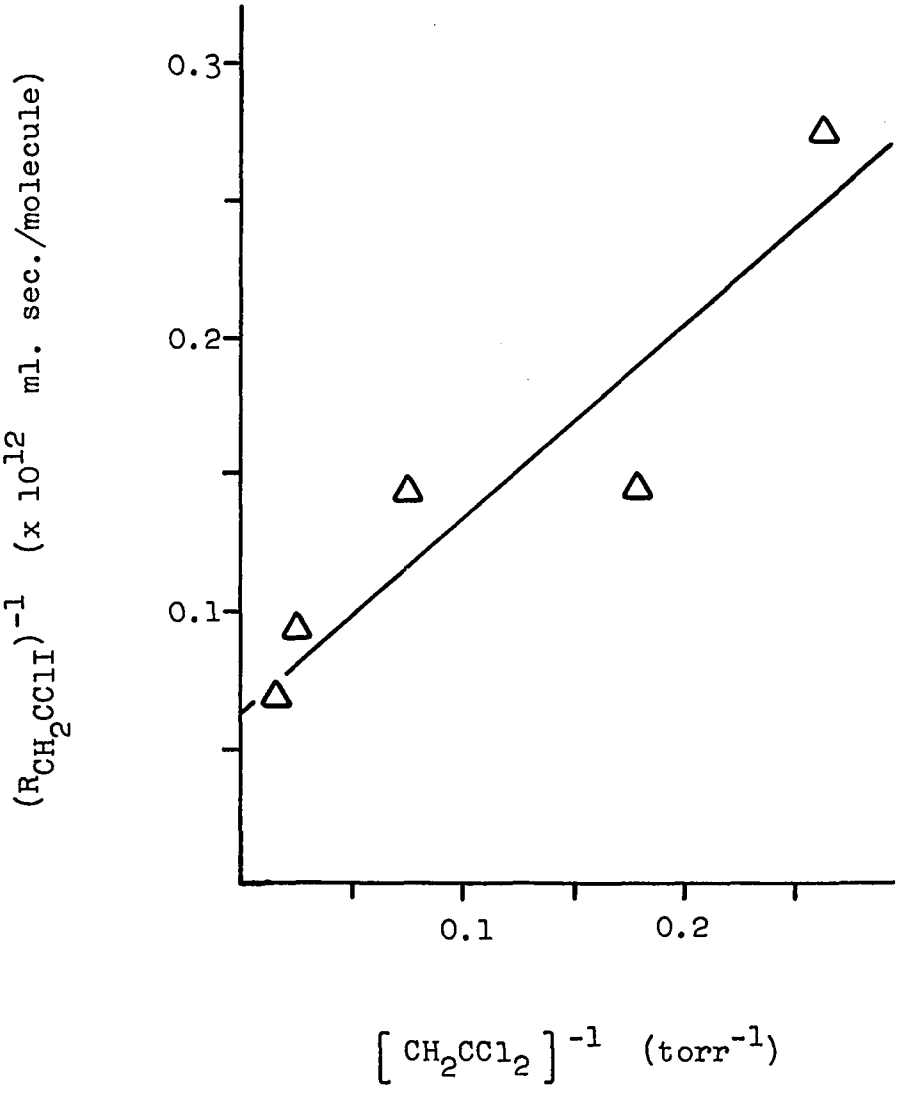
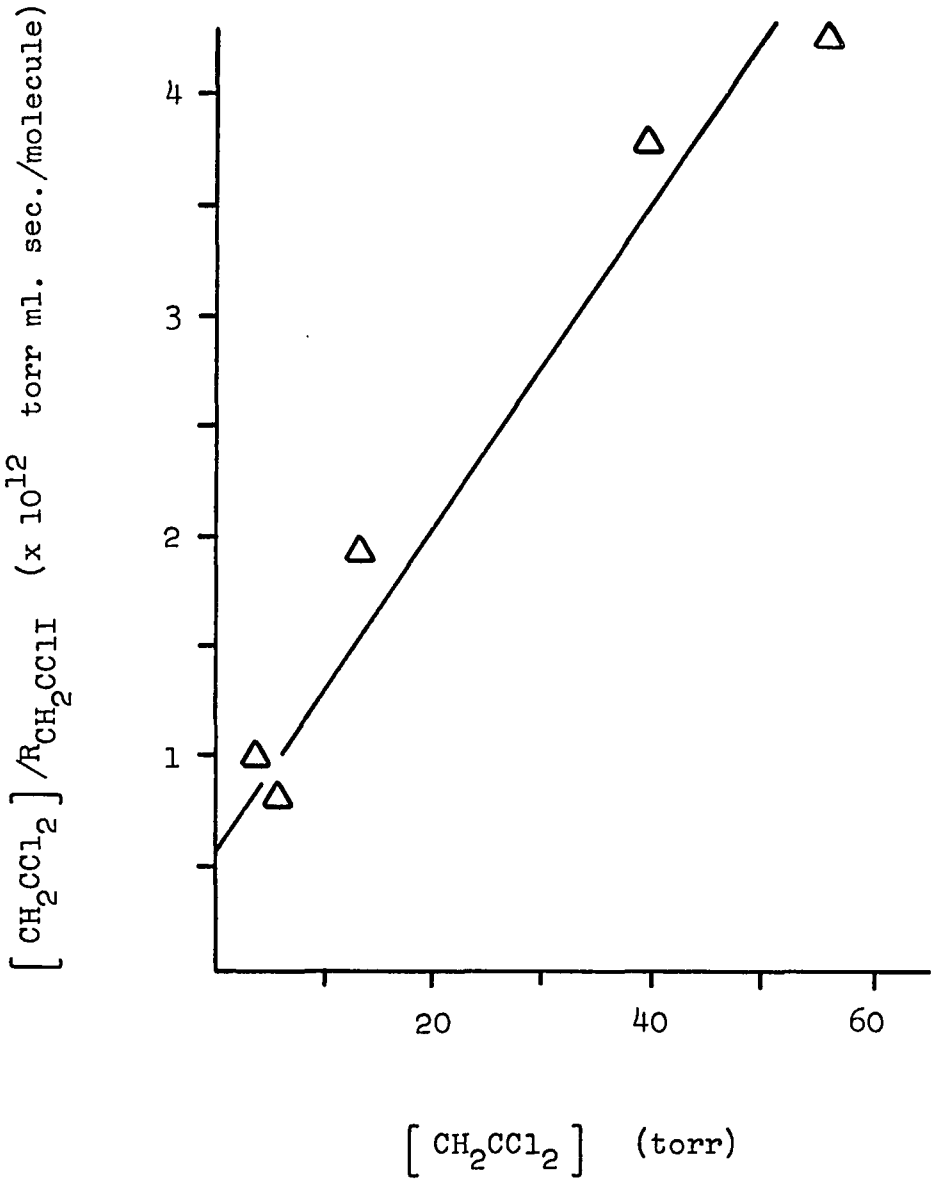


Figure 29B. Application of Rate Equations

for R_{CH_2CClI} at 45° C.



$$\frac{k_{24}}{k_{23}} = 3.2 \times 10^{-18}$$

and from the experiments at 45° C.:

$$\gamma_{**} = 4.5 \times 10^{-5}$$

$$\frac{k_{24}}{k_{23}} = 3.2 \times 10^{-18}$$

For chloroacetylene, the equations derived are:

$$\frac{1}{R_{C_2HCl}} = \frac{k_{27}}{\gamma_* k_{25}} + \frac{k_{25} + k_{26}}{\gamma_* k_{25}} \frac{1}{[CH_2CCl_2]}$$

$$\frac{[CH_2CCl_2]}{R_{C_2HCl}} = \frac{k_{25} + k_{26}}{\gamma_* k_{25}} + \frac{k_{27}}{\gamma_* k_{25}} [CH_2CCl_2]$$

Figures 30 and 31 show these graphs for the data from 28° C. and 45° C., respectively. From the graphs for experiments at 28° C., the following values were obtained:

$$\frac{k_{27}}{k_{25} + k_{26}} = 9.5 \times 10^{-18}$$

$$\frac{k_{25} + k_{26}}{\gamma_* k_{25}} = 4.6 \times 10^{4}$$

But, as was mentioned earlier, the ratio

$$\frac{R_{C_2HCl}}{R_{C_2H_2}} = \frac{k_{25}}{k_{26}} = 3.5$$

Figure 30A. Application of Rate Equations

for R_{C_2HCl} at 28° C.

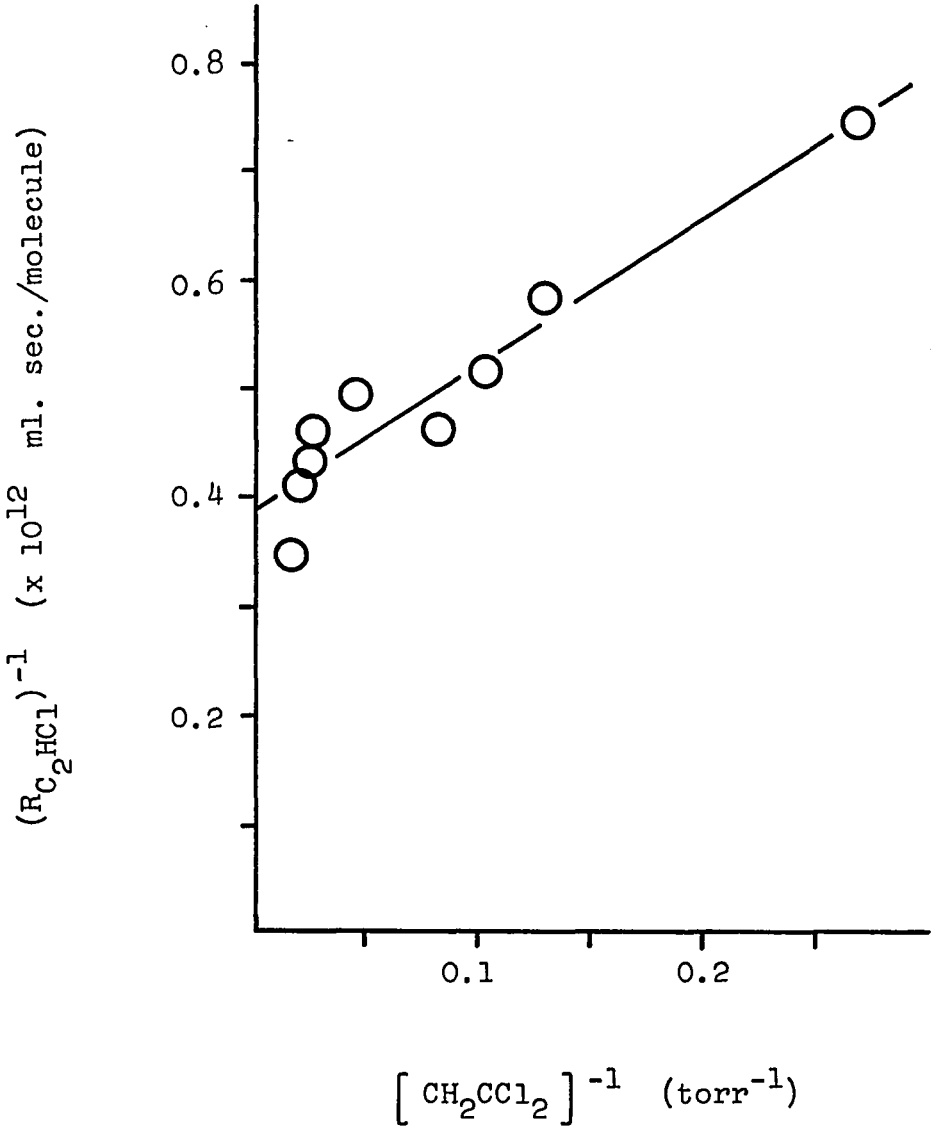


Figure 30B. Application of Rate Equations

for R_{C_2HCl} at 28° C.

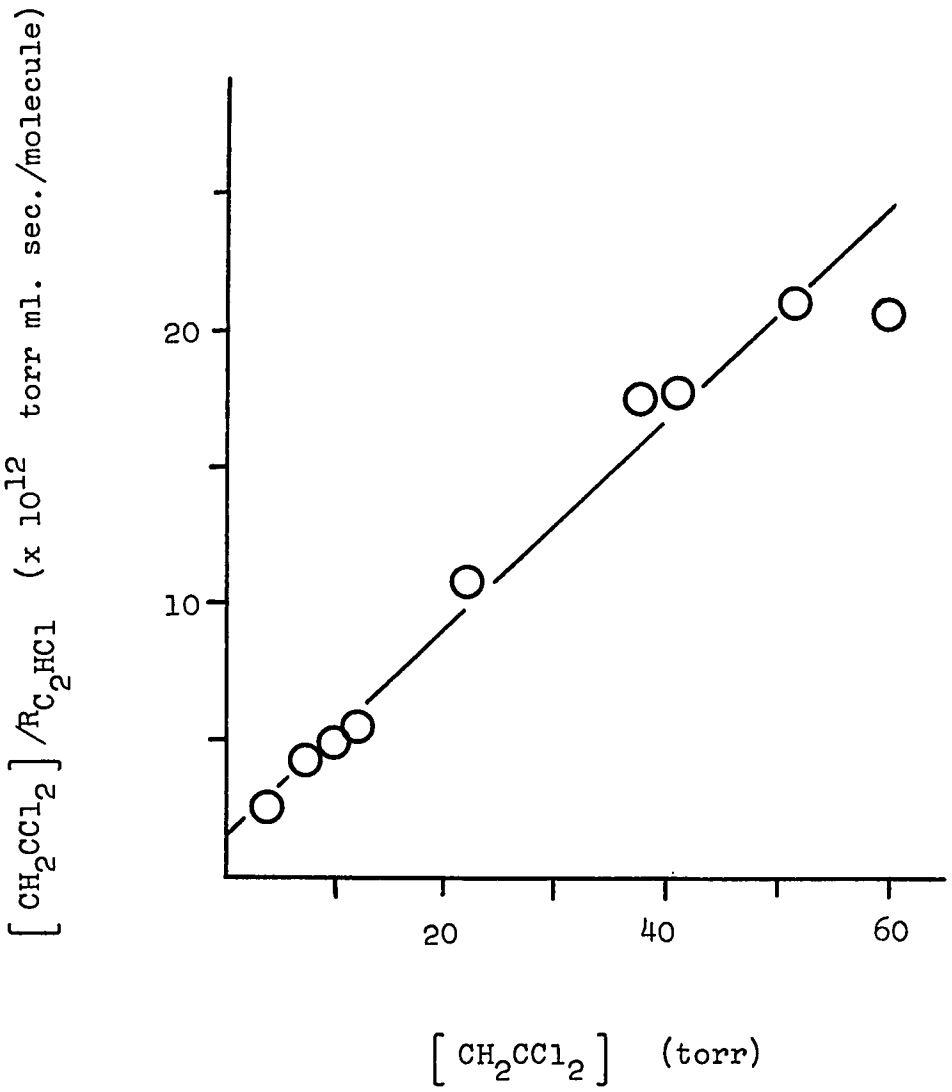


Figure 31A. Application of Rate Equations

for R_{C_2HCl} at 45° C.

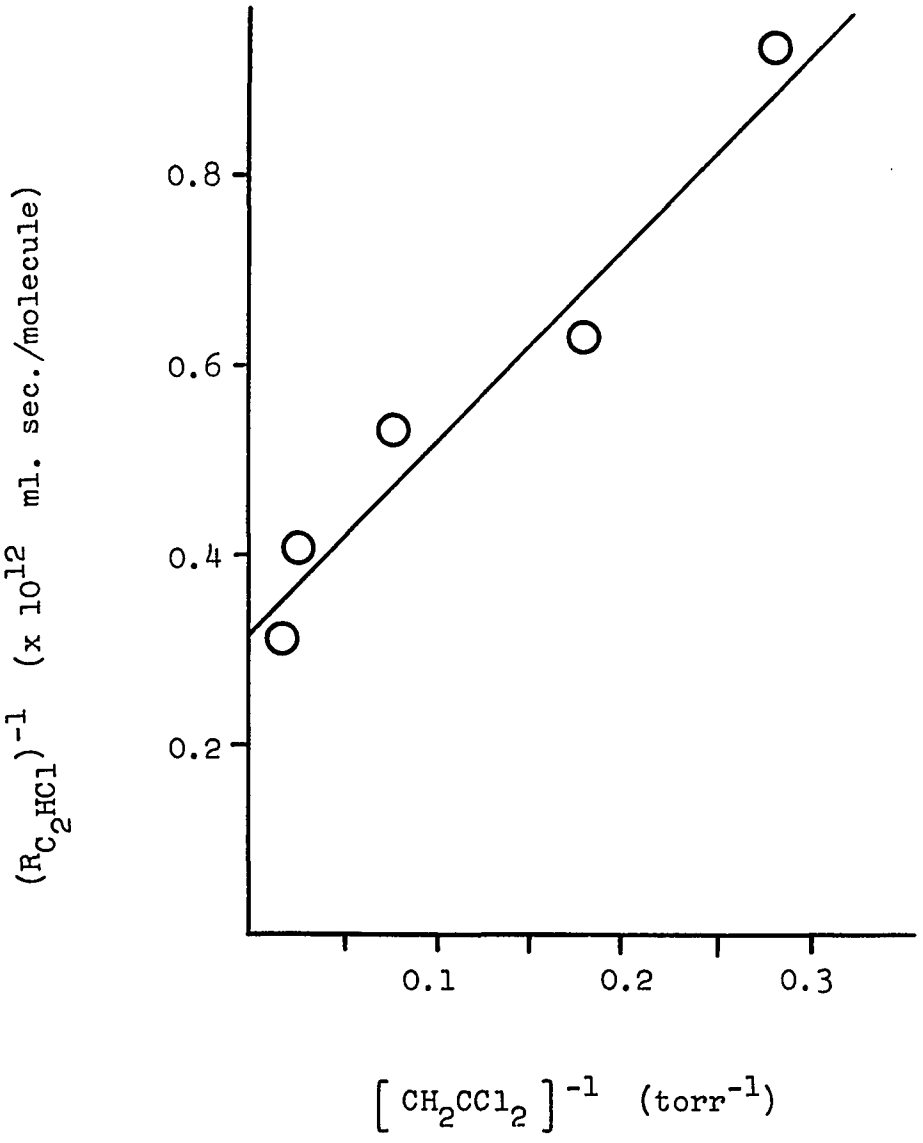
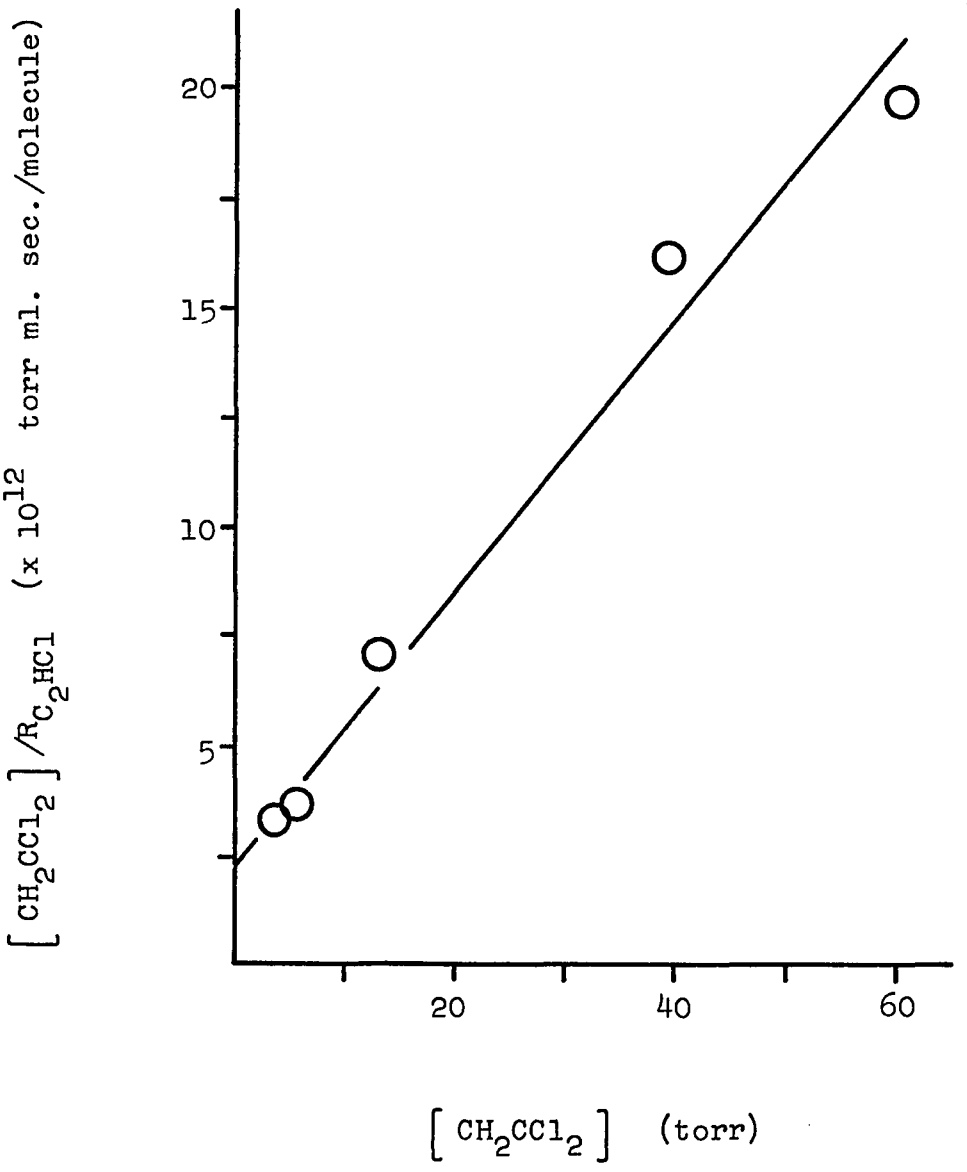


Figure 31B. Application of Rate Equations

for R_{C_2HCl} at 45° C.



Therefore, $\gamma_* = 2.8 \times 10^{-5}$

For the data from experiments performed at 45° C.,

$$\frac{k_{27}}{k_{25} + k_{26}} = 4.3 \times 10^{-18}$$

$$\frac{k_{25} + k_{26}}{\gamma_* k_{25}} = 7.1 \times 10^{4}$$

and thus, $\gamma_* = 1.8 \times 10^{-5}$

These values are listed in Table X.

From the values of the ratios of rate constants of deactivation to decomposition, $k_{27}/(k_{25} + k_{26})$ for chloroacetylene and k_{24}/k_{23} for chloroiodoethylene, the lifetimes of the excited states were calculated. This involved the standard assumption that each collision between an excited molecule and a ground state molecule resulted in the deactivation of the excited molecule. The collisional cross-sectional area of 1,1-dichloroethylene was calculated by the method of Bellas, et al.[12]: $\sigma^2 = 33.5$ Å.^{2}. The lifetimes also are listed in Table X. These data are in agreement with the earlier observation, gained from the sulfur hexafluoride deactivation study, that the two star excited state is shorter lived than the one star excited state.

The one star excited state has a shorter lifetime at 45° C. than at 28° C. It decomposes more readily at

TABLE X

Values from the Photolysis of 1,1-Dichloroethylene

A) γ

Temperature	C_2HCl	CH_2CClI
28° C.	2.8×10^{-5}	4.7×10^{-5}
45° C.	1.8×10^{-5}	4.5×10^{-5}

B) $k_{deact}/k_{decomp(total)}$

Temperature	C_2HCl	CH_2CClI
	$k_{27}/(k_{25} + k_{26})$	k_{24}/k_{23}
28° C.	9.5×10^{-18}	3.2×10^{-18}
45° C.	4.3×10^{-18}	3.2×10^{-18}

C) Lifetime (sec.)

Temperature	C_2HCl	CH_2CClI
28° C.	2.5×10^{-8}	0.84×10^{-8}
45° C.	1.1×10^{-8}	0.82×10^{-8}

higher temperatures. The decomposition of this excited molecule, thus, has an energy of activation. Application of the Arrhenius equation to these data gives a value of

1.7 kcal./mole as the energy of activation. There is no change in the lifetime of the two star excited state with the small change in temperature involved. Thus, the decomposition of the more energetic excited molecule seems unaffected by changes in temperature.

R_{CH_2CClI}/R_{C_2HCl} was observed to increase with pressure (see Figure 26, pages 118-119). From the mechanism above, the equation derived for this ratio is:

$$\frac{R_{CH_2CClI}}{R_{C_2HCl}} = \frac{\gamma_{**}k_{23}}{\gamma_{*}k_{25}} \frac{(k_{25} + k_{26}) + k_{27}\left[CH_2CCl_2\right]}{k_{23} + k_{24}\left[CH_2CCl_2\right]}$$

It is obvious that this equation is quite complex and does not allow a simple plot. Nevertheless, two extreme cases can be considered. At zero pressure, the equation simplifies to

$$\frac{R_{CH_2CClI}}{R_{C_2HCl}} = \frac{\gamma_{**}(k_{25} + k_{26})}{\gamma_{*}k_{25}}$$

At high pressures, as $k_{25} + k_{26}$ becomes negligible compared to $k_{27}\left[CH_2CCl_2\right]$ and k_{23} compared to $k_{24}\left[CH_2CCl_2\right]$, the equation predicts that an asymptote should be approached. At the asymptote,

$$\frac{R_{CH_2CClI}}{R_{C_2HCl}} = \frac{\gamma_{**}k_{23}k_{27}}{\gamma_{*}k_{24}k_{25}}$$

Figure 26, pages 118-119, shows the graphs of the change in R_{CH_2CClI}/R_{C_2HCl} with pressure of dichloroethylene at 28° C. and 45° C. For both temperatures, at zero pressure the ratio is 3.2. The plots also indicate that the ratio approaches a maximum with increasing dichloroethylene pressure, as predicted in the equation above.

For the data at 28° C., this maximum seems to be reached at a value for R_{CH_2CClI}/R_{C_2HCl} of about 5.7. Thus, the data yield:

$$\frac{\gamma_{**}(k_{25} + k_{26})}{\gamma_{*}k_{25}} = 3.2$$

$$\frac{\gamma_{**}k_{23}k_{27}}{\gamma_{*}k_{24}k_{25}} = 5.7$$

From this, it can be calculated that

$$\frac{k_{24}(k_{25} + k_{26})}{k_{23}k_{27}} = 0.56$$

a value which is in reasonable agreement with the figure of 0.34 obtained from the data in Table X, page 136.

From Figure 26, at 45° C. the asymptote seems to be at about 4.5. Consequently, the data yield:

$$\frac{\gamma_{**}(k_{25} + k_{26})}{\gamma_{*}k_{25}} = 3.2$$

$$\frac{\gamma_{**}k_{23}k_{27}}{\gamma_{*}k_{24}k_{25}} = 4.5$$

from which is calcultated

$$\frac{k_{24}(k_{25} + k_{26})}{k_{23}k_{27}} = 0.71$$

This is in excellent agreement with the value of 0.75 obtained from the data in Table X.

Thus, two completely independent approaches have yielded, within experimental, identical values for this ratio of rate constants. That such good agreement was reached may be considered a further indication of the correctness of the proposed mechanism.

THE *CIS* - *TRANS* ISOMERIZATION

INTRODUCTION

1,2-Dichloroethylene is one of the simplest compounds to exhibit cis - trans isomerism. For this reason, it was one of the first pairs of compounds in which the isomerization reaction was studied. It still is being studied now, more than four decades later.

Thermal Isomerizations

Ebert and Büll[32] were the first to investigate the thermal, gas phase isomerization. In a 1931 preliminary note (which was never followed by a full article), they reported that the equilibrium mixture, starting from either pure isomer, contained 63% cis-dichloroethylene.

Olson and Maroney[76] investigated the isomerization simultaneously induced by heat and light from a quartz mercury arc. They determined the composition of equilibrium mixtures at various temperatures. The results of the isomerization induced by heat alone were virtually the same as those performed under the influence of both light and heat. From their data, it can be calculated that the energy of activation of the isomerization reaction is 44 kcal./mole.

In 1936, Mahncke and Noyes[63] investigated the effect

of ultraviolet light from an aluminum spark on cis- and trans-dichloroethylene. They found evidence that chlorine atoms were being produced during the photoisomerization reaction. It was proposed that rather than proceeding via a freely rotating dichloroethylene excited state, the isomerization reaction was caused by the addition of a free chlorine atom to the starting material, accompanied by a simultaneous ejection of a chlorine atom from the molecule in an S_{N_2}-type reaction.

Jones and Taylor[50] studied the thermal isomerization of trans-dichloroethylene. In order to obtain reproducible results, they found it necessary to season the reaction cell. This reduced the rates of reaction observed. The seasoning would be destroyed by exposure to air. They reported that the unimolecular energy of activation was 41.9 ± 4.5 kcal./mole. The value given for the pre-exponential factor was 4.9×10^{-12}.

Jones previously, in otherwise unpublished work, had attempted to determine the Arrhenius constants for the isomerization of cis-dichloroethylene. But, he was unable to obtain consistent results, attributing this failure to the fact that cis-dichloroethylene would not deposit a carbonaceous layer of seasoning on the cell walls. Jones estimated that the energy of activation for the cis isomer was 27 - 37 kcal./mole.

In 1941, Tamamushi, et al.,[111] reported their inves-

tigation of the thermal isomerization. Apparently, they did not season the reaction cell. They found that the rate of isomerization was augmented by the addition of ethane or carbon dioxide to the reaction cell. But these gases had nowhere near the effect that the addition of oxygen or nitric oxide had. They reported a value of 16 kcal./mole for the energy of activation, and stated that the pre-exponential factor was very small.

This article complete the first decade of investigation into the isomerization of 1,2-dichloroethylene. World War II did not allow for such luxuries. It would be over fifteen years before another paper on the topic appeared. In that first decade, it was determined that, unlike the alkenes reported by Kistiakowski, the more stable isomer of 1,2-dichloroethylene is the cis isomer, comprising 60 - 65% of the equilibrium mixture in the gas phase. The value of the energy of activation was still open to question.

In 1957, Rabinovitch and Hulatt[89] published a note on the thermal isomerization of trans-dichloroethylene. They found that the results of numerous experiments had errors of up to 50%. They stated that the scattering in their data made it impossible to support any particular mechanism.

Molera and Ariza[68] again studied the thermal isomerization of trans-dichloroethylene, using a seasoned cell. For the energy of activation they found a value of 51.6

kcal./mole. The frequency factor was about 10^{15} sec.$^{-1}$.

Chlorine Atom Catalyzed Isomerizations

The turn of the decade saw the investigation of the isomerization turn more towards the idea proposed by Mahncke and Noyes[63] a quarter of a century earlier. In 1961, Wijnen[130] published a note on the photolysis of cis-dichloroethylene. He observed the formation of trans-dichloroethylene as a major reaction product. The following mechanism was proposed to account for the isomerization:

$$\text{cis-}C_2H_2Cl_2 + Cl \longrightarrow C_2H_2Cl_3^*$$

$$C_2H_2Cl_3^* \longrightarrow \text{cis-}C_2H_2Cl_2 + Cl$$

$$C_2H_2Cl_2^* \longrightarrow \text{trans-}C_2H_2Cl_2 + Cl$$

Further information on the chlorine atom catalyzed isomerization reaction comes from photochlorination studies. Dainton, et al.[7] proposed the following mechanism to explain their data on the photochlorination of both cis- and trans-dichloroethylene:

$$Cl_2 + h\nu \longrightarrow 2\,Cl$$

$$Cl + C_2H_2Cl_2 \longrightarrow C_2H_2Cl_3^*$$

$$C_2H_2Cl_3^* \longrightarrow x\ \text{tr-}C_2H_2Cl_2 + (1-x)\ \text{cis-}C_2H_2Cl_2 + Cl$$

$$C_2H_2Cl_3^* + Cl_2 \longrightarrow y\ \text{tr-}C_2H_2Cl_2 + (1-y)\ \text{cis-}C_2H_2Cl_2 + Cl_3$$

$$C_2H_2Cl_3^* + Cl_2 \longrightarrow C_2H_2Cl_3 + Cl_2^*$$

The value calculated for x was 25% and that for y was 43%. Both isomerization reactions were found to be independent of temperature.

From the photochlorination of cis-dichloroethylene, Dainton, et al.,[8] determined that for the addition of a chlorine atom to cis-dichloroethylene the energy of activation is 1.2 ± 0.7 kcal./mole and the pre-exponential factor is 2 ± 3 x 10^{10} liters/mole sec.

In a later paper on the same subject, Dainton[9] added another possible deactivation reaction for the excited trichloroethyl radical.

$$C_2H_2Cl_3^* + C_2H_2Cl_2 \longrightarrow C_2H_2Cl_3 + C_2H_2Cl_2$$

The inclusion of this reaction in the mechanism changes the values for x and y to 34% and 38%, respectively. The lifetime of the excited trichloroethyl radical was estimated to be 3 x 10^{-7} sec.

Knox and Riddick[56] also investigated the photochlorination of the 1,2-dichloroethylenes, but included propane in their reaction system. The abstraction of a primary hydrogen from propane, and the subsequent formation of 1-chloropropane, was used as a standard for rates of reaction. The following reaction scheme was found adequate to fit their data:

$$Cl + C_2H_2Cl_2 \longrightarrow C_2H_2Cl_3^*$$

$$C_2H_2Cl_3^* \longrightarrow x\ \underline{cis}\text{-}C_2H_2Cl_2 + (1-x)\ \underline{tr}\text{-}C_2H_2Cl_2 \quad Cl$$

$$C_2H_2Cl_3^* + M_i \longrightarrow C_2H_2Cl_3 + M_i$$

$$C_2H_2Cl_3^* \longrightarrow C_2H_2Cl_3$$

where M_i represents any of the various molecular species present in the reaction system. Knox found that irrespective of which isomer of 1,2-dichloroethylene the starting material was, the decomposition of the excited trichloroethyl radical produced 78% <u>cis</u>- and 22% <u>trans</u>-dichloroethylene. These values are in agreement with Dainton's original work,[7] but not with the revised values[9] which were published the following year.

For the rate constant of decomposition, Knox gave a value of,

$$k_{decomp} = 1.8 \times 10^{10}\ e^{-1.33\ kcal./RT}$$

Different rate constants were reported for the addition reactions of chlorine atoms to <u>cis</u>- and <u>trans</u>-dichloroethylene molecules:

$$k_{\underline{cis}} = 8 \times 10^{10}\ e^{-190\ cal./RT}$$

$$k_{\underline{trans}} = 3 \times 10^{10}\ e^{+170\ cal./RT}$$

No explanation could be given for the negative energy of activation for the addition to <u>trans</u>-dichloroethylene. The size of the energies of activation for the addition, about 0.2 kcal./mole, are a factor of ten smaller than

those reported by Dainton.

The last reaction in Knox's mechanism, the "unimolecular deactivation" of the excited trichloroethyl radical, was included to account for the observation that of the excited trichloroethyl radicals formed, 20% from cis-dichloroethylene and 10% from trans-dichloroethylene cannot decompose. But, Knox added, this reaction probably is an artifice which results from the pressure dependence of the decomposition reaction.

Later, Knox and Waugh[57] performed photochlorinations of the 1,2-dichloroethylenes, some in the presence of propane and inert deactivators, others in the absence of propane. They concluded that the mechanism previously given by Knox and Riddick[56] explains the observations. However, they revised downward by 30% the percentages given for excited trichloroethyl radicals which are subject to "unimolecular deactivation."

Wai and Rowland[124] studied the isomerization caused by the reaction of thermalized ^{38}Cl atoms, formed by the nuclear reaction $^{37}Cl(n,\gamma)^{38}Cl$, with cis- and trans-dichloroethylene. The analysis was done by radio gas chromatography, detecting only compounds containing ^{38}Cl atoms. As the radioactive isomers are formed only in the isomerization, the ratio of cis to trans ^{38}Cl isomers could be measured directly for either starting material.

They found that the ratio in which trans-$CHCl{=}CH^{38}Cl$ and cis-$CHCl{=}CH^{38}Cl$ are formed is constant at all pres-

sures (up to 600 torr), and from either isomer as the initial reactant. The observed value for the ratio of trans to cis isomers was 0.50 ± 0.05, or 67 ± 2% cis-CHCl=CH^{38}Cl. The lifetime of the excited 1,2-dichloro-1-^{38}chloroethyl radical was estimated to be 5 - 7 x 10^{-10} sec.

A different method of obtaining trichloroethyl radicals was used by Rajbenbach, et al.[52] They produced cyclohexyl radicals by γ-irradiation of cyclohexane. The cyclohexyl radicals then reacted with 1,1,2,2-tetrachloroethane. Abstraction of a chlorine atom produced the 1,1,2-trichloroethyl radical, which then decomposed into cis- or trans-dichloroethylene.

Their data show that the cis isomer composed 77 - 83% of the dichloroethylene produced, the appearance of the trans isomer increasing with increasing temperature. This data, which seems to contradict both Dainton and Knox, however, is questionable because of the occurrence of secondary reactions. The cyclohexyl radical, as evidenced by the appearance of both isomers of 1-chloro-2-cyclohexylethylene, adds onto the double bond of dichloroethylene. It may preferentially add onto one isomer more than the other, thus changing the ratio of cis- to trans-dichloroethylene. Also, the addition of cyclohexyl radicals may be reversible. The ratio of cis- to trans-dichloroethylene produced by the decomposition of the 1,2-dichloro-2-cyclohexylethyl radical may not be the same as that produced by the decomposition of the 1,1,2-trichloroethyl radical.

It is known that chlorine atoms are not the only radicals which catalyze the cis - trans isomerization of dichloroethylene. Tritium atoms,[122] bromine atoms[48] and chlorodifluoromethyl radicals,[31] among others, have been shown to cause the isomerization. It does not seem improbable that the addition of cyclohexyl radicals to 1,2-dichloroethylene would be reversible, and therefore, catalyze the isomerization.

But, as Knox and Waugh[57] say at the conclusion of their paper, "the problem [of deciphering the isomerization] will be cleared up only when data of some tenfold higher precision becomes available."

RESULTS AND INTERPRETATION

In the photolysis of either isomer of 1,2-dichloroethylene, the other isomer always is observed as a product. As was mentioned earlier, chlorine atoms also are produced in these photolyses. But, chlorine atom reactions have been shown to be the cause of the isomerizations reported in the photochlorination of symmetric dichloroethylenes.[7,56] It is reasonable, therefore, to investigate whether the isomerizations observed here are of the same type.

trans-1,2-Dichloroethylene

Filter Studies

The data in Table XI show the results of two filter studies performed on trans-dichloroethylene. One series was performed at an initial pressure of trans-dichloroethylene of 15 torr; the other, at 30 torr. Rates are given relative to the base of 1.00 for chloroacetylene. Values for acetylene are not given because those data were not very accurate. It must be admitted, however, that the ratio of acetylene to chloroacetylene seemed somewhat larger than the value reported earlier. This ratio does not appear to be wavelength dependent.

In the last column of Table XI are given values for

TABLE XI

Rates of Production (Relative to Chloroacetylene = 1.00) from Filter Studies on trans-1,2-Dichloroethylene in the Presence of Iodine

A) Pressure of trans-Dichloroethylene = 15 torr

Filter Used	Wavelength Range (Å.)	cis-$C_2H_2Cl_2$	tr-C_2H_2ClI	cis-C_2H_2ClI	$\frac{\text{tr-}C_2H_2ClI}{\text{cis-}C_2H_2ClI}$	$\frac{\text{cis-}C_2H_2Cl_2}{\text{cis- \& tr-}C_2H_2ClI}$
none	2000-4000	42.7	4.05	0.657	6.2	9.1
9-54	2200-4000	40.9	3.12	0.858	3.6	10.3
9-54	2200-4000	43.4	3.66	1.07	3.4	9.2
9-53	2600-4000	26.5	1.94	0.477	4.1	11.0
0-54	3000-4000	24.0	1.67	0.631	2.6	10.4
0-54	3000-4000	64.1	5.56	1.66	3.3	8.9

TABLE XI -- CONTINUED

B) Pressure of *trans*-Dichloroethylene = 30 torr

Filter Used	Wavelength Range (Å.)	*cis*-$C_2H_2Cl_2$	*tr*-C_2H_2ClI	*cis*-C_2H_2ClI	$\frac{\text{tr-}C_2H_2ClI}{\text{cis-}C_2H_2ClI}$	$\frac{\text{cis-}C_2H_2Cl_2}{\text{cis- \& tr-}C_2H_2ClI}$
none	2000-4000	85.8	10.5	2.25	4.6	6.7
none	2000-4000	85.8	11.5	3.10	3.7	5.9
none	2000-4000	59.6	8.45	1.82	4.6	5.8
none	2000-4000	79.7	8.67	2.26	3.8	7.3
9-54	2200-4000	98.4	6.10	1.25	4.9	13.4
9-54	2200-4000	106.	12.2	2.27	5.4	7.3
0-54	3000-4000	70.5	8.38	1.96	4.3	6.8
0-52	3400-4000	59.1	7.69	1.62	4.8	6.3
0-52	3400-4000	37.7	6.17	1.98	3.1	4.6

the ratio $R_{\underline{cis}\text{-}C_2H_2Cl_2}/R_{C_2H_2ClI(total)}$. Despite the variations in the ratio $R_{\underline{cis}\text{-}C_2H_2Cl_2}/R_{C_2HCl}$ and regardless of the presence or absence of a filter, the value of $R_{\underline{cis}\text{-}C_2H_2Cl_2}/R_{C_2H_2ClI(total)}$ is amazingly constant at either pressure, having a value of about 10 ± 1 at 15 torr and, omitting the results from one experiment, about 6.0 ± 1.4 at 30 torr. Thus, there seems to be a connection between the production of chloroiodoethylene and the production of <u>cis</u>-dichloroethylene, the isomerization process.

However, the production of chloroiodoethylene is also a measure of the amount of chlorine atoms produced via the primary processes

$$C_2H_2Cl_2^{*} \longrightarrow C_2H_2Cl + Cl \qquad (15)$$

$$C_2H_2Cl_2^{**} \longrightarrow C_2H_2Cl + Cl \qquad (17)$$

Because chlorine atoms previously have been shown to be a chain carrier in the isomerization process, it seems reasonable that the same type of isomerization process is occurring here. Giving support to this idea of a chain process is the fact that the amount of isomer produced far exceeds the sum of all other products (see Table XI).

In the case of <u>trans</u>-dichloroethylene, there are no indications that the following primary step occurs:

$$C_2H_2Cl_2^{**} \longrightarrow C_2H_2 + 2\,Cl \qquad (29)$$

Were this reaction to occur, one would expect to see changes in the ratio $R_{\underline{cis}\text{-}C_2H_2Cl_2}/R_{C_2H_2ClI(total)}$ as the ratio $R_{C_2H_2ClI(total)}/R_{C_2H_2}$ changes, for changes in the chlorine atom production accompanying this acetylene production would affect the production of the isomer, but not the production of chloroiodoethylene. Recalling that $R_{C_2H_2}/R_{C_2HCl}$ is constant (see Table VI, page 88), Part A of Table XI shows a 300% change in $R_{C_2H_2ClI(total)}/R_{C_2HCl}$, and thus a 300% change in $R_{C_2H_2ClI(total)}/R_{C_2H_2}$. Yet, no change in the ratio $R_{\underline{cis}\text{-}C_2H_2Cl_2}/R_{C_2H_2ClI(total)}$ is observed.

Moreover, the wavelength threshold for Reaction 29 is 2650 Å. It cannot occur at wavelenths longer than that. Yet, $R_{\underline{cis}\text{-}C_2H_2Cl_2}/R_{C_2H_2ClI(total)}$ is the same in regions where Reaction 29 is not possible as where it could occur. Thus, it may be concluded that throughout the wavelength range of this investigation, Reaction 29 does not occur. Acetylene production from trans-dichloroethylene is not accompanied by chlorine atom production.

Table XI also contains the ratio of trans- to cis-1-chloro-2-iodoethylene. This ratio has a value of 4, identical to the value observed when cis-dichloroethylene is photolyzed in the presence of iodine. It is a confirmation of the statement made previously that this ratio is invariant and is a justification for calculating the total

chloroiodoethylene rate by multiplying by five fourths the rate of production of trans-chloroiodoethylene.

Proposal of a Mechanism

The simplest mechanism explaining the chlorine atom induced, chain propagated isomerization is:

$$\text{trans-}C_2H_2Cl_2^{*} \longrightarrow C_2H_2Cl + Cl \qquad (15)$$

$$\text{trans-}C_2H_2Cl_2^{**} \longrightarrow C_2H_2Cl + Cl \qquad (17)$$

$$Cl + \text{trans-}C_2H_2Cl_2 \longrightarrow C_2H_2Cl_3^{*} \qquad (30)$$

$$C_2H_2Cl_3^{*} \longrightarrow \text{cis-}C_2H_2Cl_2 + Cl \qquad (31)$$

$$C_2H_2Cl_3^{*} \longrightarrow \text{tr-}C_2H_2Cl_2 + Cl \qquad (32)$$

$$C_2H_2Cl_3^{*} + C_2H_2Cl_2 \longrightarrow C_2H_2Cl_3 + C_2H_2Cl_2 \qquad (33)$$

This mechanism contains all the elements of a chain reaction:

a) initiation -- Réactions 15 and 17

b) propagation (the actual chain reaction) -- Reactions 30 through 32

c) termination (breaking the chain) -- Reaction 33

The ratio of cis-dichloroethylene to chloroiodoethylene represents the average number of isomerizations per chlorine atom produced. This is a reflection of the chain length, but is not, in itself, the actual value of the chain length. Both Reactions 31 and 32 are propagation steps. The ratio accounts only for Reaction 31. The

chain length could be obtained by multiplying the ratio by $(k_{31} + k_{32})/k_{31}$.

The values observed for the ratio of cis-dichloroethylene to chloroiodoethylene are about 10 at 15 torr and 6 at 30 torr. These results are consistent with the mechanism shown above. Initially, increasing the pressure of the starting material favors:

a) the initiation reaction, producing more chlorine atoms.
b) the addition of chlorine atoms to trans-dichloroethylene, forming excited trichloroethyl radicals, Reaction 30.

Consequently, the graphs of the rate of isomerization, Figures 32 - 34, initially show increases. At high enough pressures, however, these advantages are offset by the increased deactivation of the excited trichloroethyl radical, Reaction 33. This increase in the deactivation reaction breaks the chains of the isomerization sooner, shortening the chain length. Thus, in the filter studies, $R_{\underline{cis}\text{-}C_2H_2Cl_2}/R_{C_2H_2ClI(total)}$ is smaller at the higher pressure. As a result of these opposing effects, more but shorter chains, there is a maximum rate of isomerization at about 17 torr. This is observed in both cis- and trans-dichloroethylene, as is seen in Figures 31 - 33.

Application of a Rate Equation

From the mechanism on page 155, the rate of isomerization can be described as

Figure 32. Rate of Isomerization in the Photolysis of <u>trans</u>-$C_2H_2Cl_2$. Scavenger: I_2

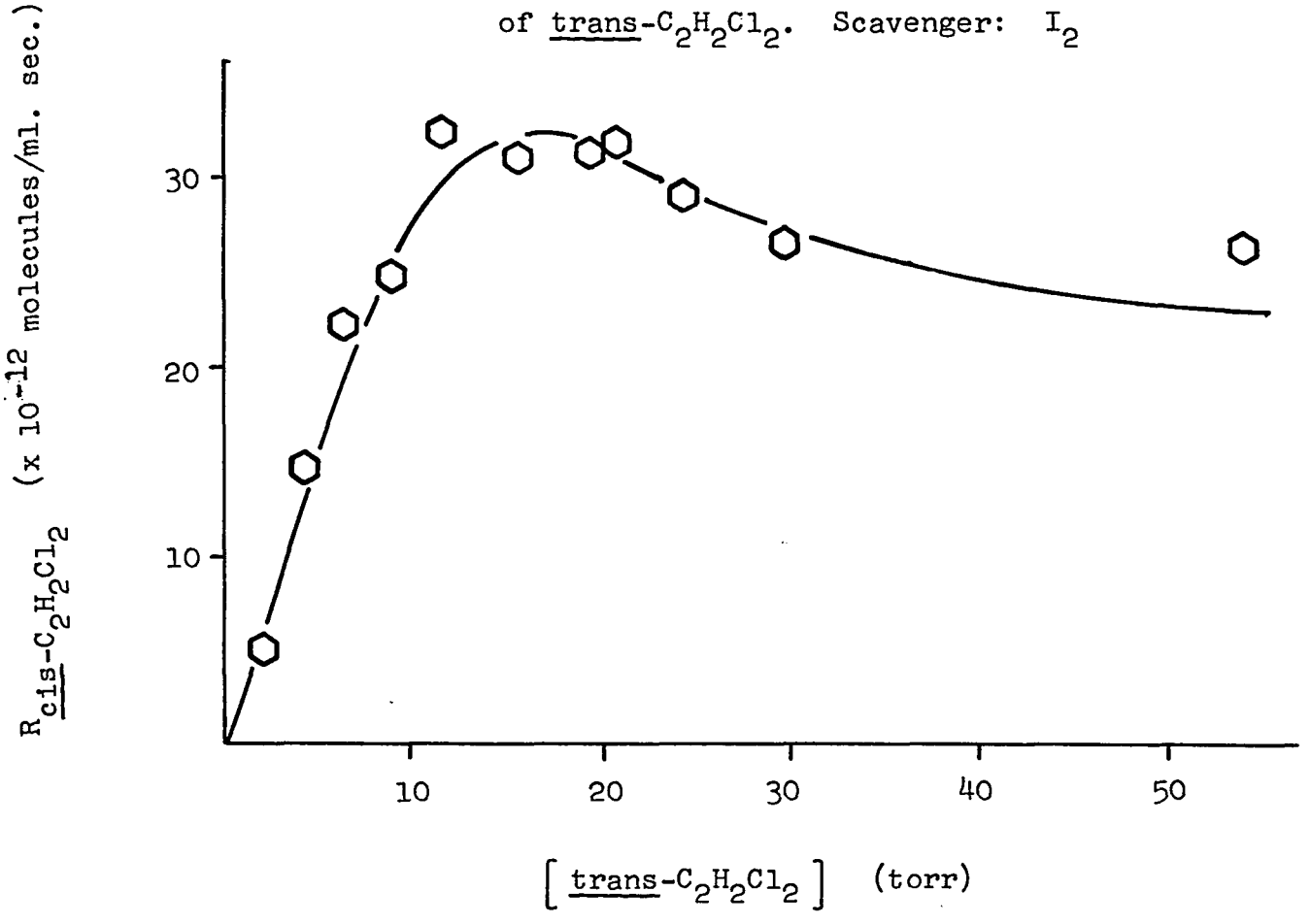


Figure 33. Rate of Isomerization in the Photolysis of <u>trans</u>-$C_2H_2Cl_2$. Scavenger: HCl (1)

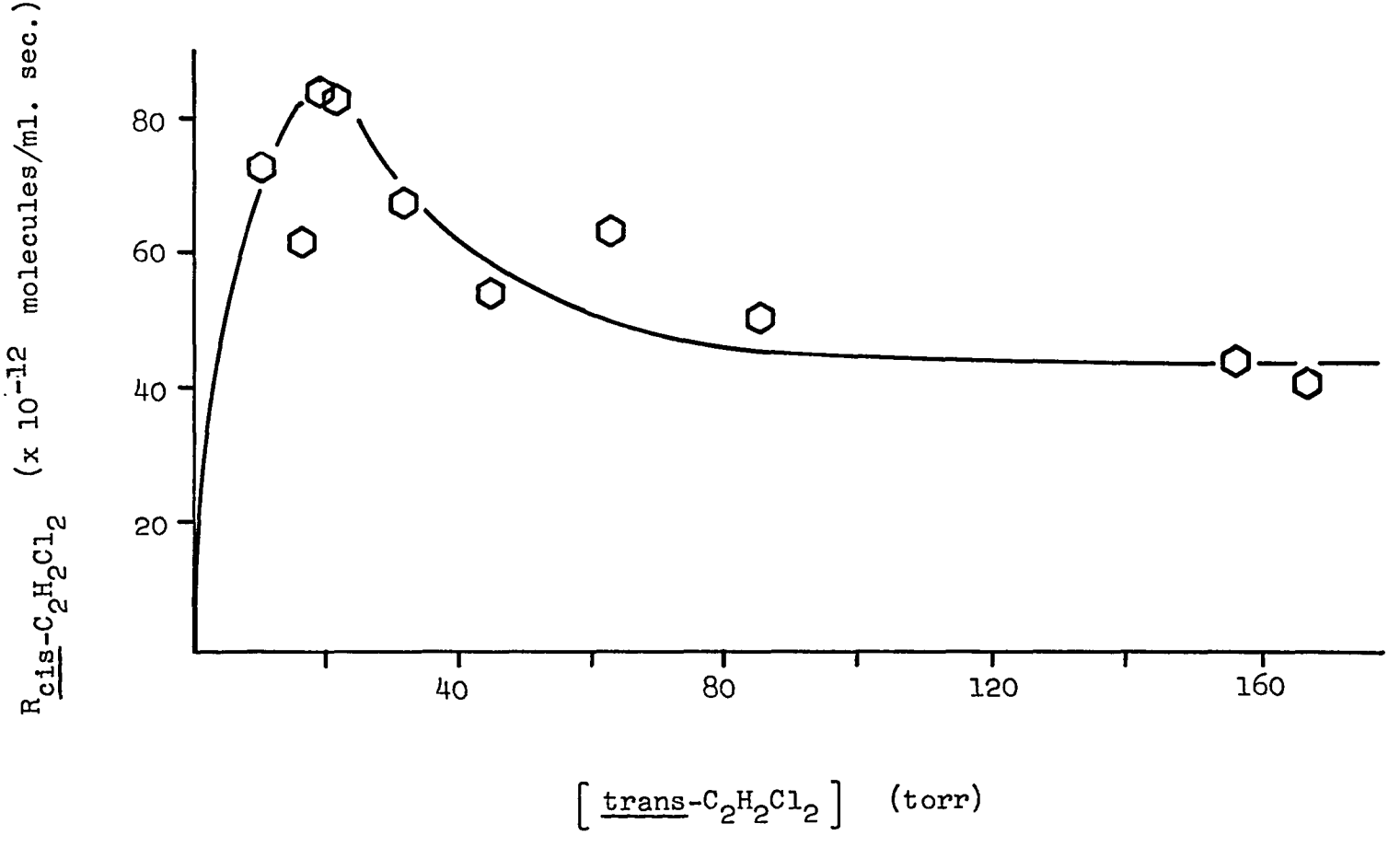
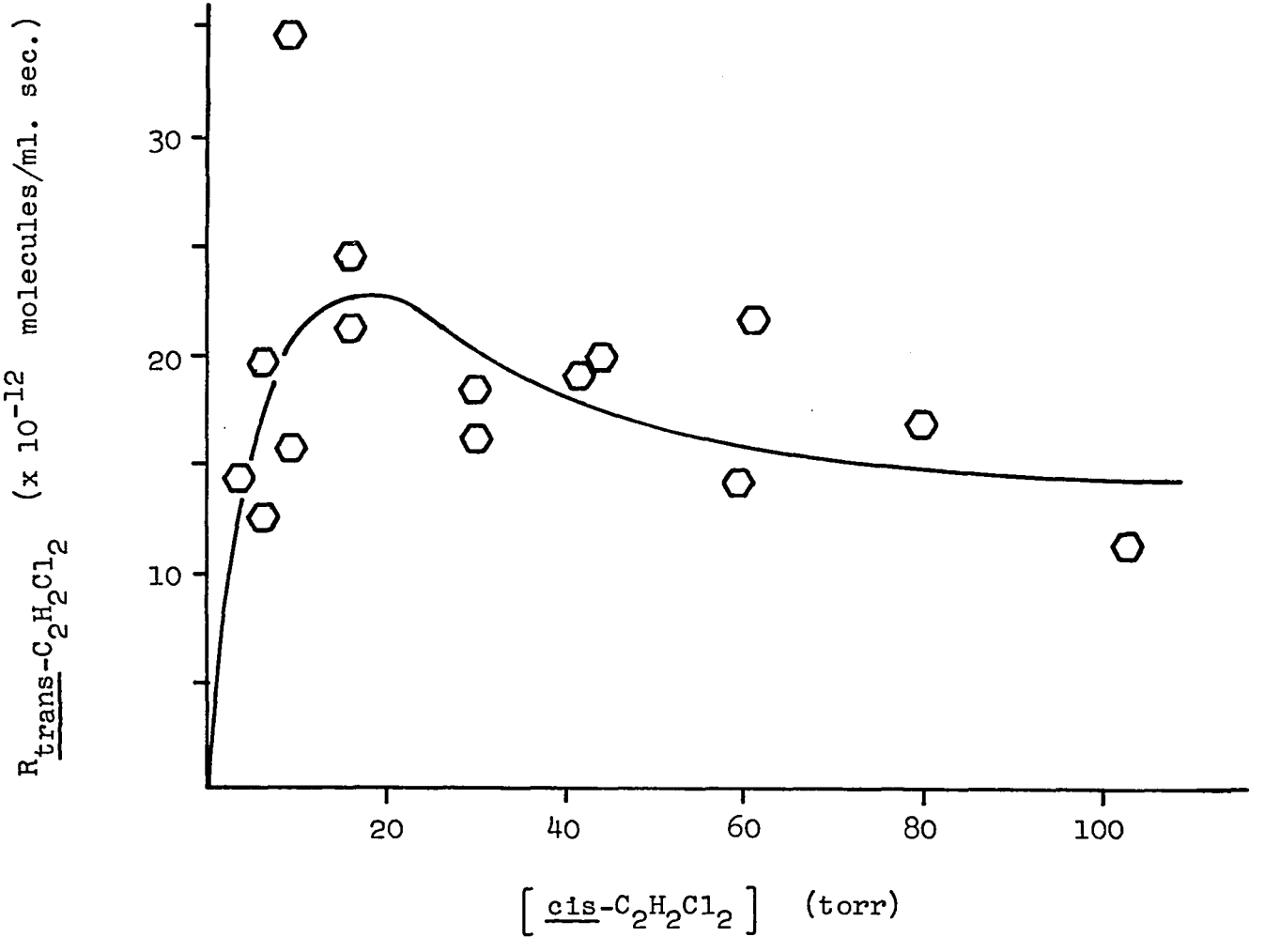


Figure 34. Rate of Isomerization in the Photolysis of cis-$C_2H_2Cl_2$. Scavenger: I_2



$$R_{\underline{cis}\text{-}C_2H_2Cl_2} = k_{31}\left[C_2H_2Cl_3^*\right]$$

For a chain reaction, the steady state approximation is applied to the entire chain process, not to the individual evanescent species. Thus,

$$R_{initiation} = R_{termination}$$

$$k_{15}\left[C_2H_2Cl_2^*\right] + k_{17}\left[C_2H_2Cl_2^{**}\right] = k_{33}\left[C_2H_2Cl_3^*\right]\left[C_2H_2Cl_2\right]$$

But, $$R_{C_2H_2ClI} = k_{15}\left[C_2H_2Cl_2^*\right] + k_{17}\left[C_2H_2Cl_2^{**}\right]$$

so that

$$\left[C_2H_2Cl_3^*\right] = \frac{R_{C_2H_2ClI}}{k_{33}\left[C_2H_2Cl_2\right]}$$

Substitution of this relationship in the original equation for the rate of isomerization, and rearranging, gives

$$\frac{R_{C_2H_2ClI}}{R_{\underline{cis}\text{-}C_2H_2Cl_2}} = \frac{k_{33}}{k_{31}}\left[\underline{trans}\text{-}C_2H_2Cl_2\right] \qquad \text{XIII}$$

The data from the one pressure study using iodine as a scavenger and from the two using hydrogen chloride as a scavenger were applied to this equation. Graphic representation of the data are given in Figures 35 - 37. While the data for the second hydrogen chloride series are too scattered to allow the drawing of a line with a reasonable degree of certainty, the other two series do give straight lines. The slopes of these lines gives as values for

Figure 35. Application of the Rate Equation for the Isomerization of <u>trans</u>-$C_2H_2Cl_2$. Scavenger: I_2

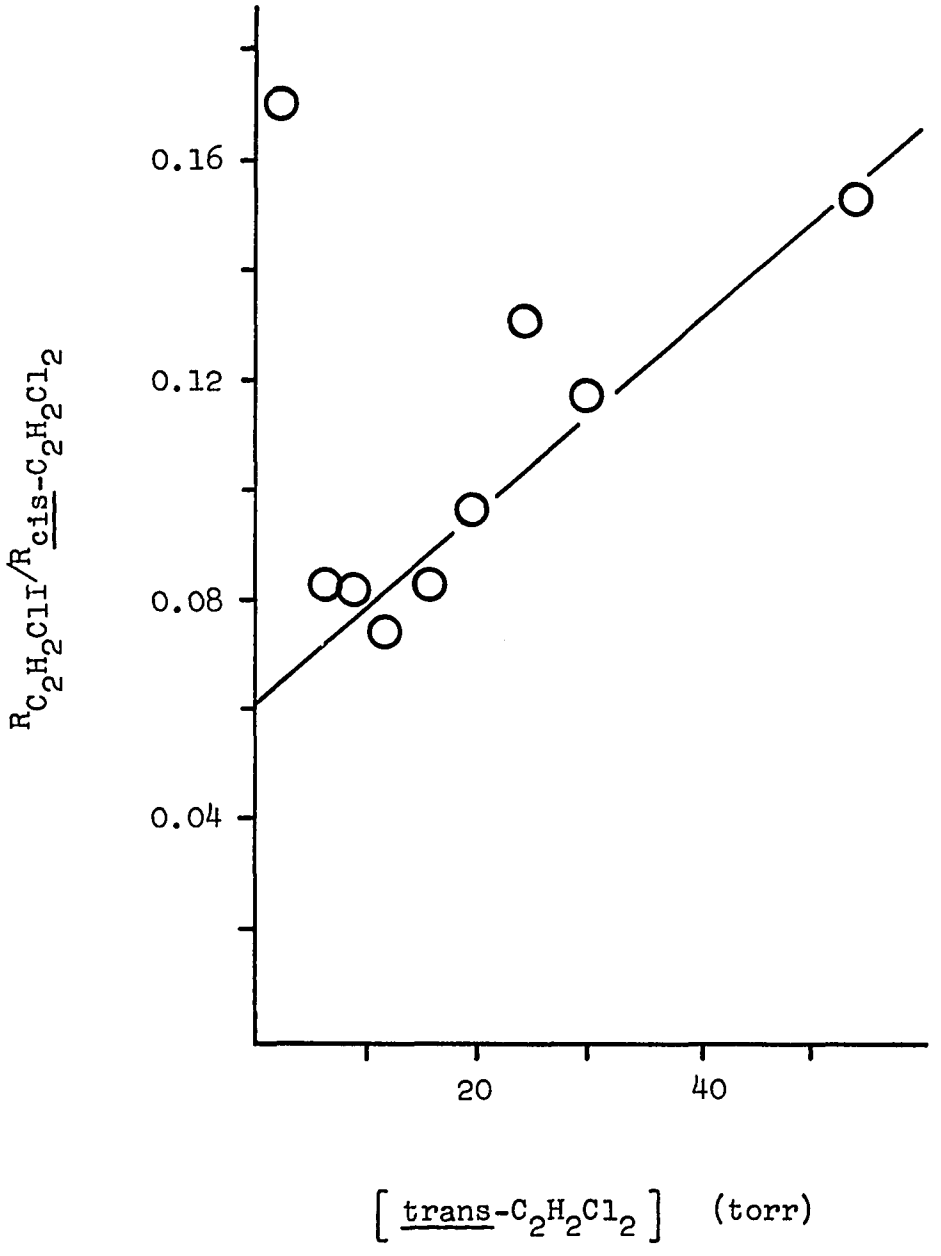


Figure 36. Application of the Rate Equation for the Isomerization of <u>trans</u>-$C_2H_2Cl_2$. Scavenger: HCl (1)

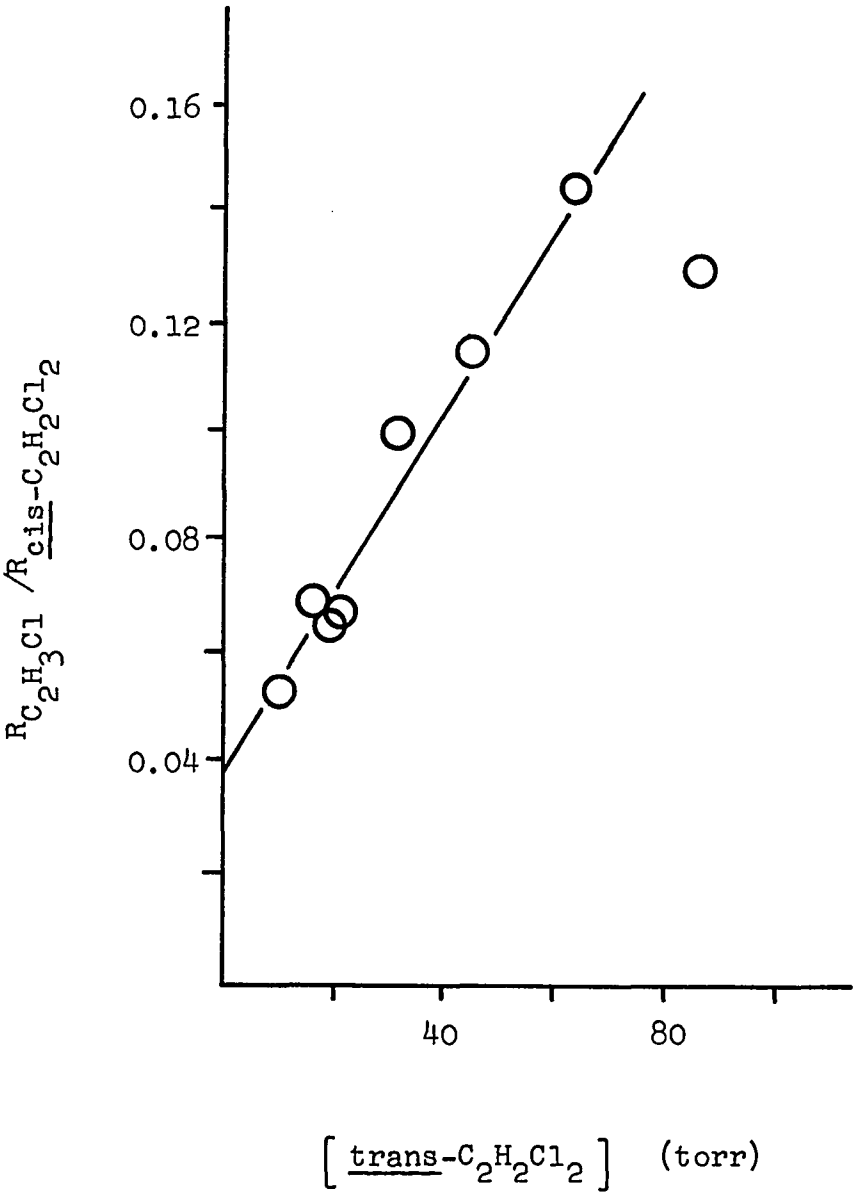
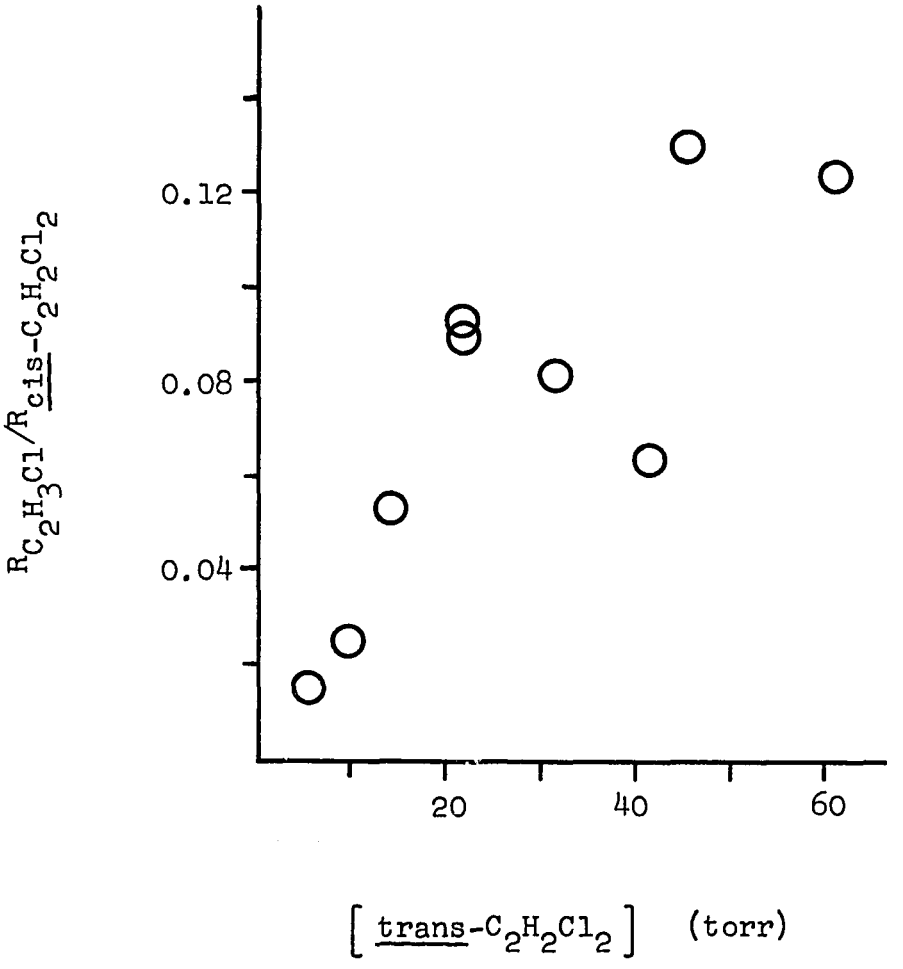


Figure 37. Application of the Rate Equation for the Isomerization of <u>trans</u>-$C_2H_2Cl_2$. Scavenger: HCl (2)



k_{33}/k_{31}: 5.1×10^{-20} for the iodine series and 5.2×10^{-20} for the first hydrogen chloride series. A linear least squares analysis of the data from the second hydrogen chloride series gave an almost identical value for the slope of the line: 5.5×10^{-20} and, as in the other two series, a small intercept.

According to Equation XIII, there should be no intercept, i.e., the intercept should be zero. In actuality, values of 0.66 for the iodine series and 0.032 ± 0.007 for the hydrogen chloride series were observed. Although the mechanism must be somewhat more complicated than the one from which Equation XIII was derived, the fact that the intercepts are very small and that there is a linear increase in the ratio $R_{C_2H_2ClI}/R_{\underline{cis}\text{-}C_2H_2Cl_2}$ with <u>trans</u>-dichloroethylene pressure clearly indicate that Reactions 31 and 33 play the major role in the isomerization process. This statement is reinforced by the fact that the iodine scavenged series gave the same value for k_{33}/k_{31} as the hydrogen chloride scavenged series did.

The oversimplification in the mechanism which most likely led to the appearance of intercepts in the graphs of Equation XIII was allowing for only one method of terminating the chain, namely, Reaction 33. There are other ways possible for breaking the chain. The chlorine atom, as well as the excited trichloroethyl radical, is a chain carrier. The mechanism has limited the chlorine atom to addition to the double bond. But various recombination

and abstraction reactions also are possible. Other reactions for the excited trichloroethyl radical also can be envisioned. These additional reactions, if they are relatively pressure independent, could account for the intercepts observed.

In addition, it is not unlikely that the deactivation reactions also lead to isomerization. Grabowski and Bylina[41] have shown that this occurs in the deactivation of the lowest lying triplet of both 1,2-dichloroethylenes. Though production of the isomer by deactivation would be minor compared to the chain process, it could be a factor in the intercept.

Were a complete derivation of a rate equation calculated, one which would include all of these possible termination reactions, the equation obtained would be extremely complex, having many terms. Graphing would not be a suitable means of analysis. A purely mathematical treatment would have to be used, viz., a least squares solution.

In order to solve the simultaneous equations which the least squares solution generates, a computer must be used. An example of the complexity of such rate equations in which more than one termination step is included in the mechanism is shown in Appendix B. In the same appendix is listed the program used to perform these calculations and a brief explanation of what the program is having the computer do.

The results of these purely mathematical considerations of the data were not good. Many of the coefficients calculated by the computer were negative. The computer, lacking rationality and a discerning eye, was not able to give less credence to points which appear far from the line being computed, as a person can do with a linear graph. Perhaps, this is why negative values were obtained. Perhaps, it is only that the data are not good enough for such a rigorous treatment. It is a well known fact that data from chain processes are difficult to reproduce. Or, perhaps, the wrong termination steps were chosen. Whatever the reason, the results are clear -- the mathematically obtained relative rate constants are unacceptable.

In any case, although the graphs, by having positive intercepts, indicate that the mechanism proposed is too simple, it should be realized that the intercepts are very small. Thus, whatever reactions have been omitted are not too important.

In Table XII are listed the values for the relative rate constants, $k_{deactivation}/k_{isomerization}$ (k_{33}/k_{31} for trans-dichloroethylene) and the intercepts obtained from the graphs. The value of the intercept seems to be dependent to some extent upon the scavenger used. The results from the slopes of the three pressure studies are in excellent agreement. The average value for k_{33}/k_{31} is 5.3×10^{-20} ml./molecule.

TABLE XII

Rate Constants for the Excited Trichloroethyl Radical

Isomer Photolyzed	Deactivator	Scavenger	Graph on Page	Intercept	$\frac{k_{deactivation}}{k_{isomerization}}$
					k_{33}/k_{31}
trans	trans	I_2	161	6.6×10^{-2}	5.1×10^{-20}
trans	trans	HCl (1)	162	3.8×10^{-2}	5.2×10^{-20}
trans	trans	HCl (2)	163	2.5×10^{-2}	5.5×10^{-20}
					k_{33}/k_{32}
cis	cis	I_2	169	2.2×10^{-2}	3.3×10^{-20}
cis (filters)	cis	I_2	171	0.21×10^{-2}	3.1×10^{-20}
					k_{34}/k_{31}
trans	CF_4	I_2	175	12.3×10^{-2}	1.1×10^{-20}

cis-1,2-Dichloroethylene

For cis-dichloroethylene, the only scavenger used was iodine. An equation similar to Equation XIII and having the same faults as that equation can be derived.

$$\frac{R_{C_2H_2ClI}}{R_{\underline{trans}\text{-}C_2H_2Cl_2}} = \frac{k_{deact}}{k_{isom}} \left[\underline{cis}\text{-}C_2H_2Cl_2 \right]$$

The graph of the data from experiments without filter is shown in Figure 38. Again, there is an intercept. The value obtained for k_{deact}/k_{isom} is 3.3×10^{-20}. The intercept has a value of 0.022. These values are included in Table XII, page 167.

Pressure studies also were performed on cis-dichloroethylene using filtered light. Unlike trans-dichloroethylene, cis-dichloroethylene does produce chlorine atoms as coproducts of acetylene.

$$\underline{cis}\text{-}C_2H_2Cl_2^{**} \longrightarrow C_2H_2 + 2\,Cl \qquad (3)$$

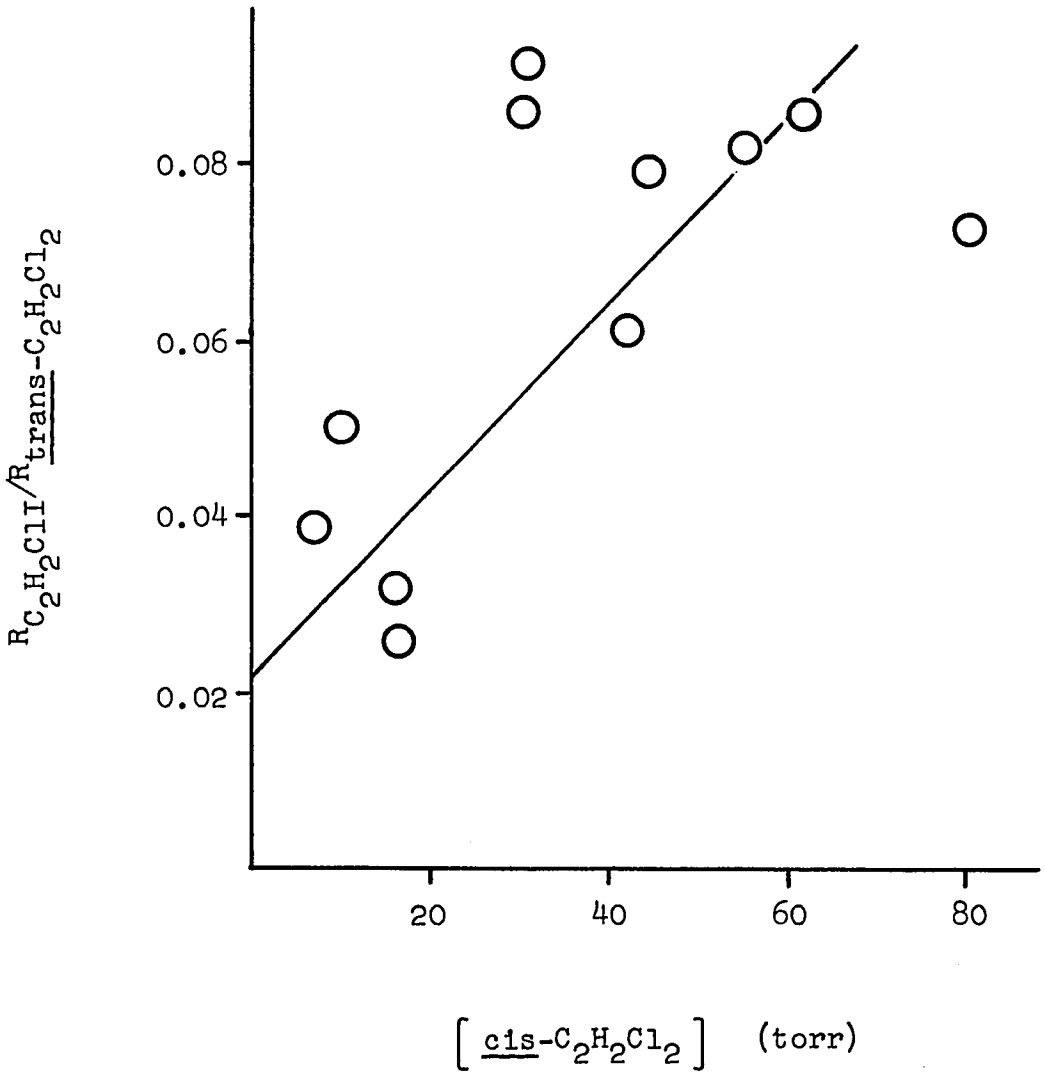
$$\underline{cis}\text{-}C_2H_2Cl_2^{**} \longrightarrow C_2H_2Cl^{\circ} + Cl \qquad (4a)$$

$$C_2H_2Cl^{\circ} \longrightarrow C_2H_2 + Cl \qquad (4b)$$

For these reactions to occur, a minimum energy equivalent to light of 2650 Å. is required. They cannot occur when filter 9-53, 0-54 or 0-52 is used.

For experiments performed using these filters, the

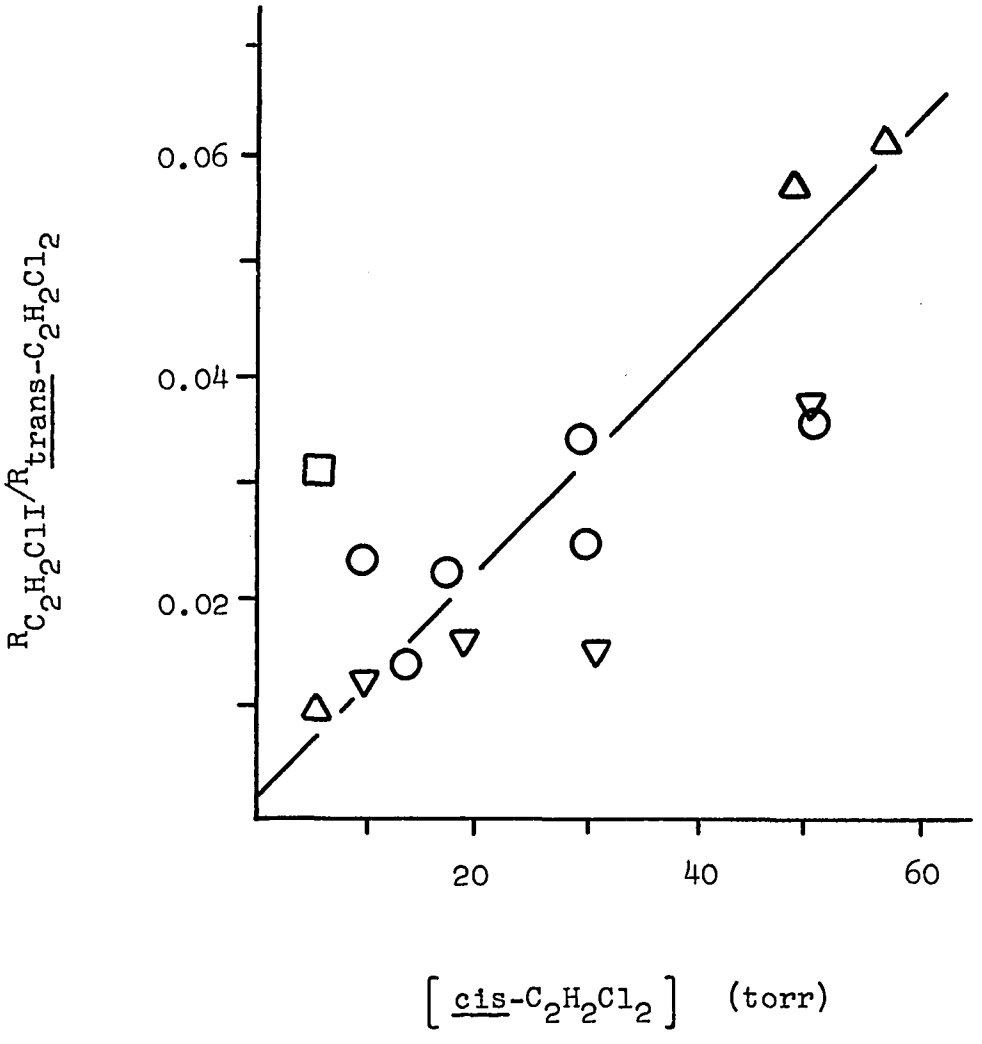
Figure 38. Application of the Rate Equation for the Isomerization of <u>cis</u>-$C_2H_2Cl_2$: No Filter



values of $R_{C_2H_2ClI}/R_{\underline{trans}\text{-}C_2H_2Cl_2}$ will be markedly different from those observed previously. This difference is due to the additional chains initiated by Reactions 3 and 4 in experiments using unfiltered light. Although Reactions 3 and 4 can occur when filter 9-54 (wavelength cutoff: 2200 Å.) is used, it was found that they do not occur (see page 50). This is confirmed by the fact that the values of $R_{C_2H_2ClI}/R_{\underline{trans}\text{-}C_2H_2Cl_2}$ are similar to those of the other filter experiments but not those of the unfiltered experiments. With filter 9-54, the production of chlorovinyl radicals is responsible for all the chains. Hence, the data from filter 9-54 experiments were plotted on the same graph as the data from the other filter experiments. This graph is shown in Figure 39.

The relative rate constants and the intercept from the filter data also are in Table XII, page 167. The value obtained for k_{deact}/k_{isom}, 3.1×10^{-20}, is in excellent agreement with that obtained from experiments performed without filters. This is to be expected because both are constants for reactions of the excited trichloroethyl radical. However much the change in light frequency may influence the formation of excited states leading to primary decomposition, all that matters here is that a chlorine atom adds onto a <u>cis</u>-dichloroethylene molecule, forming an excited trichloroethyl radical. Once the excited radical is formed, it reacts as is its nature to

Figure 39. Application of the Rate Equation for the Isomerization of <u>cis</u>-$C_2H_2Cl_2$: With Filters



react.

However, there is a great difference in the values of the intercepts, 0.002 in the presence of filters, compared to 0.022 in the absence of a filter. As was said previously, the intercept, at least in part, is a measure of termination reactions other than the deactivation of the excited trichloroethyl radical. These termination steps are dependent upon the concentration of the chain carriers. In the unfiltered experiments, Reactions 3 and 4 occur, producing acetylene and two chlorine atoms. Moreover, the higher intensity of the light produces more excited dichloroethylene molecules. The concentration of chain carriers, therefore, is greater in these experiments than in experiments using unfiltered light. Thus, a higher intercept is expected.

Assuming that cis- and trans-dichloroethylene are equally efficient deactivators of the excited trichloroethyl radical, k_{31}/k_{32} can be calculated. This is done by dividing the k_{deact}/k_{isom} obtained for trans-dichloroethylene by that obtained for cis-dichloroethylene. The resulting value is: $k_{31}/k_{32} = 1.6$.

Study with an Inert Deactivator

In the tetrafluoromethane deactivation series, the initial pressure of trans-dichloroethylene was kept constant at 20 torr. The change in the rate of isomerization should reflect the increasing deactivation caused by the

tetrafluoromethane.

$$C_2H_2Cl_3^* + CF_4 \longrightarrow C_2H_2Cl_3 + CF_4 \quad (34)$$

The tetrafluoromethane also will deactivate the excited states of trans-dichloroethylene which produce chlorine atoms. Thus, the graph in Figure 40 shows that in the first 75 torr the decrease in isomer production is akin to the square of the concentration of tetrafluoromethane, as would be expected for the double deactivation. After 100 torr, the rate of isomerization seems to approach some asymptotic limit.

The addition of Reaction 34 to the mechanism gives a rate equation with a y-intercept, the concentration of trans-dichloroethylene being kept constant.

$$\frac{R_{C_2H_2ClI}}{R_{\underline{cis}\text{-}C_2H_2Cl_2}} = \frac{k_{33}}{k_{31}}\left[\underline{trans}\text{-}C_2H_2Cl_2\right] + \frac{k_{34}}{k_{31}}\left[CF_4\right] \quad XIV$$

This is plotted in Figure 41, page 175. The value for k_{34}/k_{31} is 1.1×10^{-20}; the intercept has a value of 0.12. These also are listed in Table XII, page 167. By dividing the value for k_{34}/k_{31} into that obtained for k_{33}/k_{31} in the trans-dichloroethylene pressures studies, a comparison can be made of the relative efficiencies of the two compounds in deactivating the excited trichloroethyl radical. Trans-dichloroethylene is about five times as efficient in this deactivation.

Figure 40. CF_4 Deactivation Study. Rate of Isomerization of <u>trans</u>-$C_2H_2Cl_2$. Scavenger: I_2

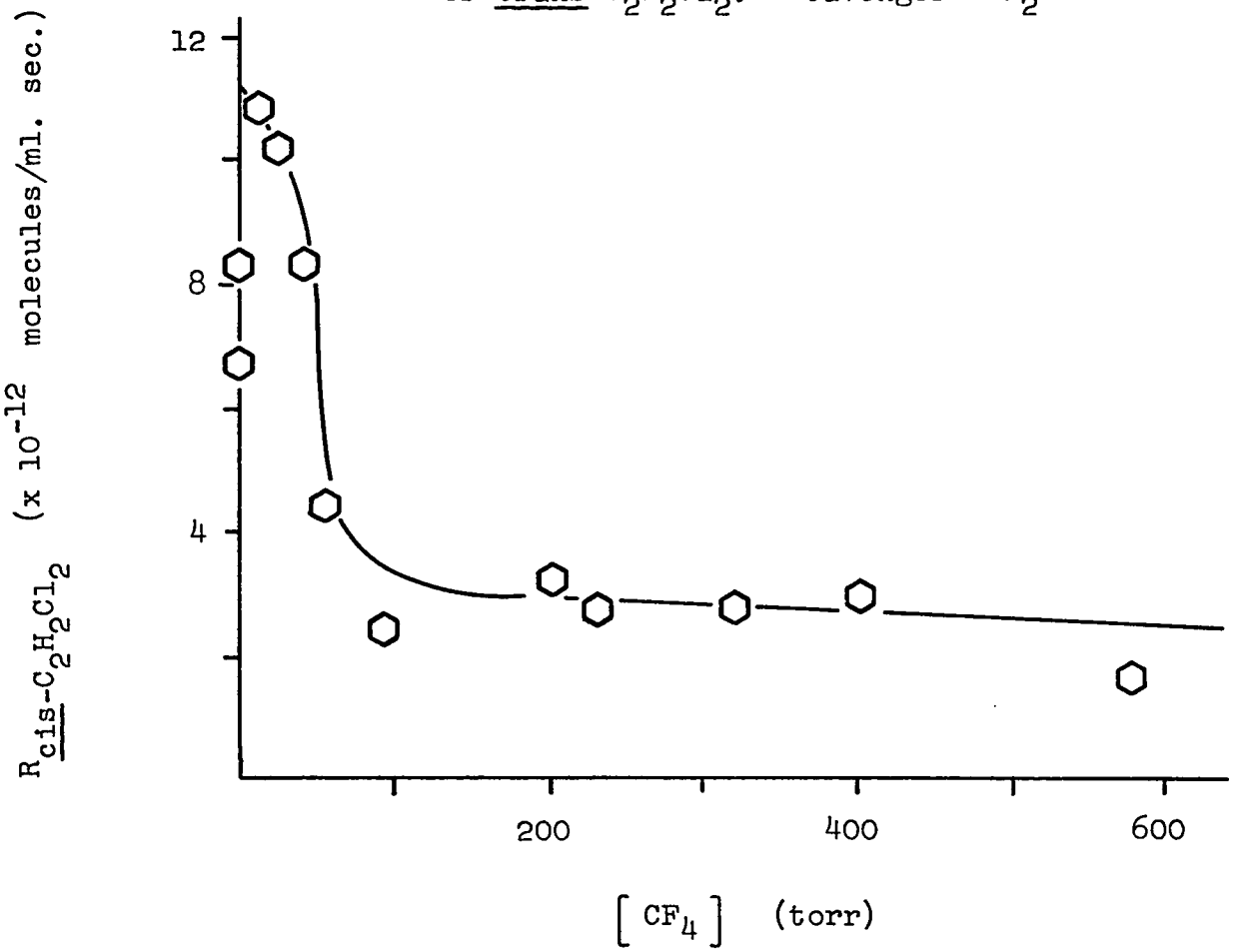
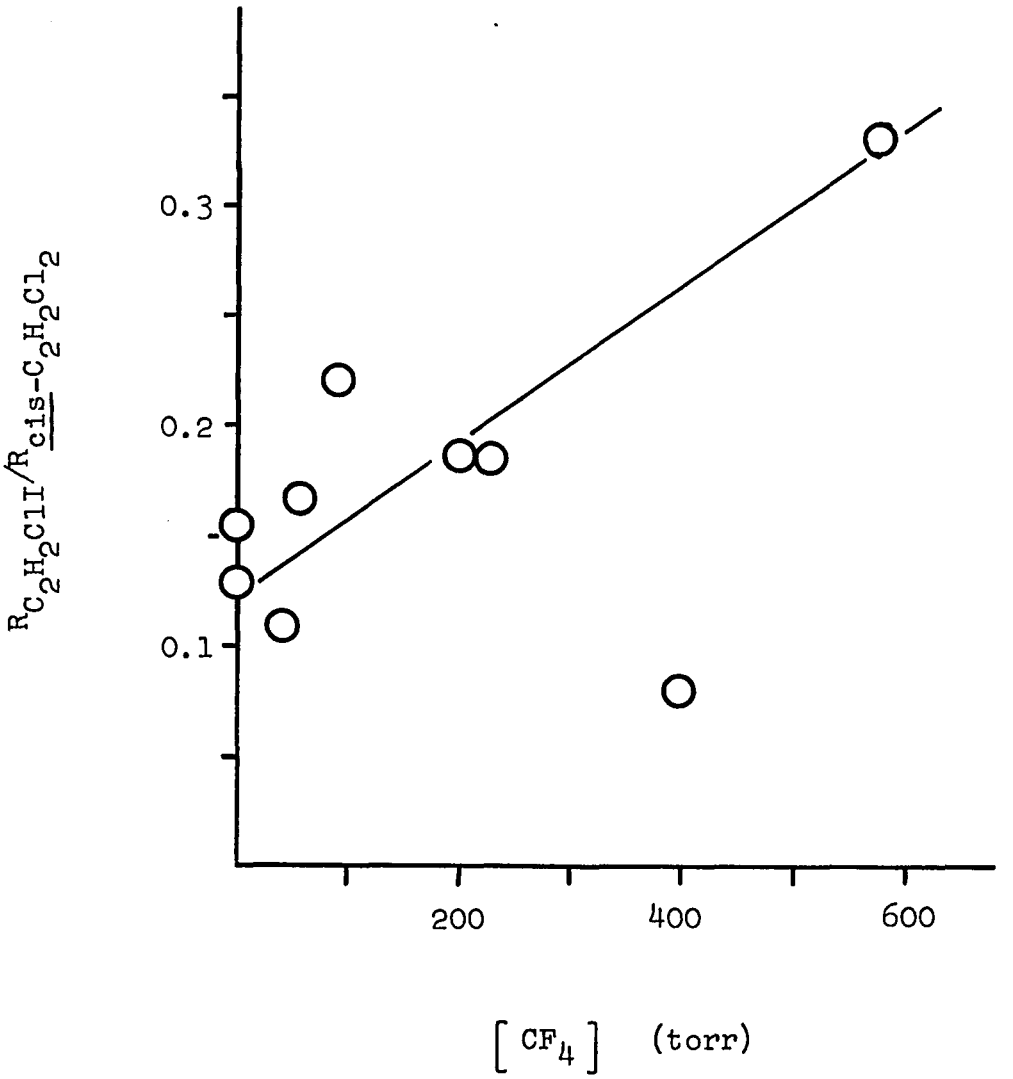


Figure 41. CF_4 Deactivation Study. Application of the Rate Equation for Isomerization. Scavenger: I_2



According to Equation XIV, the intercept should again give a value for k_{33}/k_{31}. That value, 1.9×10^{-19} ml./molecule, is more than three times the value obtained from the pressure studies. But, as in the pressure studies, there are other termination steps for which no account has been taken. These will contribute to the intercept. If the value which was established in the pressure studies for $(k_{33}/k_{31})\left[\ \underline{\text{trans}}\text{-}C_2H_2Cl_2\ \right]$ is subtracted from from the intercept, the remainder is 8.7×10^{-2}. This is similar to the value obtained for the pressure study of trans-dichloroethylene in which iodine was used as the scavenger. Again, the scavenger seems to play a role in setting the value of the intercept.

DISCUSSION

EXCITED STATES

This study was undertaken to increase the knowledge about the photolysis of substituted ethylenes. Other than considerable work on ethylene itself, there has not been much research on these unsaturated compounds. The results of this inquiry will be discussed in relation to each other and to the literature available on related compounds.

The photolysis of the three isomers of dichloroethylene has been studied. To account for the kinetics of the reactions, in each case two excited states had to be proposed. The lifetimes of most of these excited molecules were determined. They are listed in Table XIII.

TABLE XIII

Lifetimes of the Excited Species

Isomer	$C_2H_2Cl_2^*$	$C_2H_2Cl_2^{**}$	$C_2H_2Cl^\circ$
<u>cis</u>-$C_2H_2Cl_2$	2.4×10^{-9}	2.0×10^{-7}	3.8×10^{-9}
<u>trans</u>-$C_2H_2Cl_2$	n.m.	5.1×10^{-9}	n.o.
1,1-$C_2H_2Cl_2$	2.5×10^{-8}	8.4×10^{-9}	n.o.

*n.m. = not measured; n.o. = not observed.

The compound whose reactions were studied most extensively is cis-dichloroethylene. This is the reason its data are given first in Appendix A and why it was the compound whose results were reported first. Cis-dichloroethylene also is the first compound listed in Table XIII and it will be the first compound to be discussed.

cis-1,2-Dichloroethylene

As was mentioned earlier, the lower excited state is responsible for the following processes:

$$\underline{cis}\text{-}C_2H_2Cl_2^{*} \longrightarrow C_2H_2 + Cl_2 \qquad (2)$$

$$\underline{cis}\text{-}C_2H_2Cl_2^{*} \longrightarrow C_2HCl + HCl \qquad (5)$$

$$\underline{cis}\text{-}C_2H_2Cl_2^{*} \longrightarrow C_2H_2Cl + Cl \qquad (8a)$$

The higher excited state decomposes in the following manner:

$$\underline{cis}\text{-}C_2H_2Cl_2^{**} \longrightarrow C_2H_2 + 2\,Cl \qquad (3)$$

$$\underline{cis}\text{-}C_2H_2Cl_2^{**} \longrightarrow C_2H_2Cl^{\circ} + Cl \qquad (4a)$$

The excited chlorovinyl radical then may decompose further:

$$C_2H_2Cl^{\circ} \longrightarrow C_2H_2 + Cl \qquad (4b)$$

In this respect, cis-dichloroethylene is like vinyl chloride and vinyl iodide. Fujimoto, Rennert and Wijnen[34] have shown that in the irradiation of vinyl chloride with light of 1900 - 2200 Å., all product formation can be ac-

counted for by the decomposition of one excited state into acetylene and vinyl radicals:

$$C_2H_3Cl^* \longrightarrow C_2H_3 + Cl \qquad (35)$$

$$C_2H_3Cl^* \longrightarrow C_2H_2 + HCl \qquad (36)$$

These are akin to Reactions 8a and 5, respectively, of the lower excited state of cis-dichloroethylene.

Ausloos, Rebbert and Wijnen[6] found that at shorter wavelengths another process was involved in the decomposition of vinyl chloride. The overall process was represented as:

$$C_2H_3Cl + h\nu \longrightarrow C_2H_2 + H + Cl \qquad (37)$$

where Reaction 37 may proceed via an excited vinyl or chlorovinyl radical. This is analagous to the decomposition of the higher excited state of cis-dichloroethylene given by Reaction 3, 4a and 4b. Thus, there is excellent agreement between vinyl chloride and cis-dichloroethylene regarding the role which the excited states play in the formation of their respective products.

Cis-dichloroethylene has one more chlorine than vinyl chloride. Chlorine is known to be an auxochrome. Its non-bonding electrons interact with the double bond of these compounds extending the π-bond system. It is to be expected, therefore, that the absorption of light by cis-dichloroethylene will be shifted to higher wavelengths

than vinyl chloride's absorption. Vinyl chloride's absorption begins in a strong, wide band at 2200 Å. which extends into the far ultraviolet.[91,125] In spectroscopic studies, cis-dichloroethylene has been observed to absorb light of wavelengths as long as 2700 Å.[62] The spectrum of a liquid sample taken here showed the absorption of light as long as 3850 Å.

Because of this shift in absorption to longer wavelengths, two excited states are observed when cis-dichloroethylene is irradiated with near ultraviolet light, while only one is seen with vinyl chloride. The second excited state of vinyl chloride absorbs in the far ultraviolet region. Ethylene, without any chlorines, has no absorption in the near ultraviolet.[51]

In the photolysis of vinyl iodide, Roberge and Herman[92] also observed acetylene and vinyl radicals as products. They found that both molecular and radical formation occur from the same excited state:

$$C_2H_3I^* \longrightarrow C_2H_3 + I \qquad (38)$$

$$C_2H_3I^* \longrightarrow C_2H_2 + HI \qquad (39)$$

This was confirmed by Yamashita, Noguchi and Hayakawa.[131] Again, this is similar to the reactions of cis-dichloroethylene. There has been no report, however, on the far ultraviolet photolysis of vinyl iodide to confirm a process similar to Reaction 37 of vinyl chloride.

Ethyl iodide is another compound which reacts in a manner similar to cis-dichloroethylene. Schindler and Wijnen[96] have shown that the excited state formed by near ultraviolet irradiation decomposes primarily by cleavage of the carbon - iodine bond. But, about 5% of the decomposition is molecular elimination:

$$C_2H_5I^* \longrightarrow C_2H_5 + I \qquad (40)$$

$$C_2H_5I^* \longrightarrow C_2H_4 + HI \qquad (41)$$

Rebbert, Lias and Ausloos[90] investigated the photolysis of ethyl iodide at 1470 Å. They found that the main reaction was exactly analogous to Reaction 37:

$$C_2H_5I + h\nu \longrightarrow C_2H_4 + H + I \qquad (42)$$

Reaction 42 may proceed via an excited ethyl radical.

Thus, the literature data on the photolysis of halogenated ethylenes and even ethyl iodide show excellent agreement with the observations made regarding the primary processes of cis-dichloroethylene.

The absorption spectra of the 1,2-dichloroethylenes have been studied by Mahncke and Noyes,[62] Walsh[125] and Walsh and Warsop.[126,127] These spectroscopic works focused on the absorptions below 2100 Å. Broad contiua were found between 1800 and 2100 Å. These continua have absorption maxima at about 1900 Å for cis- and 1950 Å. for trans-dichloroethylene. This is in general agreement with observa-

tions made in this work. The filter studies on trans-dichloroethylene required much shorter exposure times than corresponding experiments with cis-dichloroethylene. This shows that trans-dichloroethylene has a greater absorption at higher wavelengths, which is suggested by the relative positions of the maxima.

In chlorinated ethylenes, the continua at about 1900 Å. have been associated with an excitation of the double bond. The absorption at shorter wavelengths has been ascribed to an excitation of chlorine atom electrons.[125]

In general, spectroscopists observe narrower absorption ranges than photochemists. This is due, primarily to the length of irradiation time. While spectroscopists have reported absorptions by the dichloroethylenes as high as 2700 Å., this investigation has shown that photodecomposition of the 1,2-dichloroethylenes occurs at 3400 Å. This being so, it seems reasonable to extend to longer wavelengths the observations made by spectroscopists.

If this be done, the lower excited state observed in cis-dichloroethylene would be attributed to the continuum in the 1800 - 2100 Å. region which has been associated with the excitation of the double bond. This is the logical excitation for the molecular elimination across the double bond which is observed from the lower excited state.

The absorption which spectroscopists observed at shorter wavelengths would lead to the higher excited state observed in this investigation. This excited state led exclusively to cleavage of carbon - chlorine bonds. Again, this is a logical consequence of an excitation affecting only chlorine atoms.

trans-1,2-Dichloroethylene

The above observations apply equally to trans-dichloroethylene. It is clear that these are two very similar, but not quite identical, molecules. Therefore, it would be expected that similar excited states yielding similar products would occur in both compounds. Indeed, this is observed. The lower excited state of trans-dichloroethylene produces the same products (although distributed differently) as the corresponding state of cis-dichloroethylene.

The only difference observed in their reactions is that the two star excited state of trans-dichloroethylene only shows one mode of decomposition:

$$\text{trans-}C_2H_2Cl_2^{**} \longrightarrow C_2H_2Cl + Cl \qquad (17)$$

The production of two chlorine atoms with acetylene,

$$\text{trans-}C_2H_2Cl_2^{**} \longrightarrow C_2H_2 + 2\,Cl \qquad (29)$$

either directly or via an excited chlorovinyl radical was not observed. This apparent contradiction, however, may

be only a question of semantics and could be explained by either of the following statements:

1. Reaction 29 does occur, but only to such a minor extent that it was not observed. This would be a further demonstration of the statement made previously that the product distribution from the excited states of the 1,2-dichloroethylenes are not identical.
2. Due to a wavelength shift in the absorptions of the compounds, the two star excited state of trans-dichloroethylene actually carries less energy than the corresponding state of cis-dichloroethylene. This makes it less likely that the chlorovinyl radical produced from the two star excited state has sufficient energy to decompose via a reaction similar to Reaction 4b.

Nature of the Excited States

A discussion of the excited states of cis- and trans-dichloroethylene would not be complete without an attempt to characterize the nature of the excited states involved. It seems likely that the lower excited state is a vibrationally excited ground state molecule. In recent years, there has been an outpouring of papers by, among others, groups headed by Pritchard[15,16,80-85] and Setser[22,23,25,26,42,49,53,54,98,99] on the decomposition of chemically activated alkyl halides. These are vibrationally excited ground state molecules, usually formed by the combination of substituted methyl radicals. Unless deactivated, these

excited molecules decompose by hydrogen halide elimination, similar to Reactions 5 and 14. The observed lifetime of 2.4×10^{-9} sec. for the lower excited state of cis-dichloroethylene is of the general order of magnitude expected for vibrationally excited molecules.[27]

In the case of cis-dichloroethylene, the lifetimes of both excited states were determined. The results are different enough (lifetimes differ by a factor of about 100) to establish clearly that these are two different entities. Moreover, the lifetime of the higher excited state is longer than that of the lower excited state. As the lower excited state has been designated as a vibrationally excited singlet, this seems to indicate that the two star state is a triplet molecule. Triplet states are known for their longevity. Thus phosphorescence, a triplet process, is much slower than fluorescence, a singlet process.

It would be interesting to compare the lifetimes of the corresponding excited states of cis- and trans-dichloroethylene. Unfortunately, only values for the higher excited states are available for comparison. A priori, it might be expected that because of the similarity between the two molecules these lifetimes would be close. This definitely is not the case for the higher excited states.

The fact that the product distributions observed are not identical for cis- and trans-dichloroethylene

clearly indicates that the products do not originate from the same excited state. This means that the cis and trans molecules must have maintained, at least in part, their original configuration. If this be so, then obviously, it would be purely accidental if the lifetimes were identical. Furthermore, it should be mentioned that even in the lowest vibrational state,[28] trans-dichloroethylene has a lifetime shorter by a factor of 4 than that of the lowest vibrational state of cis-dichloroethylene.

1,1-Dichloroethylene

1,1-Dichloroethylene also was found to decompose via two excited states. As in the 1,2-dichloroethylenes, the lower excited state decomposed by molecular elimination:

$$CH_2CCl_2^* \longrightarrow C_2HCl + HCl \qquad (25)$$

$$CH_2CCl_2^* \longrightarrow C_2H_2 + Cl_2 \qquad (26)$$

The higher excited state probably is the only source of chlorovinyl radicals, formed by the cleavage of a carbon - chlorine bond:

$$CH_2CCl_2^{**} \longrightarrow CH_2CCl + Cl \qquad (23)$$

These reactions are similar to those reported for 1,1-dichloroethane.

Fujimoto and Wijnen[35] found that the photolysis of 1,1-dichloro-2,2,2-trideuterioethane produces cleavage of

a carbon - chlorine bone, α,β elimination of hydrogen chloride and α,α elimination of molecular chlorine.

$$CD_3CHCl_2^* \longrightarrow CD_3CHCl + Cl \qquad (43)$$

$$CD_3CHCl_2^* \longrightarrow CD_2CHCl + DCl \qquad (44)$$

$$CD_3CHCl_2^* \longrightarrow CD_3CH + Cl_2 \qquad (45)$$

These are analogous to Reactions 23, 25 and 26, respectively. In addition, also observed in the photodecomposition of 1,1-dichloro-2,2,2-triceuterioethane was the α,β elimination of hydrogen.

$$CD_3CHCl_2^* \longrightarrow CD_2CCl_2 + HD \qquad (46)$$

This process, obviously, is not possible in 1,1-dichloroethylene. While the nature of the excited states observed in 1,1-dichloroethane were not characterized, nor their reactions assigned, the data reported required the use of more than one excited state.

Finally, in Table XIII are given for general reference the lifetimes of the excited states observed in 1,1-dichloroethylene. A comparison with those obtained for cis- and trans-dichloroethylene does not seem warranted, based upon the large differences in structure between the molecules.

PRODUCTS

Molecular Elimination Processes

It was shown above that molecular elimination is the exclusive function of the lower excited state. This species has been described as a vibrationally excited ground state molecule. For each of the three isomers of dichloroethylene, two different eliminations occur:

$$C_2H_2Cl_2^* \longrightarrow C_2HCl + HCl$$

$$C_2H_2Cl_2^* \longrightarrow C_2H_2 + Cl_2$$

Dehydrohalogenation

Examples of the dehydrohalogenation reaction abound. Aside from the decomposition of chemically and light activated molecules cited previously, dehydrohalogenation has been observed by Barton and Howlett et al.[10,11,39] in studies of the thermal decomposition of alkyl chlorides. Using shock tube pyrolysis, groups headed by Trotman-Dickenson[17,18] and Tschuikow-Roux[65,66,117-119] have investigated most of the fluoroethanes as well as CH_2ClCH_2F,[18] CH_2CF_2,[105] C_2H_3Cl[19] and C_2H_3Br.[19] In all cases, HX elimination was observed. HCl elimination predominated in the decomposition of CH_2ClCH_2F.[18] Similar results were ob-

tained in the thermal decomposition of CH_3CHFCl[64] and CH_3CF_2Cl;[64,77] HF detachment accounted for less than 5% of the products.

Sensitization also led to dehydrohalogenation in a number of compounds. It was observed in the mercury photosensitization of C_2H_3Cl,[12] C_2H_3F[110,114] and the three isomers of $C_2H_2F_2$.[114] Quick and Whittle, while investigating the reactions of the trifluoromethyl radical, found that the excited hexafluoroacetone molecule could sensitize the alkyl halides with which they were working. Thus, they observed hydrogen halide elimination from C_2H_5Br,[87] CH_2BrCH_2Br,[86] C_2H_5Cl,[86] CH_3CHCl_2,[88] CH_3CCl_3,[88] CH_3CF_2Cl,[88] $CHCl_2CHCl_2$[88] and CH_3CF_2Br.[87] However, no dehydrofluorination was observed in the latter two fluorine compounds.

Molecular detachment of hydrogen chloride already has been reported in all three dichloroethylenes. Goodall and Howlett[39] reported it in the pyrolysis of cis- and trans-dichloroethylene in the presence of free radical inhibitors. Molera and Ariza,[69] working with a seasoned cell, also observed the dehydrochlorination reaction in the pyrolysis of cis- and trans-dichloroethylene. This same reaction was observed by Futrell and Newton[36] in the α, β and γ radiolysis of the 1,2-dichloroethylenes. Wijnen[130] observed this molecular detachment in the photolysis of cis-dichloroethylene. Pimentel and coworkers[13,70] observed the vibration - rotation spectra of the HCl emitted in the laser photolysis of the three isomers of

dichloroethylene.

Dehalogenation

References to the elimination of halogen molecules are much scarcer. In 1933, Arnold and Kistiakowsky[3] observed the unimolecular decomposition of 1,2-diiodoethane by pyrolysis. This reaction produced ethylene. But, there was no comment whatsoever on whether the reaction proceeded via molecular detachment or atomic detachment.

In 1959, Shilov and Saibrova[103] observed tetrachloroethylene as a product of the pyrolysis of carbon tetrachloride. They proposed the following mechanism:

$$CCl_4 \longrightarrow CCl_3 + Cl \qquad (47)$$

$$Cl + CCl_4 \longrightarrow Cl_2 + CCl_3 \qquad (48)$$

$$2\ CCl_3 \longrightarrow C_2Cl_6 \qquad (49)$$

$$C_2Cl_6 \longrightarrow C_2Cl_4 + Cl_2 \qquad (50)$$

Today, it might be suggested that chemical activation, as well as thermal energy, was responsible for the decomposition of the hexachloroethane.

Recently, White and Kuntz[128] investigated the pyrolysis of hexachloroethane. They proposed a chain reaction initiated by the homolysis of the starting material into two trichloromethyl radicals, followed by abstraction of a chlorine atom from the parent compound. The chain propagation steps, then, are:

$$C_2Cl_5 \longrightarrow C_2Cl_4 + Cl \qquad (51)$$

$$Cl + C_2Cl_6 \longrightarrow Cl_2 + C_2Cl_5 \qquad (52)$$

They found that the addition of chlorine to the reaction decreased, but did not completely suppress, the formation of C_2Cl_4, presumedly by reversing Reaction 52. Tomkinson, Galvin and Pritchard[113] found C_2Cl_4 to be a product of the photolysis of hexachloroethane in the presence of propane. The propane served as an inhibitor of free radical reactions. This suggests that molecular detachment of chlorine does occur to some extent in the photolysis of hexachloroethane.

Similarly, Hautecloque and Nguyen[43] have investigated the photolysis of carbon tetrabromide at elevated temperatures. The products observed were C_2Br_6, Br_2 and C_2Br_4, the latter two appearing only above 250° C. The following mechanism was porposed:

$$CBr_4 + h\nu \longrightarrow CBr_3 + Br \qquad (53)$$

$$Br + CBr_4 \longrightarrow Br_2 + CBr_3 \qquad (54)$$

$$2\ CBr_3 \longrightarrow C_2Br_6 \qquad (55)$$

$$2\ CBr_3 \longrightarrow C_2Br_4 + Br_2 \qquad (56)$$

Results from the thermal decomposition of C_2Br_6 showed that this reaction could account only in part for the formation of C_2Br_4. Thus, the formation of tetrabromo-

ethylene by Reaction 56 was included. This same form of equation was used to explain the early results in chemical activation studies.[2] It seems reasonable to explain these results in a manner similar to chemical activation.

Molecular halogen elimination has been reported in the decomposition of certain halomethanes. Simons and Yarwood[106] found that the decomposition of difluorodibromomethane produces molecular bromine.

$$CF_2Br_2 + h\nu \longrightarrow :CF_2 + Br_2 \qquad (57)$$

Blomstrom, Herbig and Simmons[14] found a similar reaction in the photolysis of diiodomethane.

$$CH_2I_2 + h\nu \longrightarrow :CH_2 + I_2 \qquad (58)$$

Fujimoto and Wijnen[35] have reported the elimination of a chlorine molecule in the photolysis of 1,1-dichloro-2,2,2-trideuterioethane.

$$CD_3CHCl_2 + h\nu \longrightarrow CD_2CHD + Cl_2 \qquad (59)$$

Sekhar, Millward and Tschuikow-Roux[97] have reported trifluoroethylene as a product of the shock wave pyrolysis of CF_3CHCl_2 at temperatures of less than 1260° K. Although analogous to Reaction 59 of Fujimoto and Wijnen, the authors refused to commit themselves to a molecular elimination. Instead, a free radical process was proposed to account for this product.

This brief survey shows that there is ample evidence

in the literature for the elimination of hydrogen halides and some evidence, although to a minor extent, for the elimination of halogen molecules. The suggestion of hydrogen chloride and chlorine molecule elimination from the dichloroethylene isomers therefore is not unique, even though Cl_2 elimination had not been reported previously. It should, however, be noted that this is the first rather detailed study of the photolysis of these compounds.

Stereochemistry of Molecular Eliminations

Before discussing these steps in detail, it is important to report on the literature data regarding the nature of these elimination reactions, i.e., regarding the evidence for α,α and/or α,β eliminations. Originally, molecular eliminations were thought to occur in a four-centered reaction, with one atom coming off either carbon. However, work on the decomposition of the dideuterioethylenes by mercury photosensitization,[20,100] far ultraviolet photolysis[74] and radiolysis[5] suggested that both α,α (three-centered) and α,β (four-centered) reactions were occurring.

Because the literature data are extremely voluminous, no pretense is made of being complete. Only some of the most relevant references are given here. It is clear that the elimination of a hydrogen halide from substituted methanes must be an α,α process. Such a process has been observed in CH_3I,[24,115] CHF_3,[116] CHF_2Cl,[33,40] $CHFCl_2$[106]

and CHF_2Br.[29]

Hydrogen halide elimination observed in the following compounds must, of necessity, be an α,β process: CH_3CF_3,[2,22,38] CD_3CF_3,[71,88] CH_3CCl_3,[11,88] CH_2CF_2[105,110] and CH_3CF_2Cl.[64,77,88] In the following compounds, among others, α,α eliminations have been observed, accompanied in some by α,β eliminations: CH_2CDCl,[6] CF_3CH_2Cl,[67] CD_3CHF_2,[54] CH_3CDF_2,[120] $CH_2ClCDCl_2$,[53] CF_3CHCl_2[97] and CD_3CHCl_2.[35]

Although both α,α and α,β hydrogen halide eliminations have been observed, the situation is still rather confused. At the present time, when more than one elimination is possible, it is impossible to predict with any degree of certainty which processes occur and to what extent such processes would occur. To some extent, it seems that the type of reaction which occurs may depend upon the amount of energy put into the system. Thus, in general, both α,α and α,β processes are observed in shock tube pyrolysis experiments,[67,97,120] while energetically more moderate systems produce mainly, if not exclusively, α,β eliminations.[25,54,78,87,88] This, of course, would indicate that α,β eliminations are energetically favored over α,α eliminations.

Perhaps, the molecular elimination of hydrogen chloride from the dichloroethylenes reported here should be compared to those observed in $CH_2{=}CDCl$, a compound which is reasonably closely related to the dichloroethylenes.

The direct photolysis of 1-chloro-1-deuterioethylene in the presence of scavengers[6] produced C_2H_2 and C_2HD in approximately equal amounts, proving that both α,α and α,β eliminations occurred. Thus, α,α and α,β eliminations of hydrogen chloride may be expected from cis- and trans-dichloroethylene.

This is supported by Berry and Pimentel.[13] They studied the vibration - rotation spectra of the hydrogen chloride produced in the three dichloroethylene photoelimination chemical lasers. By observing the HCl emission from $CH_2{=}CCl_2$ and from $C(CH_3)_2{=}CHCl$, they showed that both α,α and α,β eliminations can occur from chloroethylenes. The observation of both HCl and HF laser emissions from $CHF{=}CCl_2$ shows that both α,α and α,β eliminations can be occurring from the same compound. Because both types of elimination do occur in other compounds, and because they can occur in these, they concluded that α,α and α,β eliminations of hydrogen chloride probably occur in both 1,2-dichloroethylenes.

The final determination of this problem will not be solved, however, until a dichloroethylene is synthesized with a composition in which each hydrogen and each chlorine can be identified. $CH^{35}Cl{=}CD^{37}Cl$ is one possibility. With a compound like this, one can determine exactly which hydrogen and which chlorine were lost.

Thus, the literature data indicate that hydrogen chloride eliminations are observed quite frequently and

have been suggested previously in the case of all three dichloroethylenes. Molecular chlorine elimination has not been reported previously. It should be emphasized, however, that from energetic considerations, under certain conditions, no other reaction is possible which can explain the formation of acetylene (see page 40).

The Stereochemistry of the Elimination Reactions of the Dichloroethylenes

Now, it should be interesting to take a closer look at the values observed in this investigation for the ratio of acetylene to chloroacetylene formation from the one star excited atom. This is the ratio of Cl_2 to HCl elimination. The following data were obtained:

1,1-$C_2H_2Cl_2$	0.29
trans-$C_2H_2Cl_2$	2.1
cis-$C_2H_2Cl_2$	3.1

It is clear that the Cl_2 elimination must be α,α from 1,1-dichloroethylene and α,β from cis- and trans-dichloroethylene. Elimination of HCl must be α,β for 1,1-dichloroethylene and may be either α,α and/or α,β for cis- and trans-dichloroethylene.

The fact that the ratio of Cl_2 to HCl elimination is much smaller for 1,1-dichloroethylene than for either 1,2-dichloroethylene seems to indicate that the photoeli-

mination of molecular chlorine in the dichloroethylenes occurs more readily by an α,β process.

The data clearly indicate that the ratio of Cl_2 to HCl elimination from cis- and from trans-dichloroethylene are not the same. Thus, the respective excited states of the two compounds are not the same. Earlier, this had been concluded from other considerations.

The fact that this ratio is larger for cis-dichloroethylene than for trans-dichloroethylene is not surprising. The geometry of the trans molecule definitely favors HCl elimination, both α,α and α,β. The elimination of Cl_2 is less favored becasue these atoms are trans to each other. In cis-dichloroethylene, the Cl_2 elimination is favored (the chlorine atoms are adjacent to each other), but HCl elimination should be reduced somewhat because the α,β eliminations involve H and Cl atoms which are trans to each other.

For both cis- and trans-dichloroethylene, the Cl_2 elimination is larger than the HCl elimination. This is so despite the fact that there are four possibilities for HCl elimination and only one for Cl_2 elimination in either molecule. This merely may reflect the bulkiness of the chlorine atoms which would bring them closer together, thus favoring this elimination over the elimination of hydrogen chloride.

Free Radical Processes

The scission of carbon - halogen bonds, except in the case of fluorine, is well known. The literature on it is vast. In the early studies on activation energies of dehydrohalogenation or of isomerization of halogen containing compounds, free radical reactions initiated by the cleavage of a carbon - halogen bond had to be suppressed in order to get reproducible data. This usually involved seasoning the cell or adding a free radical trap, such as propene. As a matter of fact, practically all chlorine containing compounds, on being photolyzed, produce chlorine atoms as one of the primary steps. Hence, for this process, literature references seem superfluous.

Excited Radical Formation

Thus, there is nothing surprising in observing the cleavage of a carbon - chlorine bond in the photolysis of the dichloroethylenes. As was demonstrated in the discussion of the excited states (pages 178-188), even the occurrence of carbon - halogen bond scission from the same excited state as molecular detachment is not unusual. What is of interest, though, is the manner in which the two star excited state of cis-dichloroethylene decomposes.

The mechanism for the decomposition of this excited state is:

$$\underline{cis}\text{-}C_2H_2Cl_2^{**} \longrightarrow C_2H_2 + 2\,Cl \qquad (3)$$

$$\underline{cis}\text{-}C_2H_2Cl_2^{**} \longrightarrow C_2H_2Cl^{\circ} + Cl \qquad (4a)$$

$$C_2H_2Cl_2^{**} + C_2H_2Cl_2 \longrightarrow 2\ C_2H_2Cl_2 \qquad (11)$$

$$C_2H_2Cl^{\circ} \longrightarrow C_2H_2 + Cl \qquad (4b)$$

$$C_2H_2Cl^{\circ} + C_2H_2Cl_2 \longrightarrow C_2H_2Cl + C_2H_2Cl_2 \qquad (9)$$

$$C_2H_2Cl + I_2 \longrightarrow C_2H_2ClI + I \qquad (8b)$$

In order to explain the observed results, it was necessary to postulate that the vinyl radical produced at shorter wavelengths contained excess energy which caused it to decompose according th Reaction 4b. 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 (143 lca./mole), the molecule has about 60 kcal./mole excess energy to distribute over the chlorine atom and the chlorovinyl radical.

Also, it should be mentioned that this suggestion is completely analogous to observations made in the photolysis of acetone,[45,61,72] biacetyl[101] and CH_3COOCD_3.[129] In these cases, it was reported that some of the acetyl radicals carried excess energy which forced the radical to decompose,

$$CH_3CO^{*} \longrightarrow CH_3 + CO \qquad (60)$$

before it was able to react with other radicals to yield recombination and/or disproportionation products of the type,

$$CH_3CO + R \longrightarrow CH_3COR \quad (61)$$

$$CH_3CO + R \longrightarrow CH_3CHO + \text{Olefin} \quad (62)$$

Finally, Reaction 3 may be omitted, provided it is accepted that some of the excited chlorovinyl radicals cannot be deactivated; they must decompose via Reaction 4b. This parallels the results of Ausloos, Rebbert and Wijnen,[6] who observed the following primary step in the photolysis of vinyl chloride at low wavelengths:

$$C_2H_3Cl + h\nu \longrightarrow C_2H_2 + H + Cl \quad (37)$$

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

Chlorine Atom Addition to the Double Bond

As was mentioned, chlorine atoms are produced in the primary processes. These chlorine atoms may add onto the double bond of the starting material. However, the 1,2-dichloroethylenes have reflection planes perpendicular to and bisecting their double bonds; both sides are equivalent. 1,1-Dichloroethylene has two very different sides.

In the presence of iodine, some of these trichloroethyl radicals will be scavenged. In experiments with 1,1-dichloroethylene, both 1,1,1-trichloro-2-iodoethane and 1,1,2-trichloro-1-iodoethane were observed. The CH_2ClCCl_2I was found in all the experiments. CCl_3CH_2I

was observed only occasionally. The CH_2ClCCl_2I almost invariably was the more abundant adduct product.

These data suggest that the addition occurs mainly on the methylene side of $CH_2{=}CCl_2$. However, it has been reported that in a $CCl_2\dot{C}HR$ radical, a rearrangement may occur in which a chlorine atom shifts, yielding a $\dot{C}Cl_2CHClR$ radical.[37,75,123] Thus, it may be concluded only that these data support the finding that the $CH_2Cl\dot{C}Cl_2$ radical is the more stable of the two.

Geometry of the 2-Chlorovinyl Radical

In the photolysis of either isomer of 1,2-dichloroethylene, a 2-chlorovinyl radical is produced by cleavage of a carbon - chlorine bond. The scavenging of these radicals by iodine led to both cis- and trans-1-chloro-2-iodoethylene. Moreover, the ratio of cis to trans isomers produced was the same, 1 : 4, regardless of which 1,2-dichloroethylene was decomposed. The radicals produced from cis- and trans-dichloroethylene are indistinguishable. No previous data are available regarding these reactions.

This raises the question of the geometry of the 2-chlorovinyl radical. Singer,[107] in a review on the stereochemistry of vinylic radicals gave two basic configurations:

i) linear -- the radical carbon is sp-hybridized. The 1-substituent lies along the axis of the double bond.

ii) bent -- the radical carbon is sp^2-hybridized. The configuration is basically unchanged by the loss of

the chlorine atom. If this be the configuration, there can be

a) rapid inversion -- the rate of inversion is much faster than the rate of scavenging.

b) slow inversion -- the rate of inversion is comparable to or smaller than the rate of scavenging.

To these, a third possibility must be added:

iii) bridged -- the remaining chlorine atom bridges the double bond forming a three membered ring with the unpaired electron delocalized.

Bridged bromine systems have been demonstrated in the bromination of 2-bromobutane, a bridging of a single bond,[108] as well as in the bromovinyl radical formed in the hydrobromination of 2-butyne.[1] While the chlorine atom may be too small to bridge a single bond, it might be able to bridge the double bond here.

These different structures should lead to differences in product distribution. These would be expected:

i) linear configuration -- both <u>cis</u> and <u>trans</u> isomers should be formed, their relative concentrations being determined by the stereoselectivity features of the scavenging, i.e. the interaction between the scavenger and the radical.

iia) bent configuration, fast inversion -- the product ratio should be determined by the relative populations of the two bent forms and the stereoselectivity features in the scavenging.

iib) bent configuration, slow inversion -- the product ratio should be stereospecifically determined; there will be some degree of retention of configuration.

iii) bridged configuration -- there should be only one product, the trans olefin.

In the case reported here, the same product ratio was reported form cis- and trans-dichloroethylene. Both isomers of the chloroiodoethylene were formed. These results are incompatable with cases iib and iii. This leaves cases i and iia. There is little that one can do to decide between them on the basis of the evidence. Both produce ratios which are stereoselectively determined, though case iia also is dependent upon the relative populations of the two bent forms.

Singer's review of the data available on other vinylic systems suggests that conjugated unsaturation, such as that produced by a phenyl or a nitrile group, is needed for a linear radical configuration. Thus, the 2-chlorovinyl radical seems to fit case iia, a bent configuration with rapid inversion.

ISOMERIZATION REACTIONS

Mechanism

The isomerization of both isomers of 1,2-dichloroethylene was shown to proceed predominately by a chlorine atom catalyzed chain reaction. Chlorine atoms are produced in the photodecomposition of the starting material. The addition of a chlorine atom to the double bond of the starting material produces an excited 1,1,2-trichloroethyl radical. There is free rotation about the carbon - carbon bond in the hot radical. This activated radical either is deactivated to a ground state radical or it decomposes. The decomposition is the reverse reaction of the formation of the hot radical. But, there having been free rotation in the intermediate hot radical, the product formed can be either isomer of 1,2-dichloroethylene.

This work on the isomerization reactions demonstrates that the mechanism first proposed by Wijnen[130] and Dainton[7] is valid. The cis - trans isomerization mainly proceeds via the reactions,

$$Cl + 1,2\text{-}C_2H_2Cl_2 \longrightarrow C_2H_2Cl_3^* \qquad (30)$$

$$C_2H_2Cl_3^* \longrightarrow \underline{cis}\text{-}C_2H_2Cl_2 + Cl \qquad (31)$$

$$C_2H_2Cl_3^* \longrightarrow \underline{tr}\text{-}C_2H_2Cl_2 + Cl \quad (32)$$

$$C_2H_2Cl_3^* + C_2H_2Cl_2 \longrightarrow C_2H_2Cl_3 + C_2H_2Cl_2 \quad (33)$$

The fact that the ratio $R_{\underline{cis}\text{-}C_2H_2Cl_2}/R_{C_2H_2ClI(total)}$ in the trans-dichloroethylene filter studies was constant connects the production of the cis isomer to the rate of chloroiodoethylene production, and thus, to the rate of chlorine atom production. For every chlorovinyl radical, one chlorine atom is produced.

It must be admitted that in plotting the data according to the reaction sequence given above (see Figures 35 - 37, pages 161-163), small intercepts were observed where none should have been. Because these intercepts decreased in magnitude with decreasing light intensity, it seems reasonable to assume that some minor reactions (in an already complicated mechanism) were not accounted for. These "minor reactions," being intensity dependent, most likely are radical - radical reactions. To suggest a particular reaction to account for this minor discrepency is almost pure speculation. Suffice it to say that any reaction of the type

$$C_2H_2Cl_3 + I \longrightarrow \underline{cis}\text{-}C_2H_2Cl_2 + ICl$$

$$\longrightarrow \underline{trans}\text{-}C_2H_2Cl_2 + ICl$$

might account for the observed intercepts. It is a radical - radical reaction and it is not a chain reaction pro-

cess. It, thus, is of minor importance in relation to a product which is formed by a chain process.

Branching Ratio

The data indicate that the excited trichloroethyl radical decomposes yielding 62% cis- and 38% trans-dichloroethylene. This is in fair agreement with Dainton's[9] results of 66% and 34%, and Rowland's[124] results of 67% and 33%, respectively. It is in excellent agreement with the equilibrium values of 63% and 37% reported by Ebert and Büll.[32] Knox's value of 78% and 22% are in poor agreement with all of the above data.

Recently, in a study of the decomposition of chemically activated $CH_2ClCDCl_2$, Kim and Setser[56] found that of the CHCl=CDCl produced by HCl elimination 60% was cis-dichloroethylene. The elimination product distribution does not necessarily have to be the same as that found in the decomposition of the hot trichloroethyl radical, but, apparently both processes produce the same results.

Lifetime of the Excited Trichloroethyl Radical

From the ratios of the rate constants of deactivation to isomerization for cis- and trans-dichloroethylene, an estimate can be made of the lifetime of the excited trichloroethyl radical. Combining the two ratios gives a value of 2.0×10^{-20} for $k_{deact}/k_{decomp(total)}$ of the hot radical. Using an estimate of $\sigma^2 = 38.7$ Å.^{2} as the col-

lisional cross-sectional area, a value of 4.9×10^{-11} sec. was obtained for the lifetime. This is far from Dainton's[9] value of 3×10^{-7} sec. But, it is relatively close to Knox's[56] results of 4×10^{-10} sec. and Rowland's[124] value of 6×10^{-10} sec.

In all these calculations which compare the rates of isomerization of cis-dichloroethylene to trans-dichloroethylene, it has been assumed that the two isomers are equally effective as deactivators. However, in the calculation of the cross-sectional areas of the two compounds, there was a difference of about 6%. If the two isomers have different collisional cross-sections, they cannot have the same effectiveness as deactivators. While this cannot account for the difference in the lifetime reported here and those of Knox and Rowland, it certainly is a source of error.

Deactivation Efficiency of CF_4

The relative efficiencies of tetrafluoromethane and trans-dichloroethylene as deactivators was shown on two occasions. Here, in the deactivation of the excited trichloroethyl radical, trans-dichloroethylene was found to be 4.8 times as efficient as CF_4. This ratio was 5.8 for the deactivation of the excited states of trans-dichloroethylene (primarily the two star excited state) which produce chlorovinyl radicals.

These results are not surprising. Tetrafluoromethane

is a highly symmetric molecule with only one type of bond. The transfer of energy to it is severely limited because of the paucity of vibrational and rotational modes available to it. Trans-dichloroethylene is a relatively better deactivator of $C_2H_2Cl_2^{**}$ than of $C_2H_2Cl_3^{*}$. This, too, is reasonable; there is a greater similarity and therefore more efficient deactivation between trans-dichloroethylene and its own excited state than the excited trichloroethyl radical.

Because this investigation was the first detailed study of the primary processes occurring in the photolysis of the dichloroethylenes, it is clear that many of the conclusions drawn from it could not be compared directly to other available results. It, therefore, is extremely gratifying to see that the cis - trans isomerization data obtained in this study are in excellent accord with previous observations made in completely different reaction systems. As an example, scavengers were not used in previous cis - trans isomerization studies. Such good agreement hardly would be expected if the conclusions regarding the primary processes which led to the cis - trans isomerization data would have been wrong. Indirectly, the agreement regarding the isomerization data is thus supportive of other conclusions made in this paper.

CONCLUSIONS

In the photolysis of the three isomers of dichloroethylene with near ultraviolet light (2000 - 4000 Å.), in each case two excited states were found. No two excited species are the same; there are six different molecular entities.

For the 1,2-dichloroethylenes, the lower excited state was found to decompose in the following manner:

$$C_2H_2Cl_2^* \longrightarrow C_2H_2 + Cl_2$$

$$C_2H_2Cl_2^* \longrightarrow C_2HCl + HCl$$

$$C_2H_2Cl_2^* \longrightarrow C_2H_2Cl + Cl$$

For cis-dichloroethylene, the ratio of these processes is 3.1 : 1.0 : 0.28, respectively. For trans-dichloroethylene, it is 2.1 : 1.0 : 0.27. These excited states are thought to be vibrationally excited, ground state molecules. The lifetime of this excited state of cis-dichloroethylene was found to be 2.4×10^{-9} seconds.

The higher excited state of trans-dichloroethylene decomposes only by cleavage of a carbon - chlorine bond.

$$\text{trans-}C_2H_2Cl_2^{**} \longrightarrow C_2H_2Cl + Cl$$

The formation of this excited molecule becomes more important at shorter wavelengths. Its lifetime is 5.1×10^{-9} seconds.

The higher excited state of cis-dichloroethylene

also decomposes by bond cleavage. But, its reactions are more complex.

$$\underline{\text{cis}}\text{-}C_2H_2Cl_2^{**} \longrightarrow C_2H_2 + 2\ Cl$$

$$\underline{\text{cis}}\text{-}C_2H_2Cl_2^{**} \longrightarrow C_2H_2Cl^{\circ} + Cl$$

The ratio of acetylene to excited chlorovinyl radical production is 5.0. The excited chlorovinyl radical thus formed can either decompose or be deactivated.

$$C_2H_2Cl^{\circ} \longrightarrow C_2H_2 + Cl$$

$$C_2H_2Cl^{\circ} + M \longrightarrow C_2H_2Cl + M$$

This excited dichloroethylene molecule becomes apparent only at wavelengths shorter than 2200 Å. Therefore, while the higher excited state of <u>trans</u>-dichloroethylene leads only to chloroiodoethylene production, the higher excited state of <u>cis</u>-dichloroethylene produces acetylene as well.

These higher excited states are thought to be the lowest lying triplet of each isomer. The lifetime of the excited <u>cis</u>-dichloroethylene molecule is 2.0×10^{-7} seconds; that for <u>trans</u>-dichloroethylene, 5.1×10^{-9} seconds. The lifetime of the excited chlorovinyl radical produced by the higher excited state of <u>cis</u>-dichloroethylene was found to be 3.8×10^{-9} seconds.

The chlorovinyl radicals produced from either isomer of 1,2-dichloroethylene were indistinguishable. Regardless of the method of production of these radicals, the ratio

of cis- to trans-chloroiodoethylene was 1 : 4. It is believed that the radicals formed maintain sp^2-hybridization, but invert rapidly.

The cis - trans isomerization of the 1,2-dichloroethylenes was found to proceed via a free radical chain process. Chlorine atoms produced in the primary decompositions would add onto the double bond of the starting material, forming an excited trichloroethyl radical. Free rotation about the carbon - carbon bond led to isomerization when the hot radical decomposed by ejecting a chlorine atom. Of the dichloroethylene formed by this isomerization, 62% was found to be cis-dichloroethylene. The lifetime of the excited trichloroethyl radical is 5×10^{-11} seconds.

The lower excited state of 1,1-dichloroethylene also produces acetylene and chloroacetylene,

$$CH_2CCl_2^* \longrightarrow C_2H_2 + Cl_2$$

$$CH_2CCl_2^* \longrightarrow C_2HCl + HCl$$

but in a ratio of 0.29 : 1.0. This excited state has a lifetime of 2.4×10^{-9} seconds. It requires an activation energy of about 2 kcal./mole to decompose.

It is believed that the 1-chlorovinyl radical is produced only by the higher excited state of 1,1-dichloroethylene.

$$CH_2CCl_2^{**} \longrightarrow C_2H_2Cl + Cl$$

This is the only manner in which the higher excited state decomposes. The formation of this excited state becomes more important at shorter wavelengths. It has a lifetime of 8.4×10^{-9} seconds.

APPENDIX A

Data

All Pressures are in Torr

All Rates are $\times 10^{-12}$ molecules/ml. sec.

TABLE XIV

Pressure Study on cis-1,2-Dichloroethylene, No Filter

P_{total}	$R_{C_2H_2}$	R_{C_2HCl}	$R_{tr\text{-}C_2H_2Cl_2}$	$R_{tr\text{-}C_2H_2ClI}$	$R_{cis\text{-}C_2H_2ClI}$	$R_{C_2H_2Cl_3I}$
3.7	8.98	1.09	14.4	-	-	-
6.5	7.56	1.09	19.8	-	-	-
6.7	10.4	1.55	12.6	0.390	-	0.966
9.3	11.3	1.86	34.6	-	-	1.07
9.6	10.4	1.78	15.7	0.627	-	-
16.1	14.2	2.33	24.7	0.627	0.250	-
16.4	10.4	1.64	21.3	0.441	0.183	-
30.0	14.2	2.48	18.4	1.27	0.267	-
30.2	-	2.48	16.2	1.19	0.333	1.13
41.7	13.2	2.33	19.1	0.933	-	-
44.0	15.1	2.48	20.0	1.27	0.350	1.03

(continued)

TABLE XIV -- CONTINUED

P_{total}	$R_{C_2H_2}$	R_{C_2HCl}	$R_{\underline{tr}\text{-}C_2H_2Cl_2}$	$R_{\underline{tr}\text{-}C_2H_2ClI}$	$R_{\underline{cis}\text{-}C_2H_2ClI}$	$R_{C_2H_2Cl_3I}$
59.8	13.2	2.17	14.2	0.933	-	-
61.4	18.2	3.50	21.6	1.48	0.383	0.733
80.0	13.0	2.48	16.9	0.983	0.217	-
84.1	-	2.79	-	0.933	0.200	-
102.9	14.2	1.55	11.2	-	-	-

TABLE XV

Pressure Study on cis-1,2-Dichloroethylene, Filter 9-54

P_{total}	$R_{C_2H_2}$	R_{C_2HCl}	$R_{tr\text{-}C_2H_2Cl_2}$	$R_{tr\text{-}C_2H_2ClI}$	$R_{cis\text{-}C_2H_2ClI}$	$R_{C_2H_2Cl_3I}$
9.2	0.669	0.207	2.34	no	iodine	added
9.8	0.748	0.211	2.34	0.0438	0.0181	0.0222
13.5	0.945	0.207	2.92	0.0325	0.0097	0.0222
17.2	1.02	0.258	3.97	0.0706	0.0306	0.0200
29.5	1.34	0.414	3.59	0.0989	0.0278	-
29.9*	1.58	0.414	5.20	0.103	0.0417	-
50.2	1.97	0.672	4.87	0.141	0.0625	0.0194

*This experiment was performed in four segments of 15 minutes each, more iodine being added to the cell before commencing each segment.

TABLE XVI

Pressure Study on cis-1,2-Dichloroethylene, Filters 9-53, 0-54 and 0-52

P_{total}	Filter	$R_{C_2H_2}$	R_{C_2HCl}	$R_{tr\text{-}C_2H_2Cl_2}$	$R_{tr\text{-}C_2H_2ClI}$	$R_{cis\text{-}C_2H_2ClI}$	$R_{C_2H_2Cl_3I}$
5.4	0-52	0.173	0.0199	0.262	0.00664	-	0.00778
5.5	0-54	0.154	0.0233	0.327	0.00254	-	0.00311
9.7	9-53	0.223	0.0345	0.612	0.00612	-	0.00593
10.8	0-54	0.165	0.0258	0.402	-	-	-
18.7	9-53	0.210	0.0370	0.424	0.00542	-	-
30.9	9-53	0.249	0.0534	0.899	0.0108	0.00509	0.00741
31.8	0-54	-	0.0517	-	-	-	-
47.3	9-53	0.315	0.0517	0.593	-	-	-
48.5	0-54	0.276	0.0517	0.562	0.0258	0.0115	0.00972
50.2	9-53	0.302	0.0689	0.786	0.0236	0.00648	0.00444
56.8	0-54	0.295	0.0543	0.431	0.0212	0.00347	0.00889

TABLE XVII

Pressure Study on trans-1,2-Dichloroethylene

No Filter Scavenger: I_2

P_{total}	$R_{C_2H_2}$	R_{C_2HCl}	$R_{cis\text{-}C_2H_2Cl_2}$	$R_{tr\text{-}C_2H_2ClI}$
2.1	3.41	1.76	5.07	0.692
4.4	3.70	1.66	14.9	-
6.4	4.00	1.88	22.3	1.47
8.9	-	2.07	24.8	1.62
11.6	4.69	2.02	32.7	1.91
15.6	4.55	-	31.2	2.06
19.3	-	2.17	31.5	2.43
20.7	-	2.10	32.1	-
24.3	5.28	2.22	29.3	3.06
29.7	4.40	2.12	26.7	2.50
49.8	4.11	2.31	-	-
54.1	4.55	2.41	26.4	3.24

TABLE XVIII

Pressure Study on trans-1,2-Dichloroethylene

No Filter Scavenger: HCl (1)

P_{total}	$R_{C_2H_2}$	R_{C_2HCl}	$R_{C_2H_3Cl}$	$R_{cis\text{-}C_2H_2Cl_2}$
4.2	3.95	2.13	2.90	-
10.4	4.89	2.23	3.88	73.2
11.1	-	2.18	4.04	-
16.5	5.44	3.38	4.29	61.7
19.3	-	2.47	5.41	84.0
21.6	4.84	2.50	5.71	82.6
31.8	6.33	2.99	6.74	67.5
45.0	7.90	3.95	6.20	53.7
63.3	-	5.72	9.18	63.2
85.8	7.45	2.81	6.49	50.0
156.3	-	-	-	43.8
167.1	-	3.90	6.94	40.2

TABLE XIX

Pressure Study on trans-1,2-Dichloroethylene

No Filter Scavenger: HCl (2)

P_{total}	$R_{C_2H_2}$	R_{C_2HCl}	$R_{C_2H_3Cl}$	$R_{cis\text{-}C_2H_2Cl_2}$
5.2	0.903	0.446	0.907	64.2
9.5	2.08	0.773	2.67	106.
13.9	1.50	0.744	3.84	56.8
21.6	1.65	0.773	4.28	45.9
21.8	2.35	0.684	4.09	45.9
31.5	1.44	0.607	4.28	52.4
45.3	1.35	0.654	5.12	29.3
61.0	1.63	0.773	4.70	38.0
83.6	1.99	0.714	4.56	49.8

TABLE XX

Tetrafluoromethane Deactivation Study on trans-1,2-Dichloroethylene Scavenger: I_2

$P_{tr\text{-}C_2H_2Cl_2}$	P_{CF_4}	$R_{C_2H_2}$	R_{C_2HCl}	$R_{cis\text{-}C_2H_2Cl_2}$	$R_{tr\text{-}C_2H_2ClI}$	$R_{cis\text{-}C_2H_2ClI}$	$R_{C_2H_2Cl_3I}$
20.1	-	0.741	0.365	6.72	0.827	0.144	0.502
20.1	-	0.556	0.341	8.33	0.853	0.0941	0.852
20.0	11.5	0.750	0.070	10.83	-	-	0.743
20.0	24.7	0.241	0.122	10.21	0.293	-	-
20.0	41.1	-	0.224	8.33	0.720	0.058	0.858
20.1	55.5	-	-	4.43	0.587	-	1.55
19.9	93.1	0.333	-	2.42	0.427	-	1.17
20.2	202.3	0.185	0.034	3.22	0.453	0.052	1.31
19.9	229.4	-	0.127	2.69	0.373	-	1.97
20.1	298.6	-	0.244	2.69	-	-	-
20.0	398.1	0.278	0.158	2.96	0.192	-	0.670
20.1	577.5	0.222	0.073	1.61	0.427	0.144	0.816

TABLE XXI

Pressure Study on 1,1-Dichloroethylene at 18° C.

P_{total}	$R_{C_2H_2}$	R_{C_2HCl}	R_{CH_2CClI}	$R_{CH_2ICCl_3}$	$R_{CH_2ClCCl_2I}$
3.6	0.229	0.812	5.79	-	0.196
4.8	0.426	0.957	6.52	0.268	2.61
4.9	0.572	2.03	6.52	-	1.45
11.7	0.549	2.17	8.15	-	0.725
21.8	-	3.19	12.7	-	-
40.5	0.678	2.32	5.07	1.27	0.489
42.3	1.06	3.20	13.4	0.437	0.779
48.9	0.641	3.19	12.0	0.795	2.03
60.9	0.572	1.74	12.7	1.03	-

TABLE XXII

Pressure Study on 1,1-Dichloroethylene at 28° C.

P_{total}	$R_{C_2H_2}$	R_{C_2HCl}	R_{CH_2CClI}	$R_{CH_2ICCl_3}$	$R_{CH_2ClCCl_2I}$
3.7	0.481	1.45	5.43	-	0.590
7.4	1.46	1.72	6.34	-	0.652
9.7	1.83	1.95	7.06	0.509	-
10.8	1.51	-	7.15	0.361	1.56
12.1	-	2.17	9.77	-	0.536
21.9	1.18	2.03	9.05	0.175	0.870
37.9	1.30	2.17	10.9	1.76	1.01
41.1	1.38	2.32	11.6	-	1.16
51.8	0.961	2.46	12.9	0.665	0.304
60.0	0.985	2.90	13.1	0.596	0.667

TABLE XXIII

Pressure Study on 1,1-Dichloroethylene at 45° C.

P_{total}	$R_{C_2H_2}$	R_{C_2HCl}	R_{CH_2CClI}	$R_{CH_2ICCl_3}$	$R_{CH_2ClCCl_2I}$
3.6	-	1.07	3.62	-	-
5.6	-	1.59	6.88	-	0.580
13.3	-	1.88	6.88	-	0.337
39.8	0.795	2.46	10.5	0.477	1.31
61.0	1.51	3.19	14.3	1.27	0.435

APPENDIX B

A more Complex Isomerization Mechanism

It was found that the mechanism for the isomerization did not fully represent all the reactions occurring (see page 164). Other free radical terminations were thought to be needed. The following, more complete, mechanism was proposed:

$$C_2H_2Cl_2^* \longrightarrow C_2H_2Cl + Cl \quad (1)$$

$$C_2H_2Cl + I_2 \longrightarrow C_2H_2ClI + I \quad (2)$$

$$Cl + C_2H_2Cl_2 \longrightarrow C_2H_2Cl_3^* \quad (3)$$

$$C_2H_2Cl_3^* \longrightarrow \text{Isomer-}C_2H_2Cl_2 + Cl \quad (4a)$$

$$C_2H_2Cl_3^* \longrightarrow \text{Same-}C_2H_2Cl_2 + Cl \quad (4b)$$

$$C_2H_2Cl_3^* + C_2H_2Cl_2 \longrightarrow C_2H_2Cl_3 + C_2H_2Cl_2 \quad (5)$$

$$2\ C_2H_2Cl_3^* \longrightarrow \text{disproportionation and/or recombination} \quad (7)$$

$$Cl + C_2H_2Cl_3^* \longrightarrow \text{disproportionation and/or recombination} \quad (8)$$

$$2\ Cl + C_2H_2Cl_2 \longrightarrow Cl_2 + C_2H_2Cl_2 \quad (9)$$

In the presence of an inert deactivator, tetrafluoromethane, the following reactions also may occur:

$$C_2H_2Cl_3^* + CF_4 \longrightarrow C_2H_2Cl_3 + CF_4 \quad (6)$$

$$2\,Cl + CF_4 \longrightarrow Cl_2 + CF_4 \qquad (10)$$

In this mechanism, Reactions 7 - 10 represent new termination steps.

Making use of the steady state approximation, and after considerable algebraic manipulation, the equation given on page 229 can be derived. In the equation, the following are used as simplifications in writing:

D = the concentration of the starting isomer of 1,2-dichloroethylene

Z = the rate of isomerization

M = the concentration of inert deactivator

R = the rate of formation of the chlorovinyl radical product

The rate constants also may be made to look more tractable. Actually, there are only seven sets of ratios of rate constants in the entire equation.

$K_4 = (k_{4a} + k_{4b})/k_{4a}$

$K_5 = k_5/k_{4a}$

$K_6 = k_6/k_{4a}$

$K_7 = k_7/k_{4a}^2$

$K_8 = k_8/k_3k_{4a}$

$$K_9 = k_9/k_3^2$$

$$K_{10} = k_{10}/k_3^2$$

The equation is:

$$D^2R/Z = K_4(2K_8 + K_4K_9)DZ - 2K_4K_8^2Z^2 - K_8^2RZ +$$
$$2K_8DR - K_7K_8^2Z^3 + (2K_4K_7K_9 - K_5K_8^2)DZ^2 +$$
$$(K_7 + 2K_4K_5K_9)D^2Z + K_5D^3 + K_5^2K_9D^3Z +$$
$$2K_5K_7K_9D^2Z^2 + K_7^2K_9DZ^3 +$$
$$K_4^2K_{10}MZ + K_6D^2M + 2K_4(K_6K_9 + K_5K_{10})DMZ +$$
$$2K_4K_6K_{10}M^2Z + (2K_4K_7K_{10} - K_6K_8^2)MZ^2 +$$
$$K_7^2K_{10}MZ^3 + 2K_6K_7K_{10}M^2Z^2 + K_6^2K_{10}M^3Z +$$
$$K_5(2K_6K_9 + K_5K_{10})D^2MZ + 2K_7(K_6K_9 + K_5K_{10})DMZ^2$$
$$+ K_6(K_6K_9 + 2K_5K_{10})DM^2Z$$

Of the 22 terms on the right side of the equation, the latter 11 drop out if no deactivator has been added (M = 0).

The Computation

Obviously, this equation is not suitable for graphing. To determine rate constants from an equation such as this, a least squares calculation must be done. If this is to be done within a reasonable time span, a computer has to be used.

The language which the author was taught for this purpose is "Basic." It is a highly verbal computer language. Therefore, it is easy to learn. However, it has the drawback of being very slow -- for a computer -- and being restrictive in the operations which can be done using it. There is no general method for solution of a determinant by Basic. If one has to be solved, a program must be written detailing every step to be done. In some other computer languages, for an iteritive process such as determinant solving, this is unnecessary. A simple, general program can be written. Instead of using determinants, the simultaneous equations generated by the least squares solution was solved by the method of elimination, using the largest pivotal divisor. The program is listed in Table XXIV. The computer used was a Data General Nova, Single Use Basic (12K).

The Program

The N first mentioned in lines 2 and 3 is the number of terms in the equation being solved. Consequently, it is the size of the square matrix to be solved in the least squares analysis. Lines 20 - 65 generate a set of N simultaneous equations, with all solutions having values of 1. This is used to test the least squares program. Line 10 circumvents these test equations.

Line 1030 sends the program to 2000. M7 (lines 2010 and 2020) is the number of results being analyzed,

TABLE XXIV

The Computer Program

```
   2  PRINT "N  =  ",
   3  INPUT N
   5  DIM A(N,N),B(N)
  10  GOTO  1030
  20  LET Z5 = 0
  25  FOR Z1 = 1 TO N
  27    LET Z6 = 0
  30    FOR Z2 = 1 TO N
  35      LET Z5 = Z1 + Z2 - 1
  40      IF Z5 < (N + 1) GOTO  50
  45      LET Z5 = Z5 - N
  50      LET A(Z1,Z2) = Z5
  52      LET Z6 = Z6 + Z2
  55    NEXT Z2
  60    LET B(Z1) = Z6
  65  NEXT Z1
  80  GOTO  1070
1030  GOSUB  2000
1070  PRINT "SOLUTION OF SIMULTANEOUS EQUATIONS"
1130  GOSUB  6000
1140  IF (K1 - 1) <> 0  GOTO  1180
1150  PRINT "MATRIX IS SINGULAR"
1170  STOP
```

```
1180  PRINT "SOLUTION VALUES"
1190  FOR H1 = 1 TO N
1200    PRINT H1,B(H1)
1210  NEXT H1
1220  GOSUB  7000
1230  PRINT "END OF CASE"
1240  END
2000  REM   LSTSQ
2010  PRINT "M7  =  ",
2020  INPUT M7
2025  DIM G(M7,N),H(M7),P(M7)
2026  DIM Z(M7),D(M7),R(M7),M(M7)
2040  FOR J = 1 TO M7
2050    INPUT Z(J),D(J),R(J),M(J)
2060    PRINT
2070  NEXT J
2090  PRINT ,,"DATA"
2100  PRINT " J"," Z(J)"," D(J)"," R(J)"," M(J)"
2110  FOR J = 1 TO M7
2120    PRINT J,Z(J),D(J),R(J),M(J)
2130    LET H(J) = 0
2140    FOR K = 1 TO N
2150      LET G(J,K) = 0
2160    NEXT K
2170    LET G(J,1) = D(J)*3.24*Z(J)
2180    LET G(J,2) = -2*(Z(J)↑2)
2190    LET G(J,3) = -Z(J)*R(J)
```

```
2200    LET G(J,4) = 2*D(J)*3.24*R(J)
2210    LET G(J,5) = -(Z(J)↑3)
2220    LET G(J,6) = D(J)*3.24*(Z(J)↑2)
2230    LET G(J,7) = ((D(J)*3.24)↑2)*Z(J)
2240    LET G(J,8) = (D(J)*3.24)↑3
2250    LET G(J,9) = ((D(J)*3.24)↑3)*Z(J)
2260    LET G(J,10) = 2*((D(J)*3.24)↑2)*(Z(J)↑2)
2270    LET G(J,11) = D(J)*3.24*(Z(J)↑3)
2320    LET G(J,12) = Z(J)*M(J)*3.24
2325    LET G(J,13) = ((D(J)*3.24)↑2)*M(J)*3.24
2330    LET G(J,14) = 2*D(J)*3.24*Z(J)*M(J)*3.24
2335    LET G(J,15) = 2*Z(J)*((M(J)*3.24)↑2)
2340    LET G(J,16) = (Z(J)↑2)*M(J)*3.24
2345    LET G(J,17) = (Z(J)↑3)*M(J)*3.24
2350    LET G(J,18) = 2*(Z(J)↑2)*((M(J)*3.24)↑2)
2355    LET G(J,19) = Z(J)*((M(J)*3.24)↑3)
2360    LET G(J,20) = ((D(J)*3.24)↑2)*Z(J)*M(J)*3.24
2365    LET G(J,21) = 2*D(J)*3.24*(Z(J)↑2)*M(J)*3.24
2370    LET G(J,22) = D(J)*3.24*Z(J)*((M(J)*3.24)↑2)
2380    LET H(J) = ((D(J)*3.24)↑2)*R(J)/Z(J)
2390  NEXT J
2620  FOR K = 1 TO N
2630    LET B(K) = 0
2640    FOR L = 1 TO N
2650      LET A(K,L) = 0
2660      FOR J = 1 TO M7
2670        LET A(K,L) = (G(J,K)*G(J,L)) + A(K,L)
```

```
2680        IF (L - 1) > 0  GOTO  2700
2690        LET B(K) = (G(J,K)*H(J)) + B(K)
2700      NEXT J
2710    NEXT L
2720  NEXT K
6000  LET T1 = 0
6010  LET K9 = 0
6020  FOR G1 = 1 TO N
6030    LET J0 = G1 + 1
6040    LET B1 = 0
6050    FOR H1 = G1 TO N
6060      IF ( ABS (B1) - ABS (A(H1,G1))) >= 0  GOTO  6090
6070      LET B1 = A(H1,G1)
6080      LET M2 = H1
6090    NEXT H1
6100    IF ( ABS (B1 - T1)) > 0  GOTO  6130
6110    LET K9 = 1
6115    LET K1 = K9
6120    RETURN
6130    FOR K1 = G1 TO N
6140      LET S4 = A(G1,K1)
6150      LET A(G1,K1) = A(M2,K1)
6160      LET A(M2,K1) = S4
6170      LET A(G1,K1) = A(G1,K1)/B1
6180    NEXT K1
6190    LET S4 = B(M2)
6200    LET B(M2) = B(G1)
```

```
6210    LET B(G1) = S4/B1
6220    IF (G1 - N) = 0  GOTO  6300
6230    FOR I9 = J0 TO N
6240      FOR J9 = J0 TO N
6259        LET A(I9,J9) = A(I9,J9) - (A(I9,G1)*A(G1,J9))
6260      NEXT J9
6270      LET B(I9) = B(I9) - (B(G1)*A(I9,G1))
6280    NEXT I9
6290  NEXT G1
6300  LET N2 = N - 1
6320  FOR G2 = 1 TO N2
6330    LET B2 = N - G2
6340    LET C6 = N
6350    FOR K2 = 1 TO G2
6360      LET B(B2) = B(B2) - (A(B2,C6)*B(C6))
6370      LET C6 = C6 - 1
6380    NEXT K2
6390  NEXT G2
6400  RETURN
7000  FOR J = 1 TO M7
7010    FOR K = 1 TO N
7020      LET P(J) = P(J) + G(J,K)*B(K)
7030    NEXT K
7040    LET Y6 = (P(J) - H(J)*(P(J) - H(J)) + T6
7050  NEXT J
7060  LET U = SQR (T6/M7)
7070  PRINT "THE ROOT MEAN SQUARE ERROR IS " U
```

7080 RETURN

the number of experiments performed in the series. In lines 2040 - 2070, the data is fed into the computer. The data is fed back to the operator at line 2120, giving the operator the opportunity to check them for accuracy. In lines 2170 -2380, the computer caculates the variables for each term of the rate equation, for each set of data. The actual application of the least squares method is accomplished in lines 2620 - 2720. This produces the square matrix which cannot be solved directly.

The solution is found in lines 6000 - 6400 by the method of elimination, using the largest pivotal divisor (found in lines 6040 - 6090). Each stage of elimination consists of interchanging rows when necessary (lines 6130 - 6210) to avoid division by zero. At 6100 is a test for a singular matrix. If this is passed, the results are calculated and the program returns to lines 1180 - 1210 to print the solution values. It then is sent to 7000 - 7080 to calculate and print the root mean square error, before ending.

A Sample Solution

A not untypical result is shown below. It comes from the data of the tetrafluoromethane deactivation series (Table XX, page 223). It took between 15 and 30 minutes to be computed.

DATA

J	Z(J)	D(J)	R(J)	M(J)
1	6.73	20	1.03	0
2	8.33	20	1.07	0
3	10.2	20	0.366	22.7
4	8.33	20	0.9	41.1
5	4.43	20	0.734	55.6
6	2.42	20	0.534	93.
7	3.22	20	0.566	202.5
8	2.69	20	0.466	229.3
9	2.96	20	0.24	398.1
10	1.61	20	0.534	577.6

SOLUTION OF SIMULTANEOUS EQUATIONS

SOLUTION VALUES

1	-4.5627E5
2	1.95792E10
3	6.87503E10
4	1.60608E5
5	2.34954E-4
6	8.30276E-8
7	-5.74219E-13
8	2.10601E-18
9	5.47055E-31
10	8.25128E-26
11	-6.90918E-21
12	-1.6286E4
13	-1.6902E-20

14	1.94435E-14
15	4.41707E-16
16	3.29151E-9
17	-8.21507E-22
18	-1.08995E-28
19	1.67778E-35
20	-3.81499E-32
21	3.12006E-27
22	-1.31683E-33

THE ROOT MEAN SQUARE ERROR IS 0.382518

END OF CASE

Rate constants cannot be negative, nor can a ratio of rate constants. All the negative values for ratios of rate constants make these results of no use whatever. However, the program remains for the solution of difficult equations.

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