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ABSTRACT

THE PRIMARY PROCESSES IN THE PHOTOLYSIS OF 1,2-DICHLOROPROPANE

BY

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The photolysis of 1,2-dichloropropane has been investigated in detail at room temperature and at different wavelengths. Studies over a range of exposure times permitted extrapolation of the observed product ratios to zero exposure time. Experiments in the presence and absence of inert deactivators such as SF_6 and H_2O, and of H_2S as a free radical scavenger indicated the production of three different excited states which decompose as follows :

$$CH_2ClCHClCH_3^{*} \longrightarrow \text{cis and trans } CHCl{=}CHCH_3 + HCl$$

$$CH_2ClCHClCH_3^{**} \longrightarrow CH_2{=}CHCH_3 + Cl_2$$

$$\longrightarrow CH_2{=}CClCH_3 + HCl$$

$$CH_2ClCHClCH_3^{***} \longrightarrow CH_2{=}CHCH_3 + 2\ {\cdot}Cl$$

The "one star" excited state is produced predominantly at long, the "three star" excited state at short wavelengths.

The production of cis- and trans-1-chloropropene was followed in detail, first in regard to the cis/trans ratio produced in the primary process, then in regard to variations in this ratio caused by secondary

reaction. The data yield an equilibrium value of $R_{cis}/R_{trans} = 1.5$ for the chlorine atom induced isomerization of 1-chloropropene.

Evidence is presented for the production of 1-chloropropene by chlorine atom addition to 2-chloropropene. The results of this investigation are shown to be consistent with data reported in the literature regarding similar systems.

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To my dear wife, IN-SOON, my mother, and my daughter, HYUN-JIN
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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

I. INTRODUCTION

Our investigation deals with the photolysis of halogenated propanes and in particular with the photolysis of 1,2 - dichloropropane. It is, therefore, interesting to discuss first some general principles involved in photochemical research. After this we will give a short survey of work carried out in the gas phase, on the photolysis of halogenated hydrocarbones.

1. The Absorption of Light

Most reactions carried out in the laboratory occur with molecules which are in the electronic ground states. In photochemistry, however, a reacting molecule has previously been promoted by absorption of light to an electronically excited states. To promote a molecule from the ground state to an excited state, outside energy is required. In photochemical reaction this outside energy is supplied by light. This kind of molecular excitation is best understood in terms of the quantum theory.

According to the quantum theory, light is made up of discrete particles called photons or quanta. Each photon carries an amount of energy, E, which depends on frequency, ν, or wavelength, λ, as shown in equation.

$$E = h\nu = \frac{hc}{\lambda}$$

Where h and c are the Plank constant and the velocity of light, respec-

tively. The energy of one mole of photons(definition of einstein) is given by equation.

$$E = \frac{Nhc}{\lambda}$$

Where N is the number of Avogardro. The energy at a given wavelength can be calculated by substitution of the appropriate numerical values for N, h, and c.

$$E = \frac{2.86 \times 10^4}{\lambda} \quad \text{Kcal / einstein}$$

Where λ is in nanometers. For example, an einstein of 200-nm light has an energy of 144 Kcal, whereas that of 340-nm light has an energy of 84.1 Kcal.

Considering the absorption of light energy, it would seen that an electron transition from one electron level to another should consist of one or more sharp peaks, since the energy levels of a molecule are quantized. However, the ultraviolet and visible absorption spectra of molecules are made up of broad bands in which a number of peaks are discernible. This broad absorption can be rationalized by the fact that molecules are constantly vibrating and rotating and these motions are also quantized. According to the Frank - Condon principle, the excitation of a molecule from one energy level to another occurs with almost no change in internuclear distance. This is due to the fact that the excitation happens much faster than a single molecular vibration. While an electron moves from one energy level to another, it moves from a given vibrational and rota-

tional level to some of those at next electronic level. A given sample contains a large number of molecules which are distributed among vibrational and rotational states.

The electron transitions between energy levels are governed by selection rules which are derived from the transition-moment intergral such as the equation $\langle \Psi | \vec{r} | \Psi' \rangle \neq 0$. The complete molecular wave function Ψ is approximated as a product of one-electron orbitals (ϕ), vibrational (U) and spin portion (S). The dipole moment operator $\vec{r}$ only interacts with electrons and not nuclei or electron spins, so that the transition moment intergral may be rewritten as $\langle \phi | \vec{r} | \phi' \rangle \langle U | U' \rangle \langle S | S' \rangle \neq 0$. From this, two important selection rules may be derived. First, in order that the electron transition moment $\langle \phi | \vec{r} | \phi' \rangle$ should not vanish, one of the electron wave functions should have an odd function(u) and another an even function(g), since the operator $\vec{r}$ is an odd function. A g → g or u → u transition is forbidden, while a g → u or u → g transition is allowed. Second, if the spins become unpaired during the transition, the intergral $\langle S | S' \rangle$ is zero, and a change of one electron spin would also violate the angular momentum conservation law. Therefore, singlet → triplet and triplet → singlet transitions are forbidden, whereas singlet → singlet and triplet → triplet transitions are allowed. However, in actual system forbidden transitions are frequently observed, though usually with low intensity.

In organic molecules there are four types of electronic excitation. First is a σ,σ^* transition ; this transition is difficult to study in photochemistry, because all matter absorbs at this wavelength. The second

one is a π,π^* transition, the third one is an n,σ^* and the fourth one is an n,π^* transition. These transitions are solvent-dependent, and in a polar solvent these transitions are shifted to shorter wavelengtn.

The probability of a certain transition can be determined experimentally by measuring its extinction coefficient, ε, using Beer - Lambert law. When a beam of monochromatic light, previously rendered plane - parallel, enters a sample at right angles to the plane parallel surfaces of the sample, the rate of decrease in radiant power, T, (power of transmitted light over power of incident light, called transmittance) with the length of the light path b or with the concentration c of the sample (mole per liter) will follow an exponential progression as shown in equation.

$$T = 10^{-\varepsilon bc}$$

The logarithm of the reciprocal of the transmittance is the absorbance A.

$$A = -\log T = \varepsilon bc$$

The value of the extinction coefficient is a constant dependent upon the wavelength of the light, temperature and solvent, but not upon concentration.

2. Fate of the Excited Molecule(1 - 4)

The excited molecule loses some of the absorbed energy by physical or chemical processes.

(A) Physical Processes

(1) Unimolecular Processes

A molecule interacting with radiation in the ultraviolet and visible region will undergo transition from one electronic state to another, and generate an excited singlet S_1 state in an upper vibrational level, since the excitation from S_1 to triplet states are forbidden by selection rule. Other excitations to S_2 and S_3 are also possible, but in liquid and solid these higher states rapidly degrade to S_1 state. This excited singlet S_1 state is not long - lived, it loses some of the absorbed energy without involving chemical reaction. Such processes are called physical processes. These kinds of phenomena can be explained well by a Jablonski diagram, which simply shows energies of the different states.

(a) Vibrational Relaxation

A molecule in the upper vibreational energy levels of one electronic state can cascade down to its ground vibrational energy level by releasing thermal energy to the environment. These kinds of vibrational degradations, $S_1^v \rightarrowtail S_1$ + heat, $T_1^v \rightarrowtail T_1$ + heat, are very fast ($k \simeq 10^{12} sec.^{-1}$). As briefly mentioned before, electronic transition in molecules involves not only changes in the electronic state but changes in the vibrational and rotational state as well. But the population of the vibrational S_1^0 level increases by this vibrational relaxation. Therefore, most of physical and chemical processes start from this S_1 state.

(b) Internal Conversion

A molecule in a higher electronic state can cascade down without absorption or emission of light through the vibrational levels of the lower electronic state which has the same spin multiplicity. The rate of conversion between different electronic states of like spin multiplicity, $S_1 \rightarrowtail S_0$ + heat, depends inversely on the energy seperation between them ($k \simeq 10^6 \sim 10^{12}$ $sec.^{-1}$). But this process is generally quite slow because the energy gap between the two electronic states is almost always large. Thus it is from S_1 that most interesting photochemistry begins.

(c) Intersystem Crossing

A molecule in a higher electronic state may go to a lower electronic state, which has a different spin multiplicity, without absorption or emission of light. This kind of conversion, $S_1 \rightarrowtail T_1^V$ or $T_1 \rightarrowtail S_1^V$, is of course a forbidden pathway since it violates the spin forbidden selection rule, but this process often takes place by compensations elsewhere in the system. This crossing must be isoenergetic. Thus the S_1 molecule crosses to a T_1 state at a high vibrational level and then this upper vibrational level cascade down very rapidly to its lowest vibrational level by vibrational relaxation. A singlet state usually has a higher energy than the corresponding triplet state. The reason for the temperature dependence and the exact mechanism of the pathway are not well understood. Its transition rate also depends on the energy gap between the

states. ($k \simeq 10^{-1} \sim 10^{5}$ $sec.^{-1}$ for $S_1 \rightsquigarrow T_1^V$, $k \simeq 10^{4} \sim 10^{12} sec.^{-1}$ for $T_1 \rightsquigarrow S_0^V$)

(d) Fluorescence

A molecule in the excited singlet state S_1 which did not arrive at the triplet state by collisional deactivation may emit radiation from its lowest vibrational state to return to the singlet ground state. Such processes, $S_1 \rightarrow S_0 + h\nu$, are very fast — on the order of $10^{-6} \sim 10^{-9} sec.^{-1}$ following excitation. Generally, there exist many overlapping potential curves, so that it is even possible for the excited singlet state to return to the ground state by going through a series of overlapping states. The wavelengths and quantum yield of fluorescence nomally do not depend on the exciting wavelength, because the fluorescing molecules all drop from the lowest vibrational level of the S_1 state to various vibrational levels of S_0, while excitation is from the lowest vibrational level of S_0 to various levels of S_1.

The shortest-wavelength can be emitted by the transition between the lowest vibrational levels of the two states (0 - 0 transition). Longer wavelengths of light are emitted when upper vibrational levels of the ground state are populated. When 0-0 fluorescence has the same wavelength as 0-0 absorption, it is called resonance fluorescence. If it is possible to reduce the energy of the excited state by altering either the geometry of the excited molecule or position of solvent molecule around it, 0 - 0 emission will be shifted to longer wavelength than that of 0 - 0 absorp-

tion. This kind of shift is called a Stokes shift. Occassionally a reverse of Stokes shift takes place by the absorption from a higher vibrational level of the ground states.

(e) Phosphorescence

A molecule in the excited triplet state T_1 could emit radiation from its lowest vibrational level to come back to the lower-lying ground states. As mentioned before, suppose a molecule excites from a singlet ground electronic state to a higher excited electronic state whose potential curve overlaps with that of triplet electronic excited state. The excited singlet state can now lose vibration energy by collisional deactivation, e.g., by transferring some of its vibrational energy via thermal collisions to other molecules(vibrational relaxation). When the vibrational energy level of the excited singlet state reaches the point where the singlet - triplet potential curves cross, a radiationless transition from the singlet to the triplet state can occur(intersystem crossing). This triplet state will also undergo vibrational relaxation until the lowest vibrational level is reached. The triplet state can now drop to the singlet state by emission of light. These emission processes, $T_1 \rightarrow S_0 + h\nu$ are very slow($k \approx 10^{-2} \sim 10^{4}$ $sec.^{-1}$) because of violation of the selection rule.

At room temperature in solution, this phosphorescence is often not detected because intersystem crossing of T_1 to S_0 and vibrational relaxation of T_1 by impurities and molecular oxygen compete effectively with

phosphorescence. Therefore most phosphorescence studies must be carried out at low temperature in carefully purified, outgassed, rigid media.

A molecule in the triplet state may undergo a delayed fluorescence, since the molecule can generate the singlet state by thermal vibrational reactivation and collision between two triplet molecules. The relative intensities of the emission depend on temperature because the repopulation of the singlet state can be increased at higher temperature.

(2) Bimolecular Processes

It is a common phenomenon in photochemistry that a molecule in an electronically excited state transfers its energy to a molecule in the ground state by both radiative and nonradiative methods, in a process called photosensitization. This is another way to reach an excited state without direct absorption of light. When this process takes place by collision between the excited molecule and the ground state molecule, the spin multiplicity of each molecule may change during collision. But it follows the Wigner spin conservation rule which states that the total spin does not change after energy transfer. Thus, for example, when an excited triplet donor (D^*) could interact with a ground state singlet acceptor (A_0), there should be following possibilities.

D^* A_0 D_0 A^*

$(\uparrow\uparrow)^* + \downarrow\uparrow \longrightarrow \uparrow\downarrow + (\uparrow\uparrow)^*$ singlet + triplet

$\longrightarrow \uparrow\downarrow\uparrow + \uparrow$ doublet + doublet

$\longrightarrow$ ↑↑ + ↓ + ↑ triplet + doublet + doublet

$\longrightarrow$ ↑ + ↑ + ↓↑ doublet + doublet + singlet

$\longrightarrow$ (↑↑↓↑) triplet

Other important types of intermolecular energy transfer are triplet-triplet and singlet - singlet transfer. The singlet - singlet transfer can occur over long distance (≃ 40 Å), but a triplet transfer normally requires a collision between the molecules. In photochemistry those types of energy transfer may be useful for creating desired excited states which are difficult to achieve by direct irradiation. Thus, this type of photochemistry is frequently reported in the literature.

(B) Chemical Processes

A molecule in either excited singlet or triplet state can undergo chemical reactions. The reaction products, however, will usually be produced in the electronic ground state. Sometimes, activated species are formed which may undergo chemical reactions such as abstraction, addition, fragmentation, rearrangement, recombination, disproportionation. For an example, the light induced chlorination of a hydrocarbon(5) is a chain process. The initiation of the reaction is the primary process, but the product - forming steps are secondary processes.

$Cl_2 + h\upsilon \longrightarrow 2\ \cdot Cl$ Initiation

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

$R\cdot + Cl_2 \longrightarrow RCl + Cl\cdot$ Propargation

$$Cl\cdot + Cl\cdot \longrightarrow Cl_2$$
$$R\cdot + R\cdot \longrightarrow R - R$$
$$R\cdot + Cl\cdot \longrightarrow R - Cl$$

Termination

In this section, some specific examples of the organic photochemical reaction will be surveyed.

(1) Dissociation into Free Radicals (Norrish Type I) (6)

Carbonyl compounds such as aldehydes and ketones may be excited by weak absorption in the 230 ∿ 340 nm region, which is assumed to result from a forbidden n - π^* transition involving the promotion of a non-bonding 2p electron of the oxygen atom to the carbonyl antibonding π^* orbital. The excited carbonyl compound undergoes α cleavage and produces an acyl radical and an alkyl radical by the primary process in an inert solvent or in the gas phase(7). In the reaction of unsymmetrical ketones the cleavage depends on the relative stabilities of the two possible radicals.

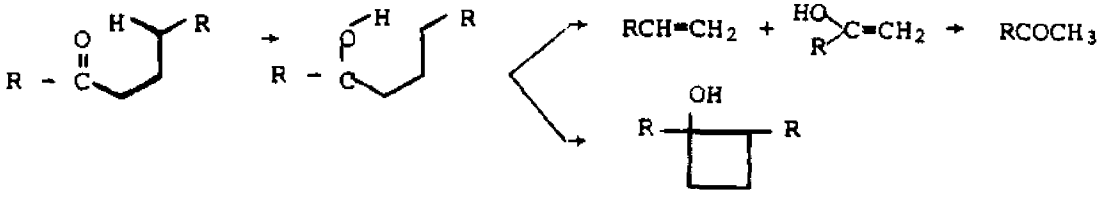
$$R - \overset{O}{\overset{\|}{C}} - R' \longrightarrow R - \overset{O}{\overset{\|}{C}}\cdot + \cdot R' \longrightarrow \text{Products}$$

(decarbonylation, recombination, and disproportionation)

(2) Decomposition into Molecules (Norrish Type II) (8)

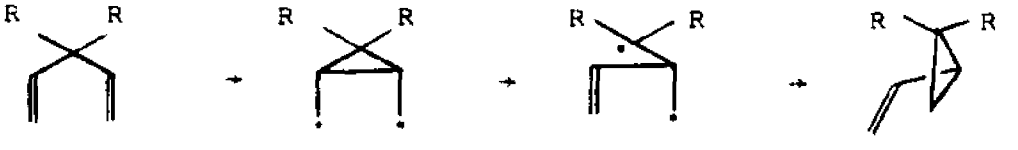
An excited carbonyl compound which has a γ-hydrogen can undergo intramolecular abstraction of γ-hydrogen via a six-membered ring transition state. The resulting diradical gives an alkene and an enol form of aldehyde or ketone which may tautomerize, or it cyclizes to a cyclobutanol

observed as a side product. The biradical can be trapped by a good hydrogen donor such as butanethiol-S-d, in which case γ-deuterated starting material is recovered(9).



(3) Intramolecular Rearrangement (10)

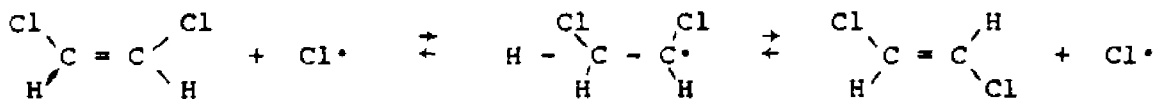
1,4 - Dienes carrying alkyl or aryl disubstituents on C-3 carbon may photochemically rearrange to vinylcyclopropanes in a reaction called the di-π-methane rearrangement. If there is no substituent at the C-3 carbon, then this rearrangement may still take place, but a different stepwise reaction involving hydrogen-radical shifts occurs because of the greater difficulty in bond breaking between C-2 and C-3 under these circumstance.



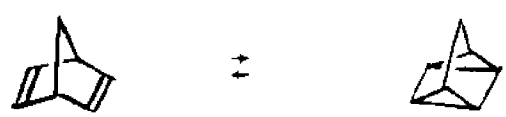
(4) Photoisomerization

The most common reaction in this category is a photosensitized cis - trans isomerization(11) of alkenes through their triplet states, since most simple monoolefins are difficult to excite by direct absorption of

light at short wavelength used in photochemical studies. But conjugated alkenes such as stilbene(12) or cyclooctenone(13) may be converted to their isomers through triplets produced by intersystem crossing. Whether these reactions go through the singlet or triplet state is still a matter of debate. But other groups(14, 15) proposed an alternative addition-elimination mechanism as given below.



An other example in this category is a valence isomerization of dienes or trienes(16, 17). Such reactions have been long known and important in the vitamin D series. It is obvious that many molecules can be constructed in this way which might be difficult to produce by other method. However, attempted valence isomerizations of this kind are not always successful.

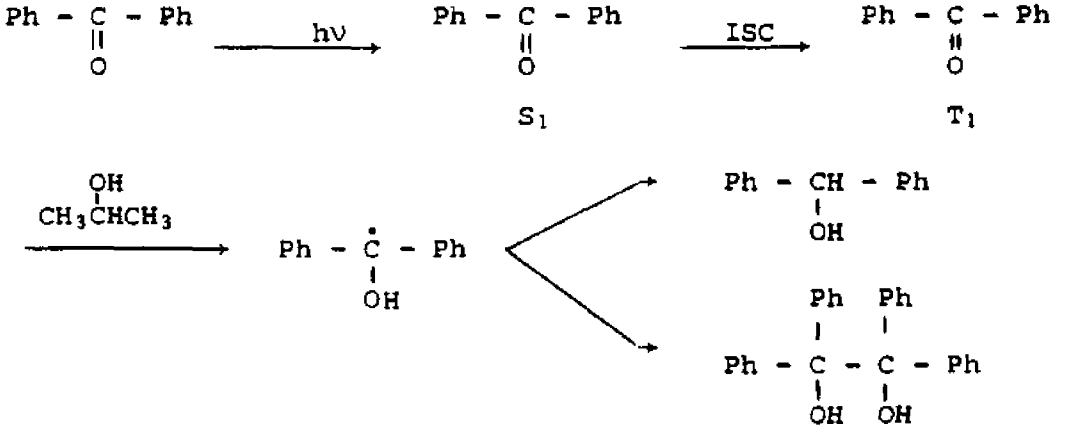


In many cases polymeric or other side products are obtained instead of desired product.

(5) Hydrogen - Atom Abstraction (Norrish Type II) (8)

Aldehydes or ketones are often reduced to the corresponding alcohol or pinacol by irradiation in hydroxylic solvents. For an example, irradiation of benzophenone in the presence of isopropyl alcohol as a solvent

produces a singlet state, which can generate a triplet state by intersystem crossing. The triplet state abstracts hydrogen from isopropanol to give the radical which can subsequently react as shown.

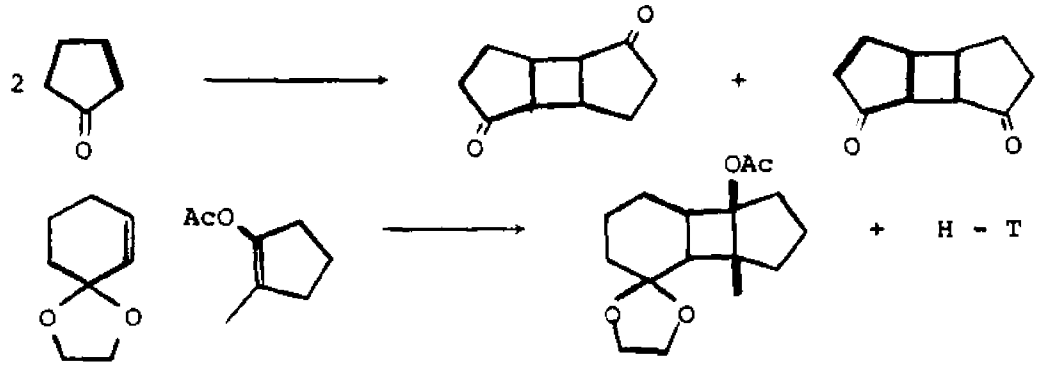


(6) Photocycloaddition (18)

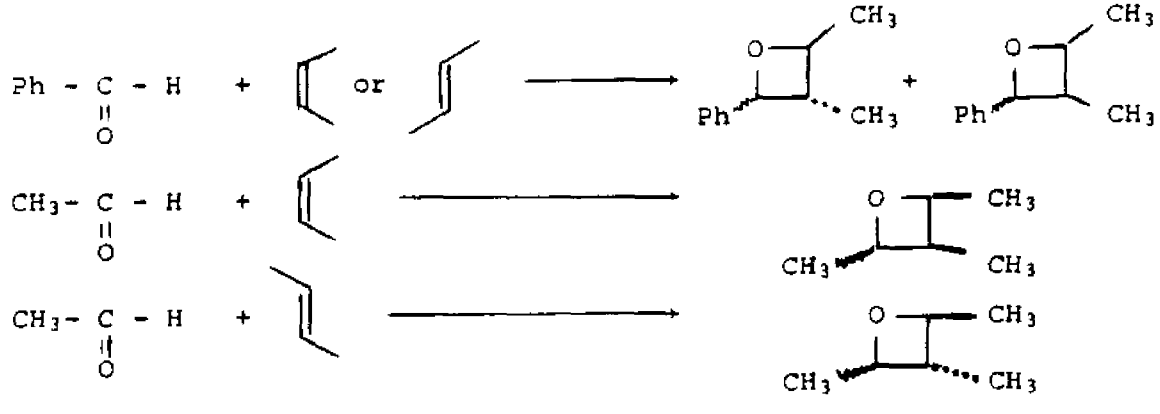
An electronically excited alkene can dimerize with a ground state molecule to form cyclobutane which reaction is a very important photoreaction from the synthetic standpoint. Unfortunately, although such reactions are nurmerous, they are not completely general, and the factors directing the course of cyclobutane formation are not clear in many cases.

Some alkenes conjugated with electron-withdrawing unsaturated groups such as carbonyl(19, 20) or nitrile(21) can produce cyclobutane as a photoproducts. In this case an α,β-unsaturated cyclic ketone such as cyclopentenone or cyclohexenone can dimerize, but an open-chain α,β-unsaturated ketone cannot, since the rate of radiationless decay of an excited molecule increases with ease of C - C bond twisting. The excited "enone"

also attacks alkenes. The exact mechanism of this reaction is not clear but with some reactants it is regiospecipic and/or stereospecific and with others it is neither. There are numerous applications of this reaction in natural product syntheses(22, 23).

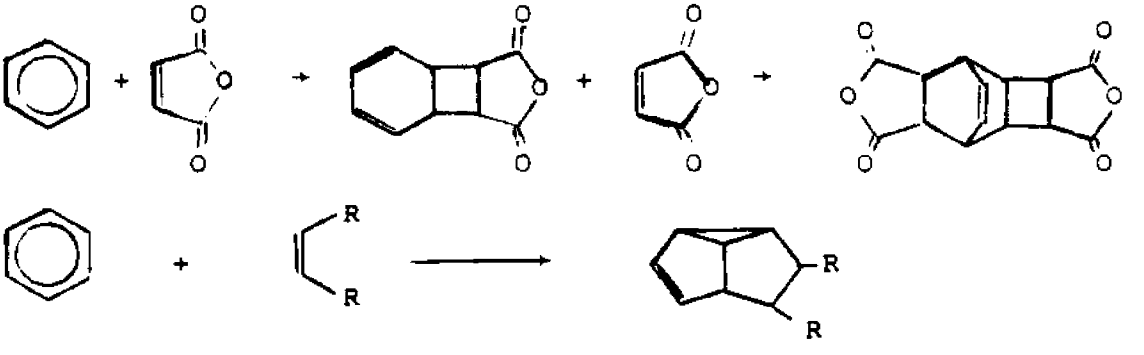


The excited carbonyl compound can add to alkene and form an oxetane. (24) This reaction is called Paterno-Buchi reaction. The stereochemistry of the reaction depends on the carbonyl compound which is used. Cycloaddition of benzaldehyde to cis- or trans- 2- butene gives a mixture of oxetanes, but the reaction with acetaldehyde maintains the stereospecificity of the isomeric 2- butenes.



Irradiation of benzene at 254 nm in the presence of alkenes may result in 1,2-, 1,3- and 1,4-cycloaddition, respectively(25 - 28). Only with a

very few systems have all types of cycloadducts been observed, and with many alkenes, one mode of reaction greatly predominates. In this cycloaddition, mode selectivity, regioselectivity, and stereoselectivity depend upon the type of alkenes. The cycloaddition of arene to alkene which has an electron withdrawing group or electron donating group produces ortho cycloaddition product predominantly. The addition of benzene to maleic anhydride gives surprisingly stable 2 : 1 photocycloadduct, produced by



sequential photochemical and thermal addition steps. The addition to simple alkenes gives 1,3-cycloaddition predominantly. Applications of these reactions have been extensively reported. (29 - 32)

(7) Photosensitization

Photosensitization is an alternative method to reach a desired excited state. There are several types of photosensitized reactions such as isomerization, addition, decomposition, oxidation, etc. One of the important reactions from practical as well as theoretical considerations is the photosensitized oxidations of alkenes. Conjugated dienes react with oxygen under influence of light to give internal peroxides(33) This reac-

tion also may be applied to certain aromatic compounds(34).

3. The Photochemistry of Alkyl Halides (2, 35)

Rowland and Molina's(36) destruction theory of the ozone layer by chlorofluoroethane stimulated considerable research interest in the photolyses of haloalkane recently, because chlorofluoroethane gas was widely used as propellants by the aerosol-dispenser industry. It was found that such compounds decompose to atomic chlorine and other products after absorbing ultraviolet light, and the chlorine atom then acts as a catalyst to deplete the upper atmosphere's protective ozone layer. The resultant depletion of the ozone would allow more ultraviolet light to reach the earth which would result in human skin cancer and worldwide damage to crops(37). In this section the photochemistry of halogenated compounds which have been investigated by quite a few research groups will be discussed.

(1) Ultraviolet Spectra (38)

The first absorption band of the alkyl halides in the ultraviolet region has been attributed to the promotion of a nonbonding p electron on the halogen atom to the lowest unfilled molecular antibonding σ^* orbital formed from the out-of-phase overlap of an sp^3 hybrid orbital of the carbon atom and a p orbital of the halogen atom. The intensity of the absorption is relatively weak due to transitions forbidden by selec-

tion rules, since the antibonding orbital possesses a large degree of p - character. The absorption maximum shifts to the longer wavelengths as the electronegativity of the halogen substituent is decreased, probably due to a decrease in the antibonding orbital energy level. This absorption frequently extends into the vacuum ultraviolet region where it may overlap the far more intense absorption associated with allowed Rydberg transitions involving the atomic orbitals of the halogen atom.

In the polyhaloalkanes the absorption intensities are greater than those in the mono-subsituted haloalkanes, and there is a shift to longer wavelength with increasing halogenation. The spectra also show a broadening of the absorption because the energy level splitting of the molecular orbital by halogen-halogen interaction results in several possible electronic transition of the type $n \rightarrow \sigma^*$.

The photochemical behavior of the halogenated compounds depends on the nature of the carbon-halogen antibonding orbital, since the transition is a valence-shell transition and since the ground state orbital is essentially nonbonding. Therefore the carbon-halogen bond dissociation might be expected by the absorption of ultraviolet light.

(2) Elimination

The alkyl halide excited by absorption of ultraviolet light can undergo two kinds of primary processes such as halogen atom elimination and molecular elemination(39, 40, 45).

$$R_2CHCH_2X + h\nu \longrightarrow R_2CHCH_2^* + X^\cdot$$

$\longrightarrow$ $R_2C{=}CH_2$ + HX

In the halogen atom elimination, free halogen atom has been detected indirectly by the transient spectra of ClO, BrO, or IO, after the flash photolysis of chloro-(41), bromo-(42), or iodomethane(43) in the presence of a large excesses of oxygen, as well as by kinetic evidence. The free methyl radical produced during the flash photolysis of methyl iodide and methyl bromide(44), has been also observed by its absorption spectrum, but the higher alkyl radicals generated from more complex alkyl halides are difficult to detect. The alkyl radicals can be trapped by the reformation of RX in the presence of excellent radical trapping agents.

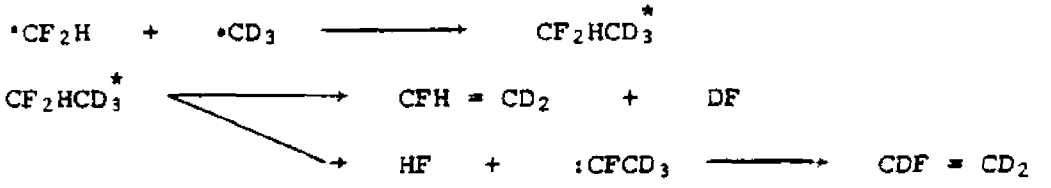
During the flash photolysis of ethyl, n-propyl, and isopropyl iodide, Thrush(45) has observed strong absorption bands due to hydrogen iodide, and suggested that this might be a primary product of the alternative molecular elimination. Schindler and Wijnen(40) found that in a vapor phase kinetic study of the continuous photolysis of ethyl iodide, ethylene formation should not be suppressed completely by added free radical scavengers such as iodine or oxygen molecule. These observation could support molecular elimination of hydrogen halide. Sandorfy(38) explained this kind of elimination on the basis of absorption spectra and ionization potential. The excitation from a lone pair orbital to antibonding orbital might generate the molecule which resembled the ion, since the excited orbital is no longer antibonding. The hole on the chlorine atom

will probably be liberated but it could well pull out a hydrogen atom to form hydrogen chloride with help of the large Rydberg orbital leading to a more complicated pattern involving molecular elimination processes. He suggests the photolysis of ethyl chloride as an example(46).

The photolysis of polyhalomethane can follow the 1,1-molecular elimination as a primary process. In the flash photolysis of mixed polyhalomethane such as bromodichloromethane or dibromodichloromethane in a large excess of oxygen(47), the transient formation of BrO, ClO can not be detected. But in the vacuum ultraviolet flash photolysis of diiodomethane(48), the I_2 molecule was observed by fluorescence. This experiment data implied 1,1-molecular elimination. If there are two types of halogen atoms, the weakest C - X bond breaks down predominantly in the photolysis. For an example, the photolysis of difluorobromomethane(CF_2BrX) (49) results in CF_2 and BrX, where X is a hydrogen, fluorine or bromine. During the flash photolysis of CF_2Br_2, CF_2HBr, CF_3Br, Yarwood and Simons (47, 50) detected the unexpected carbon mono halides by transient absorption spectra. The yields of these species, measured at peak intensity, were found to be directly proportional to the flash energy and to decrease with increased pressure of foreign gas. From this they suggest that the elimination comes from a vibrationally excited halomethyl radical. But the alternative explanation of original electronic excitation in the CHXBr species formed in the primary process, followed by internal conversion, is also possible(51). It is clear that molecular elimination from substituted methanes(52 - 56) must be a 1,1-process.

The molecular detachment reaction of HX in the photodecomposition of haloethanes has been reported frequently since Wijnen(14) first suggested the reaction in the photolysis of cis- and trans-1,2-dichloroethylene. The detachments took place from the molecule excited by ultraviolet light (57 - 63) or by far ultraviolet light(46, 64 - 68) and from vibrationally excited molecules(69 - 77). To this extent the photochemical eliminations resemble those of thermal and chemical activation systems involving the ground electronic state(78, 79). Similarly dehydrohalogenation reactions have been observed in studies of the thermal decomposition of alkyl chlorides using shock tube pyrolysis(80 - 82). Similar results were obtained in the thermal decomposition of 1-fluoro-1-chloroethane(83) and 1,1-difluoro-1-chloroethane(84). In all these cases the dehydrohalogenation played an important role.

The molecular elimination from the 1,2- position is generally accepted to proceed via a four - center transition state in both thermally and chemically activated system. However, from time to time, a three - center transition state of hydrogen halide elimination may be observed in which both the hydrogen and halogen atoms come from the same carbon atom.Generally, the detachment from halomethanes followed the three - center mechanism. But it is interesting that both 1,1- and 1,2- processes may occur simultaneously. Pritchard and coworkers(74, 85) first reported 1,1- and 1,2- elimination processes from the vibronically excited CF_2HCD_3 molecule produced by photolysis of a mixture of 1,1,3,3-tetrafluoroacetone and aceton- d_6 at 313 nm.



It seems that the 1,1 - elimination needs a somewhat higher activation energy than 1,2 - elimination, since 1,1 - elimination has been reported only in shock tube pyrolysis(85 - 88) or in photolysis at 147 nm(66).Also the structure of the molecule determines to some extent the importance of either the 1,1 - or the 1,2 - process. As an example, in compounds containing two halogen atoms attached to the same carbon atom, the 1,1 - process competes with the 1,2 - process for dehydrohalogenation.

A molecular chlorine elimination is another important primary process in the photodecomposition of dichloride compounds. Wijnen and coworkers (58, 59, 63, 89) found that dechlorination is the major process in the ultraviolet photolysis of 1,2-dichloroethylene and 1,1,2,2-tetrachloroethane, but a minor process in the photolysis of 1,1-dichloroethylene and CD_3CHCl_2. Tschuikow - Roux and coworkers(90, 91) observed that in the 147-nm photolysis of 1,2-dichloroethane and 1,1-difluoro-1,2-dichloroethane the chlorine molecular detachment is not suppressed by the radical scavenger, nitric oxide. These facts indicate that molecular 1,2-elimination is a more favorable process than 1,1- elimination. The mixed dehalochlorination was also reported by the Tschuikow - Roux group. At 147 nm CH_2FCH_2Cl not only eliminates HCl but also a significant fraction decomposes by FCl elimination(92). Increased fluorine substitution

(CF_3CH_2Cl) reduces the overall quantum yield of molecular processes at 147 nm, while FCl elimination is the major primary process at 123.6 nm (93).

Finally, molecular hydrogen elimination from halogenated compounds can take place, but it is very small amount compare to other elimination process. This dehydrogenation was observed by the Wijnen groups (63, 89) and by the Tschuikow - Roux groups(46, 68, 94).

(3) Isomerization

Absorption of a photon by a compound containing an olefinic link often results in cis-trans geometrical isomerization. 1,2-Dichloroethylene is one of the simplest compounds to exhibit cis-trans isomerism. This isomerization of 1,2-dichloroethylene stimulated considerable research interest in the area, and has posed interesting mechanistic and theoretical problem for more than four decades. The mechanism of the isomerization was proposed independently by two groups(14, 95).

In the photolysis of cis-dichloroethylene, Wijnen observed the formation of trans-dichloroethylene as a major product, and suggested a chlorine atom catalyzed mechanism. Further information on the chlorine atom catalyzed isomerization comes from photoinitiated chlorination studies. Dainton, et al. proposed the following mechanism to explain their data on the photochlorination of both cis- and trans-dichloroethylene :

$$Cl_2 \xrightarrow{h\nu} 2\ Cl\cdot$$

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

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

$$\cdot C_2H_2Cl_3^* + Cl_2 \rightarrow y \text{ trans-}C_2H_2Cl_2 + (1 - y) \text{ cis-}C_2H_2Cl_2 + \cdot Cl_3$$

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

Where the calculated x and y values were 25 % and 45 %, respectively. Both isomerization reactions were found to be independent of temperature.

Recently, the isomerization mechanism was confirmed by Ausubel and Wijnen(96). An excited 1,1,2-trichloroethyl radical produced by the addition of chlorine atom to the double bond of dichloroethylene could lead to rotation on carbon - carbon single bond. This activated hot radical either deactivated to a ground state radical or decomposed. Because the intermediate hot radical can rotate through the carbon-carbon single bond, either isomer of dichloroethylene can be produced.

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

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

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

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

The 1,2-dichloroethylene formed in the photolysis of 1,1,2,2-tetrachloroethane also exhibited the cis and trans isomerization(89) during the photolysis. At zero time the ratio of cis over trans dichloroethylene is unity, because the excited 1,1,2,2-tetrachloroethane yields both isomers at equal rate and there is no cis - trans isomerization processes

occurring at zero time. As the exposure time increases, the ratio increases and approaches 1.6. This isomerization process is also confirmed by performing deactivation studies. The ratio of cis/trans approaches unity, as the initial pressure of the deactivator, octafluorocyclobutane, increases. This, without any doubt, indicates that the excited 1,1,2-trichloroethyl radical will more effectively deactivate, go to ground state radical, and lead to no cis-trans isomerization process. These results are in excellent agreement with the result reported in the literature.

(4) Halopropanes

The photolysis of many halomethanes and haloethanes has been quite extensively investigated recently, mainly because of the possible effect which the decomposition of these compounds may have on the ozone layer in the upper atmosphere. Relatively little work has been done on the photolysis of halogenated propanes(45, 97 - 99). Dannenberg and coworkers investigated the photolysis of 1-phenyl-2-bromopropane in the liquid phase(100, 101). Such work would be of extreme interest since it may clearify some processes obtained with ethanes and methanes.

As mentioned before, recent observations are that in the near ultraviolet region the most important steps in the photolysis of chlorinated ethanes and ethylenes are the molecular elimination of chlorine and of hydrogen halide. The following conclusions have been drawn : The molecular elimination of chlorine atom from 1,2-position is the most important primary step in compounds where such a process is possible. Elimination of

a chlorine molecule from the 1,1-position either does not occur or does so only to a minor extent. Molecular elimination of hydrogen chloride is an important primary process in all chlorinated compounds, and may occur exclusively from the 1,2-position or from both 1,1- and 1,2-positions. The primary step, producing C - Cl rupture, decreases in importance with increasing chlorination in the ethanes and ethylenes which favor both Cl_2 and HCl elimination.

In order to get more information regarding the nature of the molecular elimination process, we propose to examine the photolysis of some halopropanes. In our study we have concentrated on the photolysis of 1,2-dichloropropane, although some isolated experiments were carried out with other dichloropropanes.

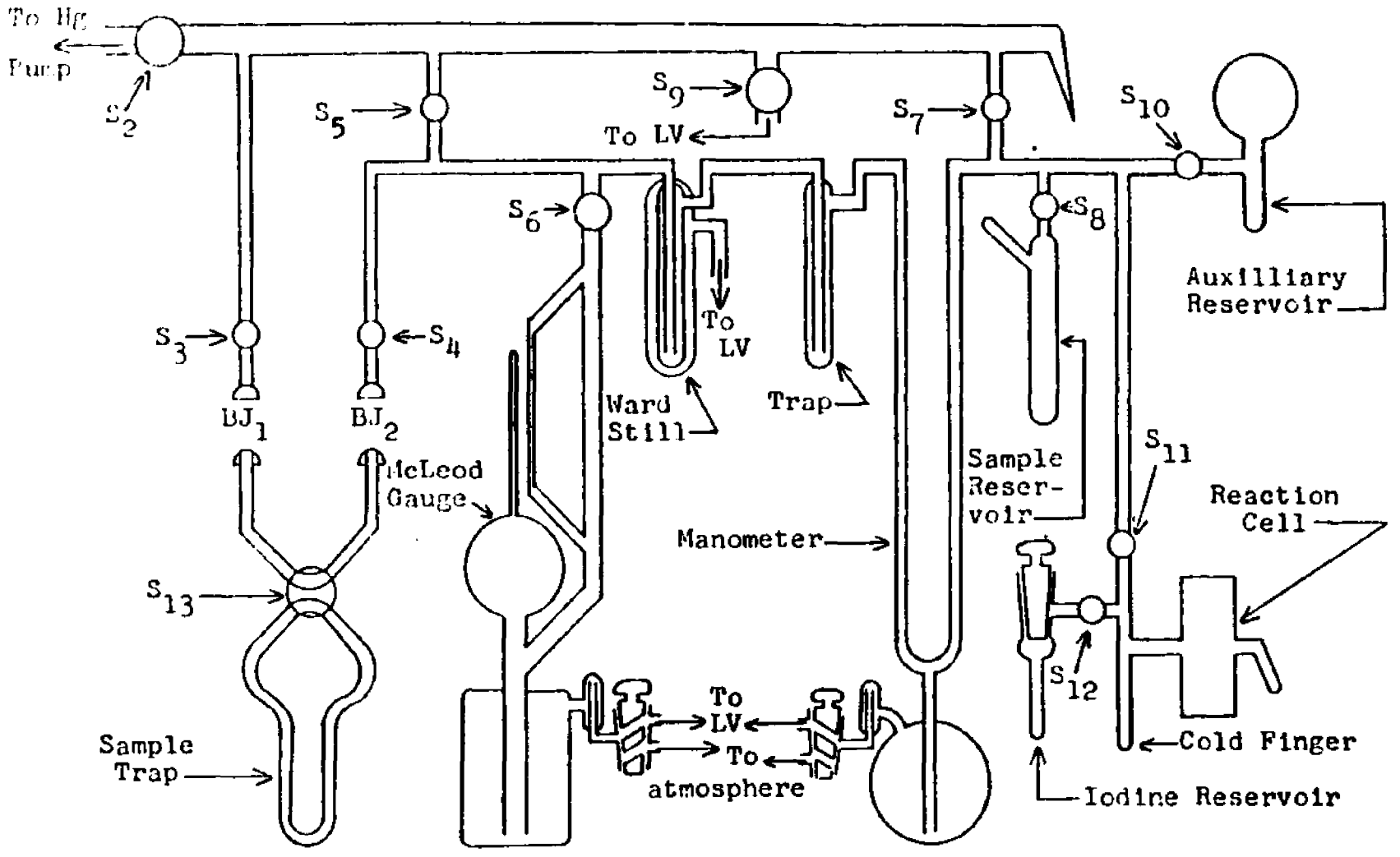
II. EXPERIMENTAL

1. High Vacuum System

The photolysis of dichloropropanes was studied in a high vacuum system, in order to carry out the photolysis in the absence of oxygen. This is extremely important since it is well known that oxygen is an excellent free radical scavenger and that the excited singlet oxygen may also generate allyl peroxide by the reaction with the propylenes produced in the photolysis. The formation of undesirable products by trace amount of oxygen would immensely complicate the interpretation of the data obtained by the experiments and would lead to wrong conclusions.

The high vacuum system consisted of two parts, the high vacuum part in which the experiments were carried out and the low vacuum part which was used to control the mercury levels in the various pressure measuring devices. These high and low vacuum parts were connected by a stopcock thus allowing the evacuation or the admission of air in case of shutdown to both parts at equal rate. A diagram of the high vacuum system is shown in Figure 1. The high vacuum part of the system was evacuated by means of a two stage mercury diffusion pump followed by a mechanical rotatory vacuum pump. The low vacuum part was evacuated by an oil pump only, since it is not necessary to maintain a vacuum of less then 1 or 2 torr.

The pressure in the high vacuum system was measured with a McLeod Gauge which was calibrated to minimum pressure of 0.001 micron. The pressure in the high vacuum system was 0.1 micron, or less, before each



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

Fig. 1. The high vacuum system.

experiment was done. The pressure of the gaseous reactants which were admitted to the quartz reaction cell was measured by a mercury manometer attached in the high vacuum system.

The quartz reaction vessel was a cylindrical cell with optically flat circular windows fused to the cell body at right angles to its axis. In quantitative photochemical work it is desirable to use flat windows on the cell and to have nearly perpendicular incidence of the light beam on the window. The fraction of light reflected at the window interface is a minimum under these conditions. The size of the tubing and windows should be consistent with the dimensions of the light beam to be used in the experiment. There should be as little unirradiated cell volume as possible so that there can be no question about the actual effective volume of the cell, which must be known, to evaluate rate constants from photochemical experiments. The pyrex tubing, which connected the cell to the high vacuum system via quartz-to-pyrex graded seals, was covered by aluminum foil in order to prevent a distorted reaction by different wavelength light. The cell was 12 cm long 5 cm in diameter and its volume was 250 ml.

All the stopcocks in the high vacuum system were teflon high vacuum stopcocks made by Ace Glass Inc. Liquid samples were kept in cold finger shaped reservoirs attached to the vacuum system. Gas samples were kept in auxilliary reservoirs with a volume of 1 liter. Gaseous compounds such as hydrogen sulfide, sulfur dioxide, etc. were transferred from lecture bottles through one of stopcock into the system. After being introduced

into the system, the various compounds were thoroughly degassed. This consisted of freezing the compound with liquid nitrogen and pumping on the reservoir with the high vacuum. These processes were repeated several times.

2. Light Source

Mercury arcs are most widely used for conventional photochemical experiments, using steadily illuminating sources of ultraviolet and visible light. There are three basic types ; the low-pressure or resonance lamp, the medium-pressure arcs, and the high-pressure mercury arcs. Each offers features which makes it particularly suited for certain experimental needs. In this study, a Hanovia model 16A13 medium-pressure mercury arc was employed as the light source. The emission spectrum of the light source ranges from 200 nm through the visible region(800 nm). But at this pressure the center of the 253.7 nm line is missing, because of self - absorption in the sheath of relatively cool mercury atoms near the inside of the walls of the arcs. This reversed radiation prevents mercury-photosensitized reactions, and makes it a very satisfactory source for direct photolysis.

The mercury arc was collimated by an aluminum shade reflector and was allowed a warm up time of at least fifteen minutes before each exposure in order to permit the lamp to reach its operating temperature and thus a uniform intensity and wavelength distribution throughout all experments was insured. The distance between the arc and photolysis cell was

kept constant at about 12 cm.

In order to examine the dependence of various products upon the wavelength of the incident light, appropriate corning filters were inserted between the arc and the cell. The transmittance spectra of these filters are shown in Figure 2.

3. Identificationcation and Analysis of Products

The photolysis products of 1,2- and 2,2- dichloropropane were identified and quantitavely determined by using a Perkin Elmer 900 gas chromatograph equipped with flame ionization detectors. A 12 foot stainless steel column packed with 70/80 mesh anakrom SE-30, was used for analysis. This packing material may be used at temperature below 250^{o}C. The column temperature was programmed at a rate of 6^{o}C / min. from - 20 to 90^{o}C.The seperation of constituents in samples composed of compounds with a wide range of boiling points can be improved and accelerated by raising the temperature of the entire column at a uniform rate during the analysis. The peak area on the gas chromatograph was measured with an Informatic automatic digital integrator (Model GRS - 100) having a solenoid printout system. In order to achieve high accuracy on small peaks, the count rate of the integrator was kept at 1000 counts/sec./mV. In order to integrate the incompletely resolved peaks, the peak -and- valley sensor was also kept at high sensitivity. Since some of the photolyzed products were gas or low boiling compounds, a special sample injection system and sample trap were used as shown in Figure 3.

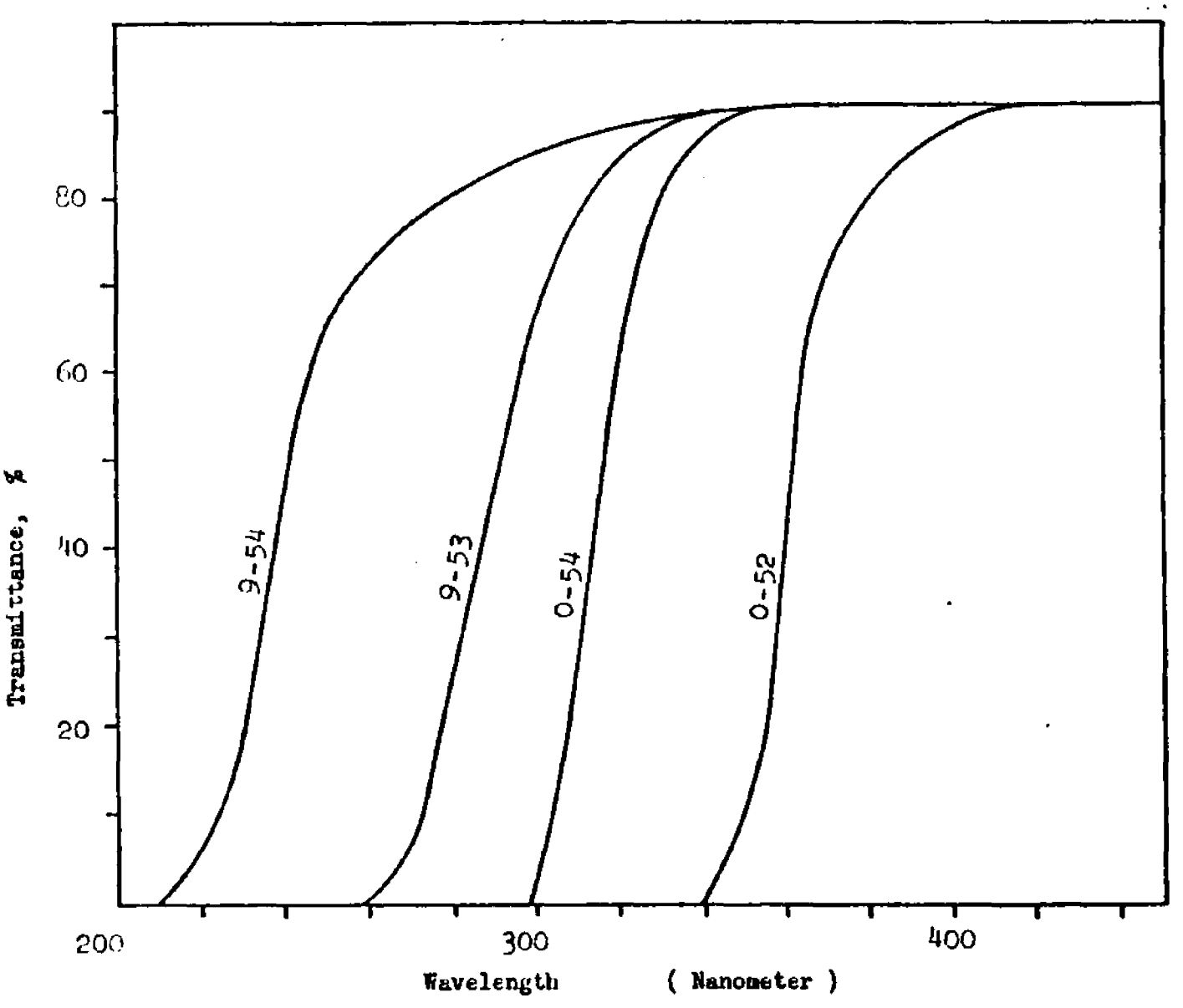


Fig. 2. The transmittance spectra of selected corning filters.

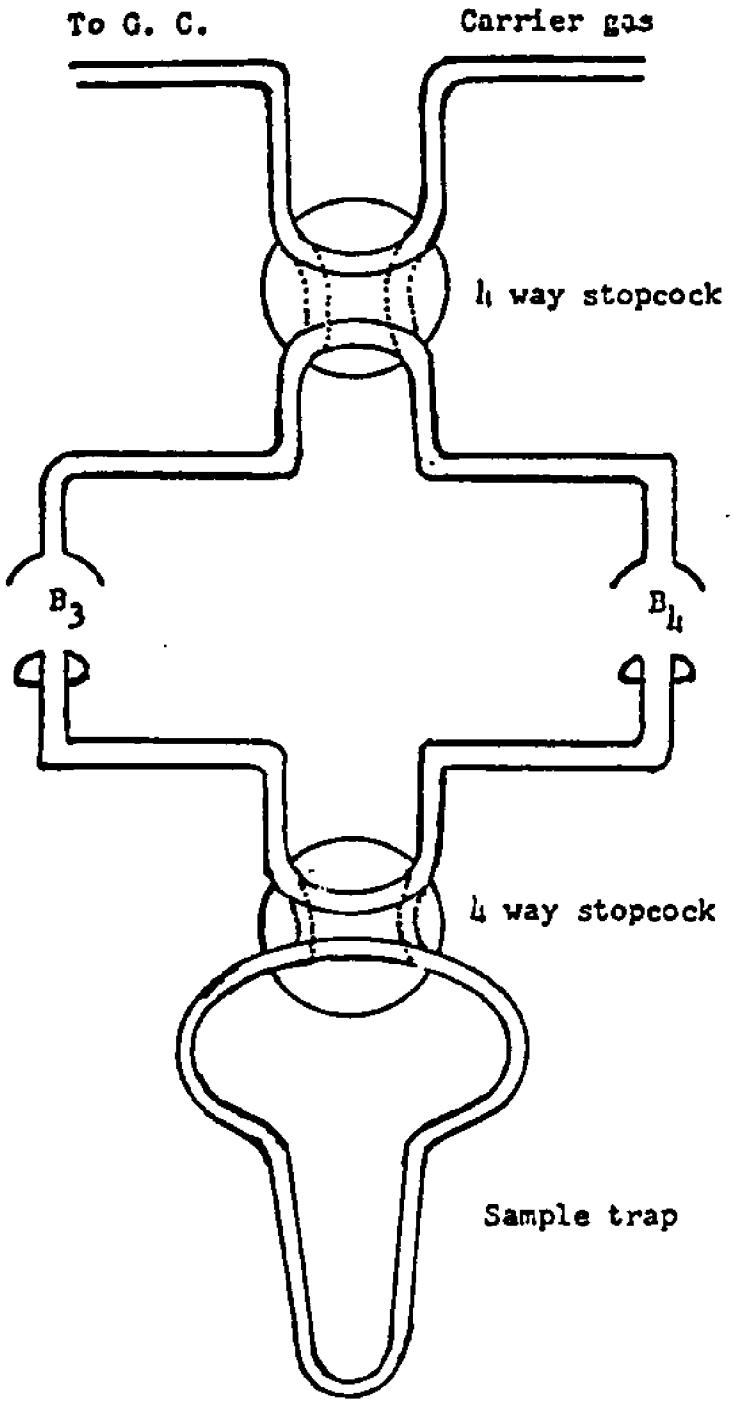


Fig. 3. Gas Chromatograph attachment and sample trap.

The major products produced by photolysis of 1,2-dichloropropane and 2,2-dichloropropane were propene, 2-chloropropene, cis- and trans-1-chloropropene, and 2-chloropropane, 2-chloropropene, respectively. In order to determine the retention time and sensitivity of the detector toward the various products, a known amount of each product was injected directly onto the column by using a Hamilton microliter syringe or a Hamilton gas tight syringe having teflon coated plungers. For every sensitivity determination three or more samples were analyzed and the results averaged. The relative deviation in these determinations was less than one percent.

In most photochemical experiments designed to develop or test mechanisms today, one restricts the amount of substrate reacted to a few percent or less to avoid complications which might arise from subsequent thermal or photochemical reactions of the primary products of the photodecomposition. The quantitative analysis of the photolysis products was always carried out in the presence of a large excess of undecomposed starting material. In order to obtain very precise quantitative determination data, samples were prepared in which all known products were diluted by the starting material to approach the condition of the analysis in the photochemical experiments.

The determination of sensitivities was performed for propene, 2-chloropropene, 2-chloropropane, trans-1-chloropropene, and mixture of cis- and trans-1-chloropropene. All were commercially available for quantitative analysis. The sensitivities of the chromatograph to the various compounds can be obtained in molecules per digiatl integrator unit. The rate

of production of the compound was then calculated by multiplying the area of the compound in the integrate units by the sensitivity of that compound and dividing this number by the illuminated volume of the reaction cell and by the exposure time. The rates are, therefore, reported in molecules per milliliter per second.

Finally it should be mentioned that more than ten experiments were usually necessary before a suitable column and suitable column temperatures were obtained. The operating conditions such as flowrate of nitrogen gas, programming temperature, etc. were always chosen so that maximum separation between the various photolyzed products would be achieved. For example, a column packed with anakrom containing 10 % silica gel separates the reaction products very well and there is a reversed retention time for 2-chloropropene and 1-chloropropenes, but it takes a long time to get rid of the starting materials from the column.

4. Chemicals

1,2-Dichloropropane from Eastman Organic Chemicals and 2,2-dichloropropane from Fluka AG were purified by fractional distillation using a spinning band column in a nitrogen atmosphere. Subsequently, after being introduced into the high vacuum system, the compound was checked for impurities by the same method as used in the analysis of the photoreaction. By this method the same amount of starting material as that to be used in the photolysis could be taken, no impurities were detected under these conditions. The other compounds obtained from the following

companies were used without further purification.

trans-1-chloropropene, 2-chloropropene ; Chemical Sample Co.

1- and 2-chloropropane, mixture of 1-chloropropene ; Pfaltz & Bauer

hydrogen sulfide, sulfur dioxide, sulfur hexafluoride ; Matheson

5. Experimental Procedure

A typical experiment was started by evacuating all the air from the high vacuum system. When the vacuum as measured on the McLeod Gauge was adequate, the system was isolated by closing stopcocks 5, 6, 7, and 10, and the mercury in the manometer was raised by opening a balljoint stopcock of the manometer to the atmosphere. The dichloropropane in the sample reservoir was allowed to expand into the tubing extending from the manometer to the quartz reaction cell. When the desired pressure was reached, the stopcock 8 of the sample reservoir was closed, and the pressure was read on the manometer attached to the system. Then the photolysis cell stopcock 11 was closed and the high vacuum manifold stopcock 7 was opened to pump out the compound remaining in the tubing. The cold finger of the reaction cell was immersed into liquid nitrogen to freeze the sample in the cell, and the stopcock 11 was opened to eliminate possible traces of air which might be present. After five minutes, stopcock 11 was closed, and the sample in the reaction cell was allowed to warm up to room temperature by removing the liquid nitrogen from the cold finger. Then the sample was ready for photolysis.

The Hanovia lamp was allowed to warm up for at least fifteen minutes

before the start of the photolysis. While the sample was being prepared and the lamp was warming up, a piece of aluminium foil was inserted between the light source and the reaction cell. As the foil was removed and the ultraviolet light started to enter the reaction cell, the stopwatch was activated manually. In order to stop the photodecomposition, either the light was turned off or the foil was replaced.

If another compound such as hydrogen sulfide, sulfur hexafluoride, etc. was necessary, the compound was added from an auxilliary reservoir. When the pressure in the reservoir exceeded that in the cell, the reservoir stopcock could be opened to admit the compound to the cell. When the desired total pressure in the cell was reached, the stopcock of the reservoir was closed and the total pressure read. After that, possible traces of air were removed by the method described above. Again the mixture was ready for photolysis.

In order to analyse the reaction mixture, a sample trap shown in Figure 3 was connected to the greased balljoint outlets below stopcocks 3 and 4 with the aid of clamps. While the photoreaction was in progress, the air in the sample trap was evacuated by opening the sample trap stopcock 13 and stopcock 3 and then stopcocks 4, 5, and 7. After the photodecomposition the stopcocks 3, 5, and 7 were closed, and the reaction mixture was collected in the evacuated U-shape sample tube at liquid nitrogen temperature for five minutes. By opening the stopcock 3 the sample trap was degassed at liquid nitrogen temperature for two minutes in order to remove any trace of air that might have leaked in through the balljoint

during the collecting process.

The sample trap was then taken to the gas chromatograph which had been adapted to allow the insertion of the sample into the flow line of the carrier gas via balljoints B_3 and B_4 as shown in Figure 3. The air in the top portion of the sample trap was passed through the column of the gas chromatograph by opening the teflon 4 - way stopcock attached in the injection port of the chromatograph. The sample was injected by turning the 4 - way stopcock of the sample trap.

The only reaction products observed in measurable amount were in the case of 1,2-dichloropropane ; propene,2-chloropropene and cis- and trans-1-chloropropene. Occasionally, at long exposure time, some trace amounts of products were observed of which retention times were consistent with trichloropropanes such as 1,2,2-trichloropropane and 1,1,2-trichloropropane and 2,2-dichloropropane. These products were not formed in measurable quantities and are obviously secondary process products. The only reaction products, observed under our experimental condition, in the case of 2,2-dichloropropane, were 2-chloropropene and 2-chloropropane. The reaction products are reported in the various tables in terms of molecules / ml for the actual exposure times of the experiments.

From these data, the product ratios were calculated and reported, first in appropriate tables, and finally plotted versus exposure time in order to obtain product ratios at zero time. Finally, we have calculated from these data the relative quantum yields of the products. For the experiments at $\lambda > 200$ nm these relative quantum yields may be taken as

actual quantum yields, since Wijnen(102) obtained an overall quantum yield of approximate 0.9 to 0.95. Although no quantum yield measurements were carried out at $\lambda > 220$ nm and $\lambda > 340$ nm, because the light absorption is quite weak in this region, it seems probable, in comparison with the data at $\lambda > 200$ nm, that also in this region the overall quantum yield may be close to unity.

III. RESULTS AND INTERPRETATION

1. Energetic Consideration

Before interpretating the experimental results in detail, it may be interesting to consider some of the primary processes which might lead directly or indirectly to the observed products from an energetical point of view. Analysis of the energetic requirements for the individual reactions will yield some information regarding their probability and even their possibility. The following reactions which might occur from the excited 1,2-dichloropropane molecules will be considered.

$$CH_2ClCHClCH_3^* \longrightarrow CH_2{=}CHCH_3 + Cl_2 \quad (A)$$

$$\longrightarrow CH_2{=}CClCH_3 + HCl \quad (B)$$

$$\longrightarrow CHCl{=}CHCH_3 + HCl \quad (C)$$

$$\longrightarrow C_3H_6Cl\cdot + Cl\cdot \quad (D)$$

$$\longrightarrow CH_2{=}CHCH_3 + 2\,Cl\cdot \quad (E)$$

$$\longrightarrow C_3H_6Cl + Cl\cdot + H\cdot \quad (F)$$

The general energy requirements of each step may be calculated by subtracting the sum of the energies required to break the various bonds from those liberated in forming the bonds of the various products. In Table 1, approximate bond energies in kilocalories per mole are given for the bonds to be considered here.

The energy requirement for step A is obtained by considering the breaking of the two C - Cl bonds (2 X 79 = 158 Kcal / mole), the formation

Table 1. Bond Energies in Kilocalories per Mole.

C - Cl	79	Cl - Cl	58
C - C	82	C = C	146
C - H	100	H - Cl	103

* Data from Kerr, J. A. Chem. Rev. 1966, 66, 465

of the Cl - Cl bond (58 Kcal / mole) and the formation of a carbon - carbon double bond formed from a single bond (146 - 82 = 64 Kcal/mole). Thus the energy requirement of step A is approximately 36 Kcal / mole. Similary the energy requirements for the other steps may be estimated. Table 2 gives these energy requirements and corresponding maximum wavelength of the incident light which would allow such steps to occur.

Table 2. Energy Requirements for Each Step in Kcal / Mole and in Nanometer of the Incident Light.

Step	energy	wavelength
A	36	750
B	12	2,380
C	12	2,380
D	79	360
E	92	310
F	115	250

2. Time Dependence of the Photolysis Procucts

Variations in exposure time were carried out in order to extrapolate the ratio of the observed products to zero time, thus, to the time where secondary reactions should be impossible, since the products under those conditions are not allowed to build up to a concentration where they might be expected to participate in reactions or be subjected to secondary photolysis. This procedure should be preferable to the use of free radical scavengers which are often used to suppress secondary processes, but which, in turn, may generate complications as will be explained later. Furthermore the wavelength dependence of the various product ratios was determined by inserting the appropriate filter between the arc and the reaction cell.

(1) Photolysis at $\lambda > 340$ nm

As can be seen in Table 2, in the photolysis of 1,2- dichloropropane at $\lambda > 340$ nm, neither step E nor step F is energetically possible. The wavelength of 340 nm is just about the border area where step D, at least energetically speaking, becomes barely possible. It is not surprising that at this wavelength no evidence was obtained to confirm the occurrence of step D. The molecular detachment steps A, B, and C are left as main sources of the reaction products.

The data obtained in the photolysis of 1,2-dichloropropane at $\lambda > 340$ nm are given in Table 3. Table 4 shows various product ratios calculated

from the data in Table 3. Cl_2 elimination/HCl elimination gives the ratio of reaction A (Cl_2 elimination) over the HCl eliminations produced by reaction B and C. The ratio, $CH_2{=}CHCH_3$ / $CH_2{=}CClCH_3$, limits itself to determine the relative importance of step A in regard to step B. Our study of these two ratios as a function of time (Table 4), clearly shows that there is little change with exposure time, indeed there is no change at all. As mentioned earlier, the time studies were undertaken to allow extrapolation of the product ratios to zero time, in order to minimize secondary processes. The fact that the ratios Cl_2 elimination / HCl elimination and $R_{CH_2=CHCH_3}$ / $R_{CH_2=CClCH_3}$, do not, or hardly, vary with time, indicates that even over 5 fold increases of exposure time secondary reactions are very unimportant. Such unimportance of secondary

Table 3. Photolysis of 1,2 - Dichloropropane at $\lambda > 340$ nm.

$P_{CH_2ClCHClCH_3}$ = 24 torr, Products in molecules/ml X 10^{-15}

Expt. No.	Time Min.	$CH_2{=}CHCH_3$	$CH_2{=}CClCH_3$	$CHCl{=}CHCH_3$ Cis	$CHCl{=}CHCH_3$ Trans
1	180	2.91	1.57	0.691	0.486
2	240	4.17	2.49	1.06	0.699
3	360	6.15	3.71	1.70	1.10
4	540	9.35	5.47	3.51	2.32
5	720	12.7	6.66	5.34	3.95
6	900	15.4	6.94	5.36	3.63

Table. 4. Product Ratios in the Photolysis of 1,2 - Dichloropropane at $\lambda > 340$ nm.

Expt. No.	Time Min.	Cl_2 Elimination / HCl Elimination	$CH_2=CHCH_3$ / $CH_2=CClCH_3$	$CHCl=CHCH_3$ / $CH_2=CClCH_3$	c-$CHCl=CHCH_3$ / t-$CHCl=CHCH_3$
1	180	1.1	1.9	0.75	1.4
2	240	0.98	1.7	0.71	1.5
3	360	0.94	1.7	0.76	1.6
4	540	0.83	1.7	1.1	1.5
5	720	0.80	1.9	1.4	1.4
6	900	0.97	2.2	1.3	1.5

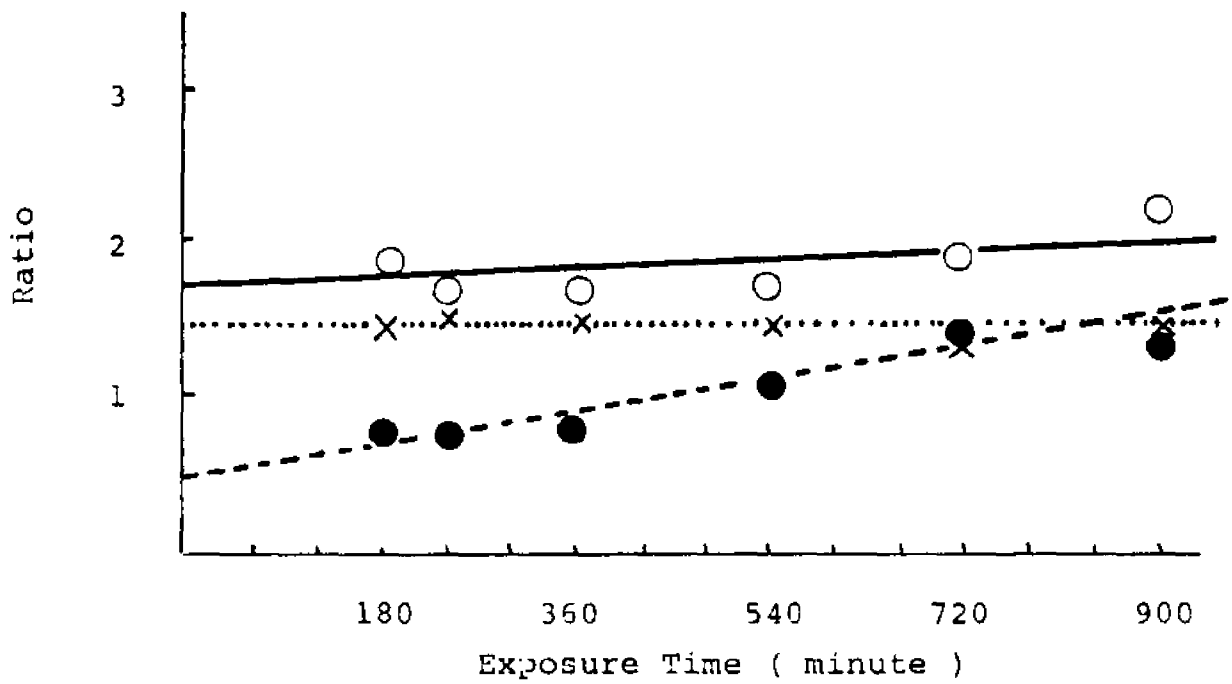


Fig. 4. Plot of the product ratios against exposure time in the photolysis of 1,2-dichloropropane at $\lambda > 340$ nm. —○—; $CH_2=CHCH_3/CH_2=CClCH_3$, —●—; $CHCl=CHCH_3/CH_2=CClCH_3$, ···×···; c-$CHCl=CHCH_3$/t-$CHCl=CHCH_3$

reactions can only be expected if the primary processes do not produce free radicals to any great extent, or indeed if the primary processes are limited to steps A, B, and C as estimated already from energy consideration.

The ratio, $c\text{-}CHCl{=}CHCH_3$ / $t\text{-}CHCl{=}CHCH_3$, is constant at about 1.5 within experimental error. This ratio represents, as will be shown later, the equilibrium concentration between cis- and trans- 1- chloropropene. The only ratio that does show a clear time dependence is the ratio, $R_{CHCl=CHCH_3}$ / $R_{CH_2=CClCH_3}$, where $R_{CHCl=CHCH_3}$ represents the total production rate of both cis- and trans-1-chloropropene. The data in Table 4 are ploted in Figure 4, showing clearly, the constant value for R_{cis} / R_{trans} of the produced 1-chloropropene, and the constant or nearly constant value for $R_{CH_2=CHCH_3}$/ $R_{CH_2=CClCH_3}$. The ratio, $R_{CHCl=CHCH_3}$ / $R_{CH_2=CClCH_3}$, shows, however, a clear time dependence. Extrapolation to zero time yields a value of 0.5 for this ratio, indicating that in the HCl elimination steps, at least initially, 2-chloropropene(66 %) rather than 1-chloropropene (33 %) is formed preferentially.

The fact that the ratio, $R_{CHCl=CHCH_3}$ / $R_{CH_2=CClCH_3}$, increases with time indicates that a secondary reaction is occurring during the photolysis. Perhaps, it is convenient here to list once more the suggested primary processes.

$$CH_2ClCHClCH_3^{*} \longrightarrow CH_2{=}CHCH_3 + Cl_2 \qquad (A)$$

$$\longrightarrow CH_2{=}CClCH_3 + HCl \qquad (B)$$

$$CH_2ClCHClCH_3^* \longrightarrow CHCl{=}CHCH_3 + HCl \qquad (C)$$

It is worthwhile to consider which of the reaction products might undergo secondary photolysis. Neither propene nor hydrogen chloride absorbs at $\lambda > 200$ nm. The chloropropenes containing only one chlorine atom in the molecule absorb light at wavelengths lower than 1,2-dichloropropane, and are, thus, not expected to undergo secondary photolysis, to any appreciable extent. This is especially so if we remember that 1,2-dichloropropane in only photolyzed to a maximum of about 1 % of its initial concentration.

The situation is, however, completely different with chlorine which starts to absorb at about 400 nm reaching a maximum at 330 nm and which has a very large absorption coefficient(103). Secondary photolysis of chlorine molecules is, therefore, extremely likely.

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

The chlorine atoms, thus produced, may react either by abstraction or by addition to a double bond. The abstraction reactions require an activation energy and are, especially at low temperature, not expected to occur to any appreciable extent. The following addition reactions must, therefore, be considered.

$$\cdot Cl + CH_2{=}CHCH_3 \longrightarrow \cdot C_3H_6Cl^* \qquad (G)$$

$$\cdot Cl + CH_2{=}CClCH_3 \longrightarrow \cdot CH_2CCl_2CH_3^* \qquad (H)$$

$$\cdot Cl + CH_2{=}CClCH_3 \longrightarrow CH_2ClC\dot{C}lCH_3^{*}$$

$$\cdot Cl + CHCl{=}CHCH_3 \longrightarrow CHCl_2\dot{C}HCH_3^{*} \qquad (I)$$

$$\longrightarrow \cdot CHClCHClCH_3^{*}$$

The addition of a chlorine atom to a double bond generates a vibrationally excited radical, since in this addition reaction the formation of the C - Cl bond and the transformation from a carbon-carbon double bond to a single bond lead to an energy excess of about 16 Kcal / mole.

Vibrationally excited radicals containing chlorine atoms have been discussed in detail especially the $C_2H_2Cl_3^{*}$ radical(96). Such a radical will either decompose again or deactivate by collision. Because the deactivational collision is not expected to be important at the low pressure of our investigation, the decomposition reaction should draw our attention. In this respect it is interesting that the $C_3H_5Cl^{*}$ radical can only decompose to return to the starting material, since a reaction such as losing a hydrogen atom from the vibronically excited $C_3H_6Cl^{*}$ radical needs an excess energy of about 35 Kcal/mole. These considerations lead to the conclusion that propene is not prone to the secondary reactions. This conclusion is in agreement with the experimental observations.

In principle chlorine atoms may add either to 2-chloropropene or to 1-chloropropenes. Orientation in addition to unsymmetrical olefins is determined at the addition step, which occurs so as to produce the most stable radical. Data about the addition of a hydrogen atom to propene show that the hydrogen atom adds preferentially to the end rather than

to the middle carbon in a ratio of about 9 : 1 (104).From these we might expect preferential addition to 2-chloropropene rather than to 1-chloropropene, since addition of a chlorine atom to the terminal carbon of 1-chloropropene would also cause a steric congestion due to the bulky chlorine atom. In addition, it should be remembered that at zero exposure time the concentration of 2-chloropropene is twice as large as that of 1-chloropropene, as indicated by the ratio of 0.5 for $R_{CHCl=CHCH_3}$ / $R_{CH_2=CClCH_3}$.

In contrast to the excited $\dot{C}_3H_6Cl^*$ radical which had only one method of decomposition, the vibronically excited $CH_2Cl\dot{C}ClCH_3^*$ radicals may decompose as follows :

$$CH_2Cl\dot{C}ClCH_3^* \longrightarrow CH_2=CClCH_3 + \cdot Cl \qquad (K)$$

$$CH_2Cl\dot{C}ClCH_3^* \longrightarrow CHCl=CHCH_3 + \cdot Cl \qquad (L)$$

In reaction L the excited radical undergoes a hydrogen migration after releasing the chlorine atom attached to the middle carbon. Reaction K is of course the reverse of the chlorine atom addition given by reaction H. Reaction H followed by reaction L would lead to an effective conversion of 2-chloropropene into 1-chloropropene. Thus with increasing exposure time the ratio, $R_{CHCl=CHCH_3}/R_{CH_2=CClCH_3}$ would be expected to increase, as indeed, experimentally observed.

The relative quantum yields of products were calculated and reported in Table 5, and some of them are plotted as a function of exposure time in Figure 5. Although the data show some scatter, they present an over-

Table 5. Relative Quantum Yields of the Products in the Photolysis of 1,2 - Dichloropropane at $\lambda > 340$ nm.

Expt. No.	Time Min.	$CH_2=CHCH_3$	$CH_2=CClCH_3$	$CHCl=CHCH_3$	
				Cis	Trans
1	180	0.51	0.28	0.12	0.09
2	240	0.51	0.29	0.12	0.08
3	360	0.49	0.29	0.13	0.09
4	540	0.45	0.26	0.17	0.12
5	720	0.44	0.23	0.19	0.14
6	900	0.49	0.22	0.17	0.12

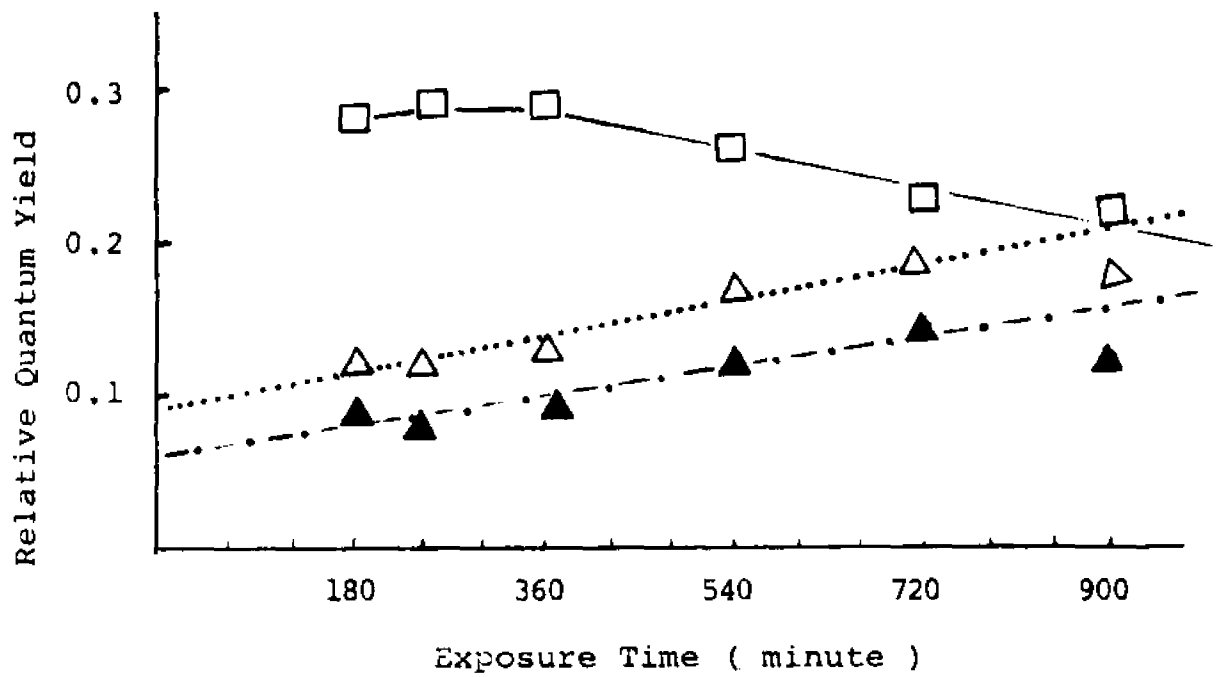


Fig. 5. Plot of the relative quantum yields against exposure time in the photolysis of 1,2-dichloropropane at $\lambda > 340$ nm.

—□— ; $CH_2=CClCH_3$, ···△··; c-$CHCl=CHCH_3$, -·▲-·- ; t-$CHCl=CHCH_3$

all confirmation of the suggested transformation of 2-chloropropene into 1-chloropropene by showing the increase of the quantum yields of cis- and trans-1-chloropropene and the corresponding decrease of the quantum yields of 2-chloropropene as a function of exposure time.

(2) Photolysis at $\lambda > 220$ nm

The data obtained at $\lambda > 220$ nm are given in Tables 6 and 7. A graphical representation of the variations in product ratios is shown in Figure 6. The relative quantum yields are presented in Table 8 and plotted in Figure 7. Generally speaking, it is amazing how similar the data

Table 6. Photolysis of 1,2 - Dichloropropane at $\lambda > 220$ nm.

$P_{CH_2ClCHClCH_3}$ = 24 torr, Products in molecules/ml X 10^{-15}

Expt. No.	Time Min.	$CH_2=CHCH_3$	$CH_2=CClCH_3$	$CHCl=CHCH_3$ Cis	$CHCl=CHCH_3$ Trans
1	120	1.98	1.24	0.285	0.238
2	180	3.48	1.80	0.974	0.475
3	240	4.61	2.47	1.15	0.575
4	300	5.82	3.08	1.77	0.776
5	360	7.68	3.57	2.15	1.19
6	420	8.14	4.67	3.51	2.93
7	480	9.27	5.89	4.13	3.02
8	600	11.6	5.41	4.61	3.06
9	720	13.7	6.62	5.30	3.45

Table 7. Product Ratios in the Photolysis of 1,2 - Dichloropropane at $\lambda > 220$ nm.

Expt. No.	Time Min.	Cl_2 Elimination / HCl Elimination	$CH_2=CHCH_3$ / $CH_2=CClCH_3$	$CHCl=CHCH_3$ / $CH_2=CClCH_3$	c-$CHCl=CHCH_3$ / t-$CHCl=CHCH_3$
1	120	1.1	1.6	0.42	1.2
2	180	1.1	1.9	0.80	2.1
3	240	1.1	1.9	0.70	2.0
4	300	1.0	1.9	0.82	2.3
5	360	1.1	2.2	0.93	1.8
6	420	0.73	1.7	1.4	1.2
7	480	0.71	1.9	1.2	1.4
8	600	0.89	2.2	1.4	1.5
9	720	0.89	2.1	1.3	1.5

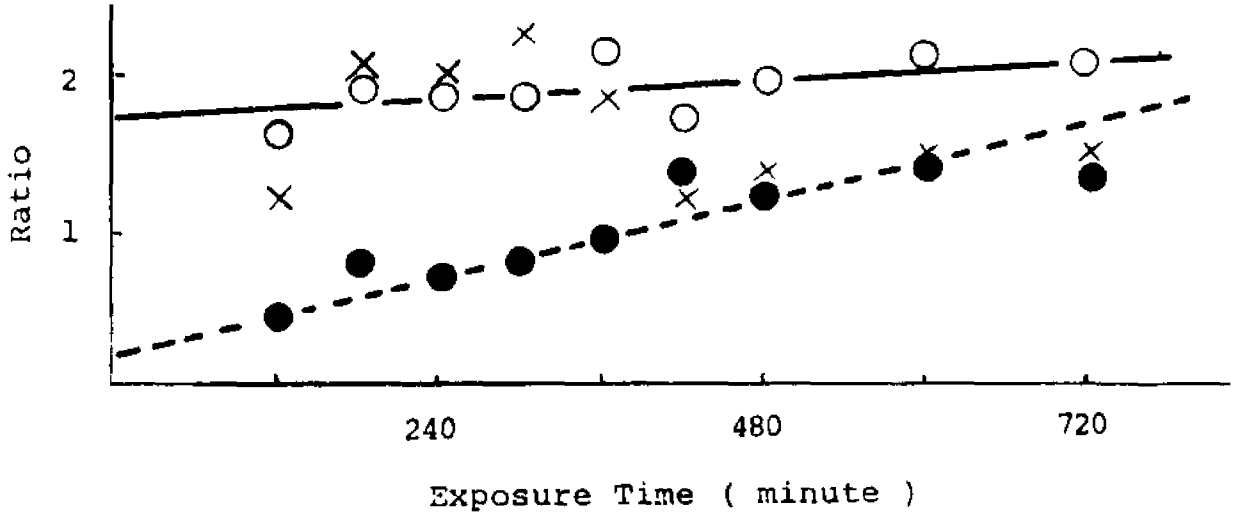


Fig.6. Plot of the product ratios against exposure time in the photolysis of 1,2-dichloropropane at $\lambda > 220$ nm. —○—; $CH_2=CHCH_3/CH_2=CClCH_3$ --●-- ; $CHCl=CHCH_3/CH_2=CClCH_3$, ···×··· ; c-$CHCl=CHCH_3$/t-$CHClCHCH_3$

Table 8. Relative Quantum Yields of the Products in the Photolysis of 1,2 - Dichloropropane at $\lambda > 220$ nm.

Expt. No.	Time Min.	$CH_2=CHCH_3$	$CH_2=CClCH_3$	$CHCl=CHCH_3$	
				Cis	Trans
1	120	0.53	0.33	0.08	0.06
2	180	0.52	0.27	0.14	0.07
3	240	0.52	0.28	0.13	0.07
4	300	0.51	0.27	0.15	0.07
5	360	0.53	0.24	0.15	0.08
6	420	0.43	0.24	0.18	0.15
7	480	0.42	0.26	0.18	0.14
8	600	0.47	0.22	0.19	0.12
9	720	0.47	0.23	0.18	0.12

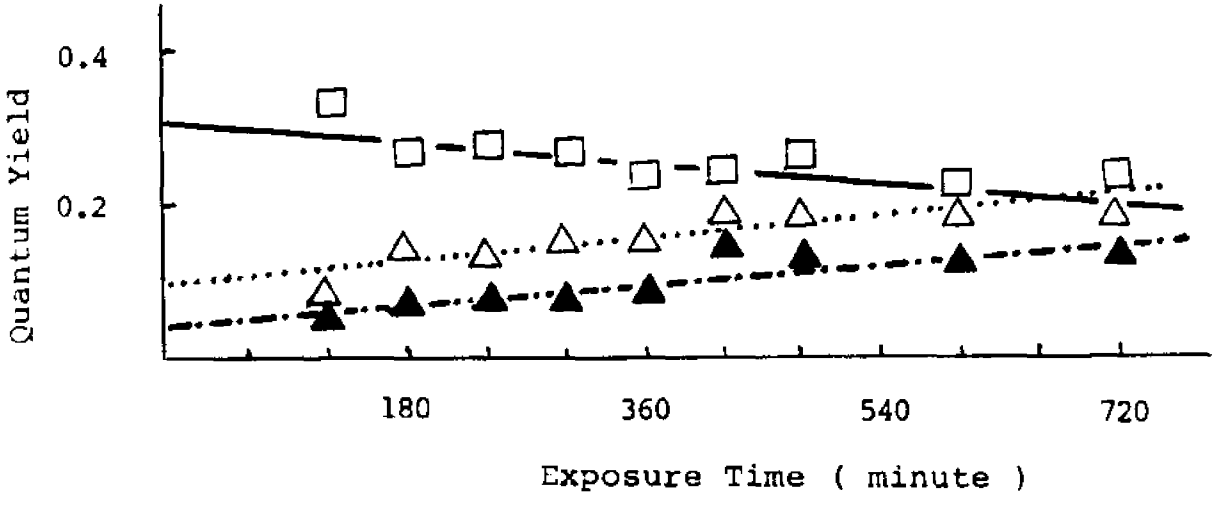


Fig. 7. Plot of the relative quantum yields against exposure time in the photolysis of 1,2-dichloropropane at $\lambda > 220$ nm.

——□—— ; $CH_2=CClCH_3$, ····△···· : c-$CHCl=CHCH_3$, – – ▲ – – ; t-$CHCl=CHCH_3$

here are which discussed at $\lambda > 340$ nm. There are no new products. The product ratios are quite similar to those reported at $\lambda > 340$ nm.

As a matter of fact the ratio, $R_{CH_2=CHCH_3}/R_{CH_2=CClCH_3}$, at zero time is 1.75 exactly as was the case at $\lambda > 340$ nm. This is a strong indication that both propene and 2-chloropropene are produced from a single excited state since their ratio seems to be wavelength independent. The ratio, $R_{CHCl=CHCH_3}/R_{CH_2=CClCH_3}$, at zero time is however, considerably smaller at $\lambda > 220$ nm(0.2) than at $\lambda > 340$ nm(0.5), indicating that 1-chloropropene is, at least in part, produced by an excited state different from the one producing propene and 2-chloropropene, and that this excited state is at a lower energy level since the production of 1-chloropropene increases, relatively speaking, toward longer wavelengths. The data regarding to cis/trans are rather scattered. We have no explanation to offer why the experimental error determining this ratio seems so much larger here than in most other series. The relative quantum yields, given in Table 8, confirm the increase of cis- and trans-1-chloropropene at the expense of 2-chloropropene as discussed at $\lambda > 340$ nm.

(3) Photolysis at $\lambda > 200$ nm

The data obtained at $\lambda > 200$ nm are given in Tables 9 and 10. In Figure 8 the ratios given in Table 10 are plotted as a function of time. There are clear and unmistakable signs of secondary reaction as indicated by the rather steep slopes of $R_{CH_2=CHCH_3}/R_{CH_2=CClCH_3}$ and of $R_{CHCl=CHCH_3}/R_{CH_2=CClCH_3}$, and the initial variations of the R_{cis}/R_{trans} ratio of

1-chloropropene.

The ratio, $R_{CH_2=CHCH_3}/R_{CH_2=CClCH_3}$, extrapolates to a value of 2.75 at zero time compared to the value of 1.75 at $\lambda > 220$ nm and at $\lambda > 340$nm. This indicates that there may be another primary step producing propene. As will be discussed later, other 1,2-dichlorocompounds show similar phenomena and a corresponding explanation would be primary step E :

$$CH_2ClCHClCH_3^* \longrightarrow CH_2=CHCH_3 + 2\ Cl^{\bullet} \qquad (E)$$

Table 9. Photolysis of 1,2 - Dichloropropane at $\lambda > 200$ nm.

$P_{CH_2ClCHClCH_3}$ = 24 torr, Products in molecules/ml X 10^{-15}

Expt. No.	Time Min.	$CH_2=CHCH_3$	$CH_2=CClCH_3$	$CHCl=CHCH_3$ Cis	Trans
1	5.0	3.92	1.28	0.275	0.321
2	7.5	6.29	1.65	0.341	0.303
3	10.0	7.52	1.95	0.520	0.403
4	12.5	8.82	2.12	0.699	0.501
5	15.0	11.0	2.42	1.04	0.699
6	17.5	12.8	2.55	1.09	0.921
7	20.0	15.4	3.26	1.83	1.22
8	25.0	18.7	3.51	1.99	1.31
9	30.0	22.7	3.57	2.41	1.61
10	35.0	26.1	4.67	3.62	3.00
11	40.0	29.9	4.69	5.02	3.34
12	60.0	35.8	3.73	4.98	3.26

This would mean that the system now generates chlorine atoms directly in addition to the atoms produced by secondary photolysis of chlorine molecules. As suggested before, the variation of the ratio, $R_{CHCl=CHCH_3}/R_{CH_2=CClCH_3}$ caused by initial attack of chlorine atoms upon 2-chloropropene should be more visible here due to the increased chlorine atom production during the photolysis. This is indeed shown in Figure 8 by the steep slope of the ratio, $R_{CHCl=CHCH_3}/R_{CH_2=CClCH_3}$.

Table 10. Product Ratios in the Photolysis of 1,2 - Dichloropropane at $\lambda > 200$ nm.

Expt.	Time	Cl_2 Elimination	$CH_2=CHCH_3$	$CHCl=CHCH_3$	c-$CHCl=CHCH_3$
No.	Min.	HCl Elimination	$CH_2=CClCH_3$	$CH_2=CClCH_3$	t-$CHCl=CHCH_3$
1	5.0	2.1	3.1	0.47	0.86
2	7.5	2.7	3.8	0.39	1.1
3	10.0	2.6	3.9	0.47	1.3
4	12.5	2.7	4.2	0.57	1.4
5	15.0	2.7	4.6	0.72	1.5
6	17.5	2.6	5.0	0.79	1.2
7	20.0	2.7	4.7	0.93	1.5
8	25.0	3.2	5.3	0.94	1.5
9	30.0	3.0	6.4	1.1	1.5
10	35.0	2.3	5.6	1.4	1.2
11	40.0	2.3	6.4	1.8	1.5
12	60.0	3.2	9.6	2.2	1.5

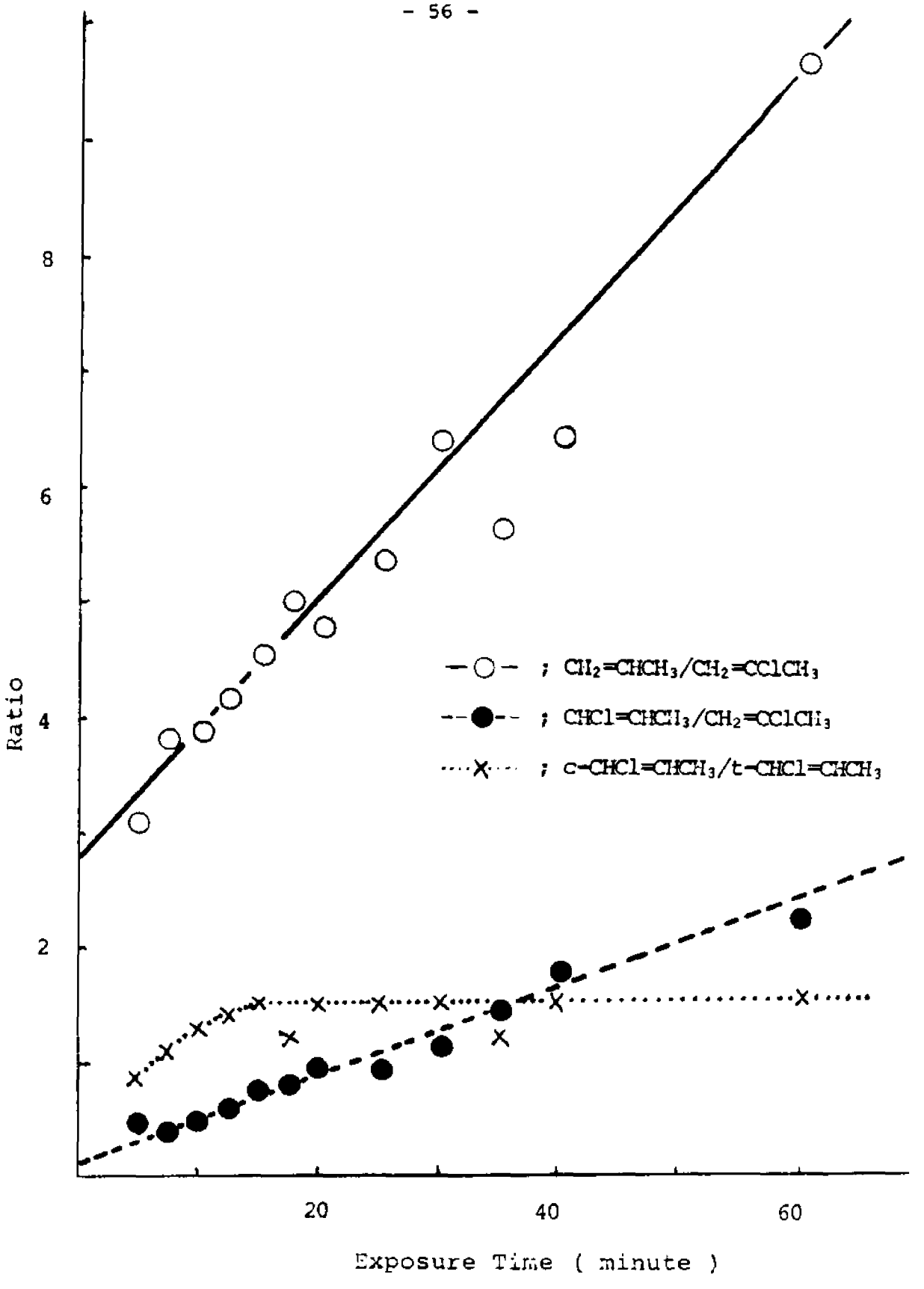
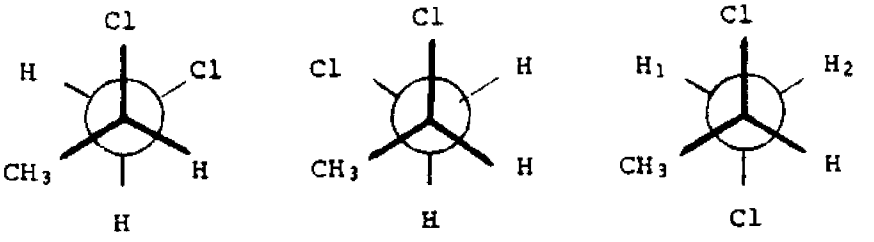


Fig. 8. Plot of product ratios against exposure time in the photolysis of 1,2-dichloropropane at $\lambda > 200$ nm.

In Figure 9 we plotted the relative quantum yields of the photolyzed products as a function of time. The relative quantum yield of propene is for all practical purpose independent of exposure time, confirming that propene does not participate in the secondary processes. The quantum yields of 1-chloropropene increase as those of 2-chloropropene decrease with exposure time. This behavior is completely in accordance with the proposed secondary mechanism.

Finally it is clearly seen in Figure 8 that the ratio, cis/trans for 1-chloropropene reaches an equilibrium value of about 1.5 as already pointed out at $\lambda > 340$ nm. This equilibrium is established by secondary reaction, since at the shortest exposure time a ratio of 0.9 was obtained. It is tempting to extrapolate the curve in Figure 8 for cis/trans to 0 at zero exposure time, which would indicate that initially only trans compound was produced. Exclusive or preferential production of the trans isomer may be rationalized by considering the conformational isomers I, II, and III, shown on page 58. Since photochemical molecular elimination from 1,2-position generally proceeds via a four-center transition state, the major pathway, syn elimination could occur from rotamers I, II, or III. Syn elimination from II or loss of H_1 from III would cause the chlorine atom and the methyl group to be eclipsed in the transition state, thus, obstructing the two pathways for syn elimination leading to cis-1-chloropropene. Because of these an excess of trans isomer should be expected

Extrapolating the cis/trans data in Figure 3 to zero time is, however,



I II III

Table 11. Relative Quantum Yields of the Products in the Photolysis of 1,2 - Dichloropropane at $\lambda > 200$ nm.

Expt. No.	Time Min.	$CH_2=CHCH_3$	$CH_2=CClCH_3$	$CHCl=CHCH_3$ Cis	$CHCl=CHCH_3$ Trans
1	5.0	0.67	0.22	o.o5	0.06
2	7.5	0.73	0.19	0.04	0.04
3	10.0	0.72	0.19	0.05	0.04
4	12.5	0.72	0.18	0.06	0.04
5	15.0	0.72	0.16	0.07	0.05
6	17.5	0.74	0.15	0.06	0.05
7	20.0	0.71	0.15	0.08	0.06
8	25.0	0.73	0.14	0.08	0.05
9	30.0	0.75	0.12	0.08	0.05
10	35.0	0.70	0.12	0.10	0.08
11	40.0	0.69	0.11	0.12	0.08
12	60.0	0.75	0.08	0.10	0.07

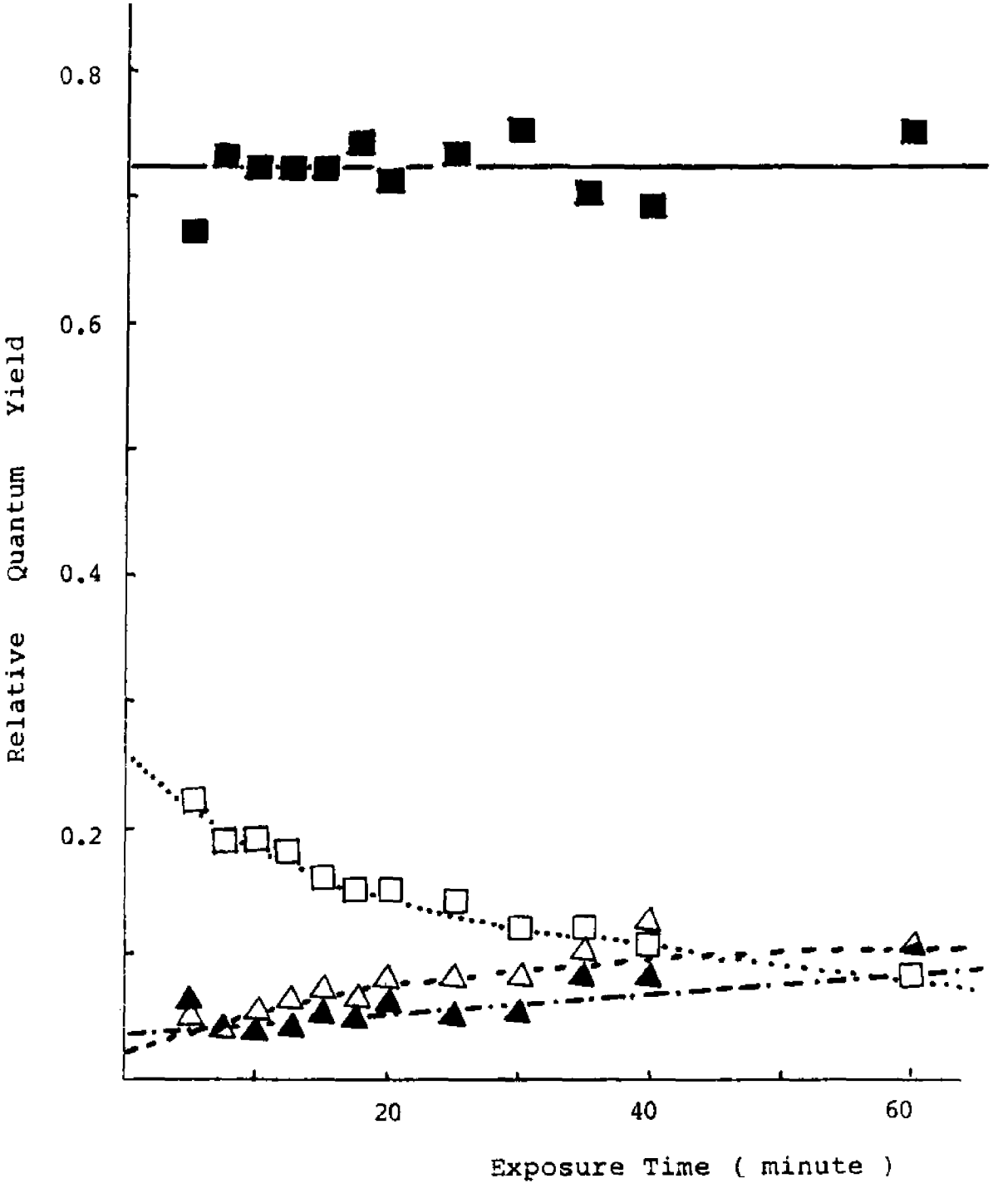


Fig. 9. Plot of the relative quantum yields against exposure time in the photolysis of 1,2-dichloropropane at $\lambda > 200$ nm.

—■— ; CH_2=$CHCH_3$, ···□··· ; CH_2=$CClCH_3$,

– –△– –; c-$CHCl$=$CHCH_3$, – ·-▲– · ; t-$CHCl$=$CHCH_3$

dangerous. It should suffice here to state that at the shortest exposure time a value smaller than unity was obtained for the ratio, cis/trans, which increased with increasing exposure time to a constant value of 1.5. Such a behavior may be explained by the following reaction sequence :

$$\cdot Cl + \text{trans-}CHCl{=}CHCH_3 \longrightarrow \cdot CHClCHClCH_3^{*}$$

$$\cdot CHClCHClCH_3^{*} \longrightarrow \text{trans-}CHCl{=}CHCH_3 + \cdot Cl$$

$$\longrightarrow \text{cis-}CHCl{=}CHCH_3 + \cdot Cl$$

Thus cis-trans isomerization of 1-chloropropene depends upon the production and subsequent decomposition of the vibrationally excited $\dot{C}HClCHClCH_3^{*}$ radical. Obviously if it would be possible to quench the vibrational excitation with a deactivator, then cis-trans isomerization would be stopped.

3. Summary of the Photochemical Processes.

The product ratios at zero time are summerized in Table 12. These data seem to indicate the formation of three excited states.

$$CH_2ClCHClCH_3 + h\nu \longrightarrow CH_2ClCHClCH_3^{***} \quad (1)$$

$$\longrightarrow CH_2ClCHClCH_3^{**} \quad (2)$$

$$\longrightarrow CH_2ClCHClCH_3^{*} \quad (3)$$

Which are suggested to decompose in the following way :

$$CH_2ClCHClCH_3^{***} \longrightarrow CH_2{=}CHCH_3 + 2\ \cdot Cl \quad (4)$$

$$CH_2ClCHClCH_3^{**} \longrightarrow CH_2{=}CHCH_3 + Cl_2 \quad (5)$$

$$\longrightarrow CH_2{=}CClCH_3 + HCl \quad (6)$$

$$CH_2ClCHClCH_3^{**} + M \longrightarrow CH_2ClCHClCH_3^{*} + M^{*} \quad (7)$$

$$CH_2ClCHClCH_3^{*} \longrightarrow CHCl{=}CHCH_3 + HCl \quad (8)$$

Reaction 7 will be discussed later.

The production of the "triple star" excited state and its subsequent decomposition into propene and chlorine atom(reaction 4) has been observed only at $\lambda < 220$ nm. The formation of the "two and one star" excited states has been observed at all wavelength regions and the decomposition reaction 5, 6, and 8 are, energetically speaking, possible at $\lambda < 700$ nm.

From the data in Table 12, the percentage of each primary step at the individual wavelength was calculated. These are reported in Table 13. The production of the "one star" excited state decreases in importance with decreasing wavelength of the investigation. This decrease is a

Table 12. Product Ratio in the Photolysis of 1,2 - Dichloropropane at Zero Exposure Time.

Ratio \ Wavelength	> 200 nm	> 220 nm	> 340 nm
$\frac{CH_2{=}CHCH_3}{CH_2{=}CClCH_3}$	2.75	1.75	1.75
$\frac{CHCl{=}CHCH_3}{CH_2{=}CClCH_3}$	0.1	0.2	0.5
$\frac{c\text{-}CHCl{=}CHCH_3}{t\text{-}CHCl{=}CHCH_3}$	—	—	1.5

relative decrease, since the production of the "two" and especially the "three star" excited states increases at shorter wavelengths.

Accepting these primary processes, the following reactions are proposed in order to explain the variation in the product ratios.

$CH_2{=}CClCH_3 + {\cdot}Cl \longrightarrow CH_2Cl\dot{C}ClCH_3^*$ (9)

$CH_2Cl\dot{C}ClCH_3^* \longrightarrow CH_2{=}CClCH_3 + {\cdot}Cl$ (10)

$\longrightarrow CHCl{=}CHCH_3 + {\cdot}Cl$ (11)

$CH_2Cl\dot{C}ClCH_3^* + M \longrightarrow CH_2Cl\dot{C}ClCH_3 + M^*$ (12)

$CHCl{=}CHCH_3 + {\cdot}Cl \longrightarrow {\cdot}CHClCHClCH_3^*$ (13)

${\cdot}CHClCHClCH_3^* \longrightarrow cis\text{-}CHCl{=}CHCH_3 + {\cdot}Cl$ (14)

$\longrightarrow trans\text{-}CHCl{=}CHCH_3 + {\cdot}Cl$ (15)

${\cdot}CHClCHClCH_3^* + M \longrightarrow {\cdot}CHClCHClCH_3 + M^*$ (16)

Reactions 12 and 16 will be discussed later.

Table 13. Contribution (in %) of Each Individual Step to the Total Primary Process at Different Wavelengths.

	> 200 nm (%)	> 220 nm (%)	> 340 nm (%)
$CH_2{=}CHCH_3 + 2\ Cl{\cdot}$	26.0	—	—
$CH_2{=}CHCH_3 + Cl_2$	45.4	59.3	53.8
$CH_2{=}CClCH_3 + HCl$	26.0	33.9	30.8
$CHCl{=}CHCH_3 + HCl$	2.6	6.8	15.4

4. Deactivation of Vibronically Excited Radicals

In the above mechanism we included reactions of vibrationally excited radicals. Experiments with an inert deactivator, sulfur hexafluoride,were, therefore, carried out in order to get information about the absence or presence of these radicals and about their participation in the determination of the final product distribution. Sulfur hexafluoride is an excellent inert deactivator ; it has many vibrational modes,and it is neither photolyzed nor fragmentized by reactions in the system. This study may also yields information regarding the nature of the excited 1,2-dichloropropane molecules yielding the products given by the reactions 4 to 8. If decomposition occurs from a vibrationally excited state then the presence of an inert deactivator should influence this process.

(1) Photolysis in the Presence of SF_6 at $\lambda > 200$ nm

In the mechanism vibrationally excited radicals are produced by chlorine atom addition to chloropropenes. It is, therefore, expected that especially data obtained at short wavelengths ($\lambda > 200$ nm) will yield useful information. After all, at $\lambda > 200$ nm chlorine atoms are produced not only by secondary photodecomposition of chlorine molecules but also by direct photolysis of 1,2-dichloropropane. If cis-trans isomerization takes place via an excited $\dot{C}HClCHClCH_3^*$ radical, then such isomerization should decrease with increasing pressure of the sulfur hexafluoride as indicated by the following processes :

$$\cdot Cl + \text{trans-}CHCl{=}CHCH_3 \longrightarrow \cdot CHClCHClCH_3^*$$

$$\cdot CHClCHClCH_3^{*} \longrightarrow cis\text{-}CHCl{=}CHCH_3 + \cdot Cl$$

$$\cdot CHClCHClCH_3^{*} \longrightarrow trans\text{-}CHCl{=}CHCH_3 + \cdot Cl$$

$$\cdot CHClCHClCH_3^{*} + SF_6 \longrightarrow \cdot CHClCHClCH_3 + SF_6^{*}$$

Once the vibrationally excited $\cdot CHClCHClCH_3^{*}$ radical has lost all, or even only a part, of its energy, it can not decompose any more and thus the isomerization chain will be stopped before thermodynamic equilibrium is reached. Actually the ratio, cis/trans, decreases with increasing deactivator pressure as shown in Figure 10, reaching a value 1.1 not far from the lowest value of 0.9 observed at the shortest exposure time. Unfortunately, it was impossible to increase the deactivator pressure

Table 14. Photolysis of 1,2 - Dichloropropane in the Presence of Sulfur Hexafluoride at $\lambda > 200$ nm. Products in molecules/ml X 10^{-15}

Expt. No.	SF_6 Pressure Torr	$CH_2{=}CHCH_3$	$CH_2{=}CClCH_3$	$CHCl{=}CHCH_3$	
				Cis	Trans
1	0	14.1	2.80	1.88	1.50
2	10	14.0	2.53	1.94	1.65
3	20	14.0	2.54	2.28	2.07
4	30	14.1	2.39	1.95	1.90
5	40	13.5	2.11	1.76	1.55

* The photolysis was carried out at an initial pressure 10 torr of 1,2-dichloropropane. The exposure time was 30 minutes.

Table 15. Product Ratios in the Photolysis of 1,2 - Dichloropropane in the Presence of Sulfur Hexafluoride at $\lambda > 200$ nm.

Expt. No.	SF_6 Pressure Torr	Cl_2 Elimination / HCl Elimination	CH_2=$CHCH_3$ / CH_2=$CClCH_3$	$CHCl$=$CHCH_3$ / CH_2=$CClCH_3$	c-$CHCl$=$CHCH_3$ / t-$CHCl$=$CHCH_3$
1	0	2.3	5.1	1.2	1.3
2	10	2.3	5.5	1.4	1.2
3	20	2.1	5.5	1.7	1.1
4	30	2.3	5.9	1.6	1.1
5	40	2.5	6.4	1.6	1.1

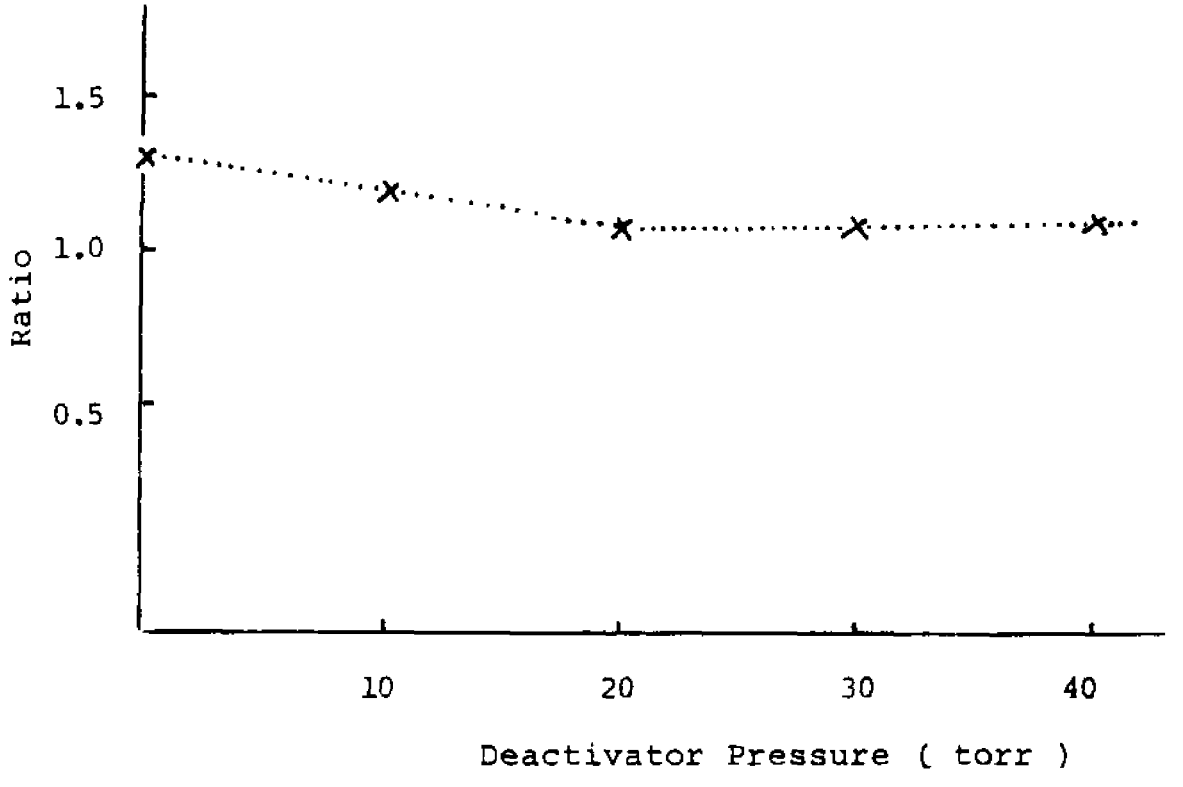


Fig. 10. Plot of the cis/trans ratio against sulfur hexafluoride pressure in the photolysis of 1,2-chloropropane at $\lambda > 200$ nm.

even more in order to determine the initial cis/trans ratio before the sequence of isomerizations started. Since in our experiments, starting materials and reaction products were collected simultaneously for injection into the gas chromatograph, a pressure of sulfur hexafluoride exceeding 40 torr might have caused accident by exploding the sample trap.

In Table 16 relative quantum yields of various products are reported as a function of SF_6 pressure. There is no doubt that the quantum yield of 2-chloropropene decreases with increasing deactivator. At the same time there is no indication of an increase in quantum yields of 1-chloropropene. Again this behavior confirms the reaction sequence given previously.

$$\cdot Cl + CH_2{=}CClCH_3 \longrightarrow CH_2\dot{C}ClCH_3^*$$

Table 16. Relative Quantum Yields of the Products as a Function of Sulfur Hexafluoride Pressure in the Photolysis of 1,2-Dichloropropane at $\lambda > 200$ nm.

Expt. No.	SF_6 Pressure Torr	$CH_2{=}CHCH_3$	$CH_2{=}CClCH_3$	$CHCl{=}CHCH_3$ Cis	$CHCl{=}CHCH_3$ Trans
1	0	0.70	0.14	0.09	0.07
2	10	0.70	0.13	0.09	0.08
3	20	0.67	0.12	0.11	0.10
4	30	0.69	0.12	0.10	0.09
5	40	0.71	0.11	0.09	0.08

$$CH_2ClCClCH_3^* \longrightarrow CH_2{=}CClCH_3 + {\cdot}Cl$$

$$CH_2ClCClCH_3^* \longrightarrow CHCl{=}CHCH_3 + {\cdot}Cl$$

$$CH_2ClCClCH_3^* + SF_6 \longrightarrow CH_2ClCClCH_3 + SF_6^*$$

In the absence of SF_6, we noticed a decrease in 2-chloropropene and a corresponding increase in 1-chloropropene with increasing exposure time. If an inert deactivator is added to the system, the vibronically excited $CH_2ClCClCH_3^*$ radical will be deactivated. Thus the quantum yield of 2-chloropropene will be decreased without increasing that of 1-chloropropene. Thus the experimental data are in excellent agreement with the proposed mechanism.

(2) Photolysis in the Presence of SF_6 at $\lambda > 220$ nm

A series of experiments with SF_6 was carried out also at $\lambda > 220$ nm. The results are reported in Table 17. Relative quantum yields of the various products and product ratios are given in Tables 17 and 18, respectively. A graphical representation of the variation in the product ratios with sulfur hexafluoride is shown in Figure 11. The data are very different from those just discussed at $\lambda > 200$ nm. The relative quantum yield of propene stays constant at $\lambda > 200$ nm but decreases sharply at $\lambda > 220$ nm with the increase in SF_6 pressure. The relative quantum yields of 1-chlorpropenes stay approximately constant at $\lambda > 200$ nm, but increase considerably at $\lambda > 220$ nm. The results in Table 18 show quite clearly that at $\lambda > 220$ nm, the 1-chloropropenes increase at expense of propene.

At first glance one is tempted to assume that chlorine atoms react with propene to form cis- and trans-1-chloropropene. But all experiments so far have shown that chlorine atoms are produced at this wavelength by secondary photolysis only. They can, therefore, not be expected to have such a pronounced effect as that shown in Table 18. Secondly, if indeed chlorine atoms would react with propene to form ultimately 1-chloropropene, we should certainly have observed this at $\lambda > 200$ nm, where chlorine atoms are produced in the primary process and where the relative concentration of propene is considerably larger, thus favoring this kind of reaction if it would occur.

In addition we would expect to see a decrease in 2-chloropropene production with increasing sulfur hexafluoride pressure due to the reaction of chlorine atoms with 2-chloropropene as explained earlier. None of

Table 17. Photolysis of 1,2 - Dichloropropane in the Presence of Sulfur Hexafluoride at $\lambda > 220$ nm. Products in molecules/ml X 10^{-15}

Expt. No.	SF_6 Pressure Torr	$CH_2=CHCH_3$	$CH_2=CClCH_3$	$CHCl=CHCH_3$ Cis	$CHCl=CHCH_3$ Trans
1	0	11.2	4.97	2.34	1.42
2	10	10.4	4.75	2.78	1.40
3	20	10.0	4.62	3.55	2.48
4	30	9.69	4.78	4.03	2.14
5	40	9.55	4.99	4.06	2.55

*The photolysis was carried out at an initial pressure 10 torr of 1,2-dichloropropane. The exposure time was 10 hours.

those effects are observed. In order to explain this kind of phenomena on the basis of the suggested mechanism, it should be remembered that the excited state producing 1-chloropropene has a lower energy than the state yielding propene. We are, therefore, suggesting that the data may be explained by a partial deactivation of the "two star" excited state, yielding propene, to produce the "one star" excited state which then may decompose into cis- and trans-1-chloropropene. This can be expressed by the following reactions :

$$CH_2ClCHClCH_3^{**} \longrightarrow CH_2{=}CHCH_3 + Cl_2 \qquad (5)$$

$$CH_2ClCHClCH_3^{**} + SF_6 \longrightarrow CH_2ClCHClCH_3^{*} + SF_6^{*} \qquad (7)$$

$$CH_2ClCHClCH_3^{*} \longrightarrow \text{cis- or Trans-}CHCl{=}CHCH_3 + HCl \qquad (8)$$

It is clear that this mechanism will increase the production of cis- and

Table 18. Relative Quantum Yields of the Products as a Function of Sulfur Hexafluoride Pressure in the Photolysis of 1,2 - Dichloropropane at $\lambda > 220$ nm.

Expt. No.	SF_6 Pressure Torr	$CH_2{=}CHCH_3$	$CH_2{=}CClCH_3$	$CHCl{=}CHCH_3$ Cis	$CHCl{=}CHCH_3$ Trans
1	0	0.56	0.25	0.12	0.07
2	10	0.55	0.25	0.14	0.07
3	20	0.48	0.22	0.17	0.12
4	30	0.47	0.23	0.20	0.10
5	40	0.45	0.24	0.20	0.11

Table 19. Product Ratios in the Photolysis of 1,2 - Dichloropropane in the Presence of Sulfur Hexafluoride at $\lambda > 220$ nm.

Expt No.	SF_6 Pressure Torr	Cl_2 Elimination / HCl Elimination	$CH_2{=}CHCH_3$ / $CH_2{=}CClCH_3$	$CHCl{=}CHCH_3$ / $CH_2{=}CClCH_3$	c-$CHCl{=}CHCH_3$ / t-$CHCl{=}CHCH_3$
1	0	1.3	2.3	0.76	1.7
2	10	1.2	2.2	0.88	2.0
3	20	0.94	2.2	1.3	1.4
4	30	0.88	2.0	1.3	1.9
5	40	0.82	1.9	1.3	1.6

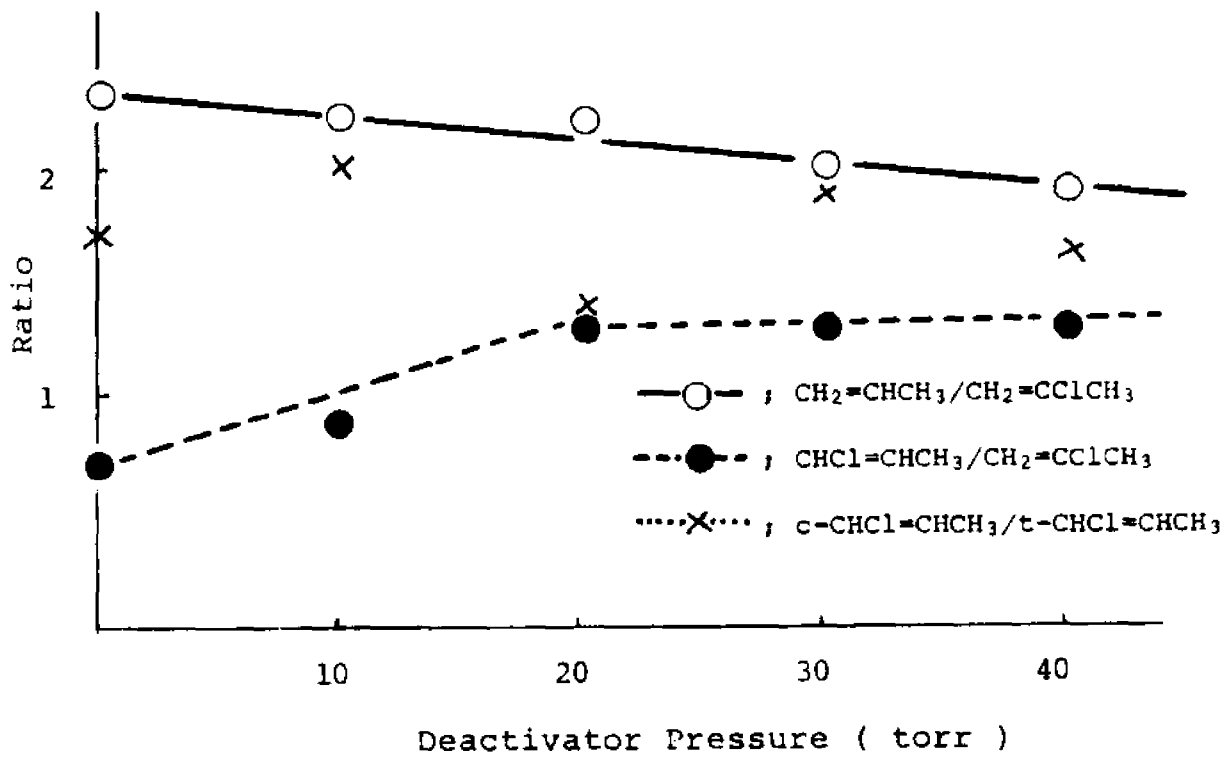


Fig. 11. Plot of product ratios against sulfur hexafluoride pressure in the photolysis of 1,2-dichloropropane at $\lambda > 220$ nm.

trans- 1- chloropropene at the expense of propene with increasing sulfur hexafluoride pressure as observed.

Some additional information regarding reactions 5, 7, and 8 has been obtained by carring out the photolysis at different pressures of 1,2-dichloropropane. Obviously the pressure range is relatively small since the vapor pressure of 1,2-dichloropropane at room temperature is only about 40 torr. These data are given in Tables 20 and 21. The production rate increases with increasing 1,2-dichloropropane pressure as expected, since the absorption of light is a function of the initial pressure. It is extremely interesting that with increasing pressure the rates of production /torr of both propene and 2-chloropropene decrease. Such a behavior is really quite normal and may be explained either by nonlinearity between pressure and absorbed light or by self-quenching of the excited states producing propene and 2-chloropropene. Nonlinearity between

Table 20. Product Formation as a Function of Initial 1,2 - Dichloropropane Pressure at $\lambda > 200$ nm. Products in molecules/(ml•sec.)X10^{-12}

Expt. No.	Pressure Torr	$CH_2=CHCH_3$	$CH_2=CClCH_3$	$CHCl=CHCH_3$ Cis	Trans	Cis + Trans
1	9	6.28	1.29	0.273	0.293	0.566
2	14	8.20	1.98	0.603	0.467	1.07
3	24	12.5	3.25	0.867	0.672	1.54
4	34	15.9	3.78	1.15	0.987	2.14
5	40	19.3	4.25	1.41	1.30	2.71

* The experiments were carried out at 10 minutes exposure time.

light absorption and pressure would not be expected at the relatively low pressure of this investigation and would, furthermore, also cause a decrease in cis- and trans-1-chloropropene yields which is not observed.

Self-quenching of the excited state producing propene and 2-chloropropene is, thus, much more likely, especially, since we have been able to observe deactivation by sulfur hexafluoride and, as will be shown later, by water. The production rate of total cis- and trans-1-chloropropene is, within experimental error, independent of the initial pressure of 1,2-dichloropropane. This may be explained by accepting that the excited state producing 1-chloropropene is so short-lived that it can not be deactivated within the pressure range of this study. Another explanation, preferred by us, is to accept that the deactivational decrease in 1-chloropropene is compensated by for by an increased production of the excited state yielding 1-chloropropene as shown in the reaction sequence 5, 7, and 8.

Table 21. Product Formation per Torr as a Function of Initial 1,2-Dichloropropane Pressure. Products in molecules/(ml·sec.·torr) X 10^{-11}

Expt. No.	Pressure Torr	$CH_2{=}CHCH_3$	$CH_2{=}CClCH_3$	$CHCl{=}CHCH_3$ Cis + Trans
1	9	6.98	1.43	0.629
2	14	5.86	1.41	0.764
3	24	5.21	1.35	0.642
4	34	4.68	1.11	0.629
5	40	4.83	1.06	0.678

5. Suppression of Free Radical Processes

We have carried out time studies to allow us to extrapolate the product ratios to zero time where secondary processes are impossible. Another method to prevent secondary reaction is to carry out the photolysis in the presence of a free radical scavenger. Of course it would be interesting to compare the results obtained from these two studies. Thus, several scavengers were tested for their use in the photolysis of 1,2-dichloropropane. Nitric oxide reacted with our column packing material and furthermore its use as a scavenger for chlorine atoms is rather questionable. Iodine caused a distortion of the product distribution through its strong absorption of ultraviolet light. Moreover, it was difficult to get authentic samples to compare the retention time of the chloroiodine products formed. Therefore, we decided to use hydrogen sulfide as a free radical scavenger, and performed two series of experiments, one at λ > 220 nm and the other one at λ > 200 nm.

(1) Photolysis in the Presence of H_2S at λ > 220 nm.

The primary processes at λ > 220 nm consist exclusively of the molecular detachment steps producing propene, molecular chlorine, and hydrogen chloride. At this wavelength free radical reactions are introduced only by secondary photodecomposition of chlorine molecule. The data obtained from the photolysis of 1,2-dichloropropane in the presence of hydrogen sulfide are given in Tables 22 and 23. The product ratios are

plotted in Figure 12. Where it can be seen that the ratio, CH_2=$CHCH_3$ / CH_2=$CClCH_3$, at zero time is exactly equal to 1.75 as observed in the absence of hydrogen sulfide at $\lambda > 220$ nm and at $\lambda > 340$ nm.

The ratio, cis/trans, of 1-chloropropene varies from 0.39 at 120 minutes to 0.62 at 720 minute exposure time, and extrapolates to a value 0.3 at zero time. This is extremely interesting since it confirms that the ratio, about 1.5 was equilibrium ratio as clearly shown in Figure 4, where no change occurred with exposure time. The low value of the ratio obtained here confirms the data obtained at $\lambda > 200$ nm in the absence of a free radical scavenger. In Figure 8, the data at low exposure time extrapolate to a value smaller than unity. An extrapolation to a value of 0.3 obtained here from the scavenger experiment is completely compatible

Table 22. Photolysis of 1,2 - Dichloropropane in the Presence of Hydrogen Sulfide at $\lambda >$ 220 nm. Products in molecules/ml X 10^{-15}

Expt No.	Time Min.	CH_2=$CHCH_3$	CH_2=$CClCH_3$	$CHCl$=$CHCH_3$	
				Cis	Trans
1	120	2.50	0.540	2.42	6.14
2	240	4.38	0.636	3.41	8.20
3	360	8.11	0.737	5.27	11.8
4	480	9.03	0.906	6.92	13.6
5	600	11.3	0.893	8.83	14.9
6	720	14.7	0.791	9.25	14.8

*The photolysis was carried out at an initial 1,2-dichloropropane pressure of 20 torr in the presence of 2 torr of hydrogen sulfide.

Table 23. Product Ratios in the Photolysis of 1,2 - Dichloropropane in the Presence of Hydrogen Sulfide at $\lambda > 220$ nm.

Expt. No.	Time Min.	Cl_2 Elimination / HCl Elimination	$CH_2=CHCH_3$ / $CH_2=CClCH_3$	$CHCl=CHCH_3$ / $CH_2=CClCH_3$	c-$CHCl=CHCH_3$ / t-$CHCl=CHCH_3$
1	120	0.28	4.63	15.8	0.39
2	240	0.36	6.89	18.3	0.42
3	360	0.38	9.23	23.2	0.45
4	480	0.42	10.0	22.6	0.51
5	600	0.46	12.6	26.6	0.59
6	720	0.59	18.1	30.5	0.62

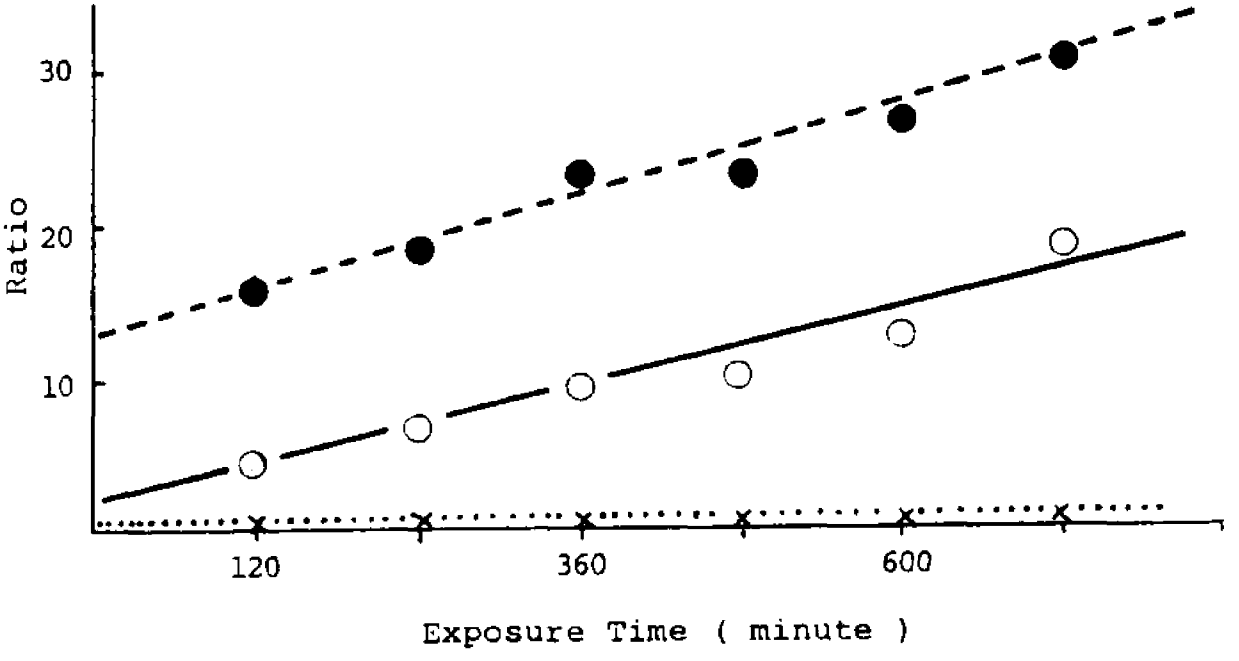


Fig. 12. Plot of product ratios against exposure time in the photolysis of 1,2-dichloropropane in the presence of H_2S at $\lambda > 220$ nm.

—○— ; $CH_2=CHCH_3/CH_2=CClCH_3$, - - ● - - ; $CHCl=CHCH_3/CH_2=CClCH_3$,
···×··· ; c-$CHCl=CHCH_3$/t-$CHCl=CHCH_3$

with the data in Figure 8. Thus the hydrogen sulfide data confirm clearly that initially the trans-1-chloropropene is produced in larger amounts than the cis compound and that cis-trans isomerization is a free radical process which can be stopped by the addition of a free radical scavenger such as hydrogen sulfide. In this case it is clear that the cis-trans isomerization :

$$\cdot Cl + \text{cis- or trans-}CHCl{=}CHCH_3 \longrightarrow \cdot CHClCHClCH_3^*$$

$$\cdot CHClCHClCH_3^* \longrightarrow \text{cis-}CHCl{=}CHCH_3 + \cdot Cl$$

$$\cdot CHClCHClCH_3^* \longrightarrow \text{trans-}CHCl{=}CHCH_3 + \cdot Cl$$

is prevented from occurring in the presence of hydrogen sulfide by the reaction :

$$\cdot Cl + H_2S \longrightarrow HCl + HS\cdot$$

There are, however, some differences. First the ratio, $CH_2{=}CHCH_3$ / $CH_2{=}CClCH_3$ shows a rather steep slope as can be seen in Figure 12. In order to compare the result obtained in the absence of hydrogen sulfide with that in the presence of it, the ratio, without-H_2S/with-H_2S, was calculated and is given in Table 24. Table 24 gives, thus, for each compound the ratio, R_x(in the absence of H_2S)/R_x(in the presence of H_2S). A value of unity would mean that the data are identical regardless of whether hydrogen sulfide is present or absent. The data in Table 24 are plotted as a function of exposure time in Figure 13, from which it may be seen that hydrogen sulfide affects the production of 2-chloropropene

Table 24. Product Ratios in the Photolysis of 1,2 - Dichloropropane in terms of Without-H_2S / With-H_2S at λ > 220 nm.

Expt. No.	Time Min.	CH_2=$CHCH_3$	CH_2=$CClCH_3$	$CHCl$=$CHCH_3$	
				Cis	Trans
1	120	0.79	2.3	0.12	0.038
2	240	1.1	3.9	0.34	0.070
3	360	0.95	4.9	0.41	0.10
4	480	1.0	6.5	0.60	0.22
5	600	1.0	6.1	0.52	0.21
6	720	0.92	8.4	0.57	0.23

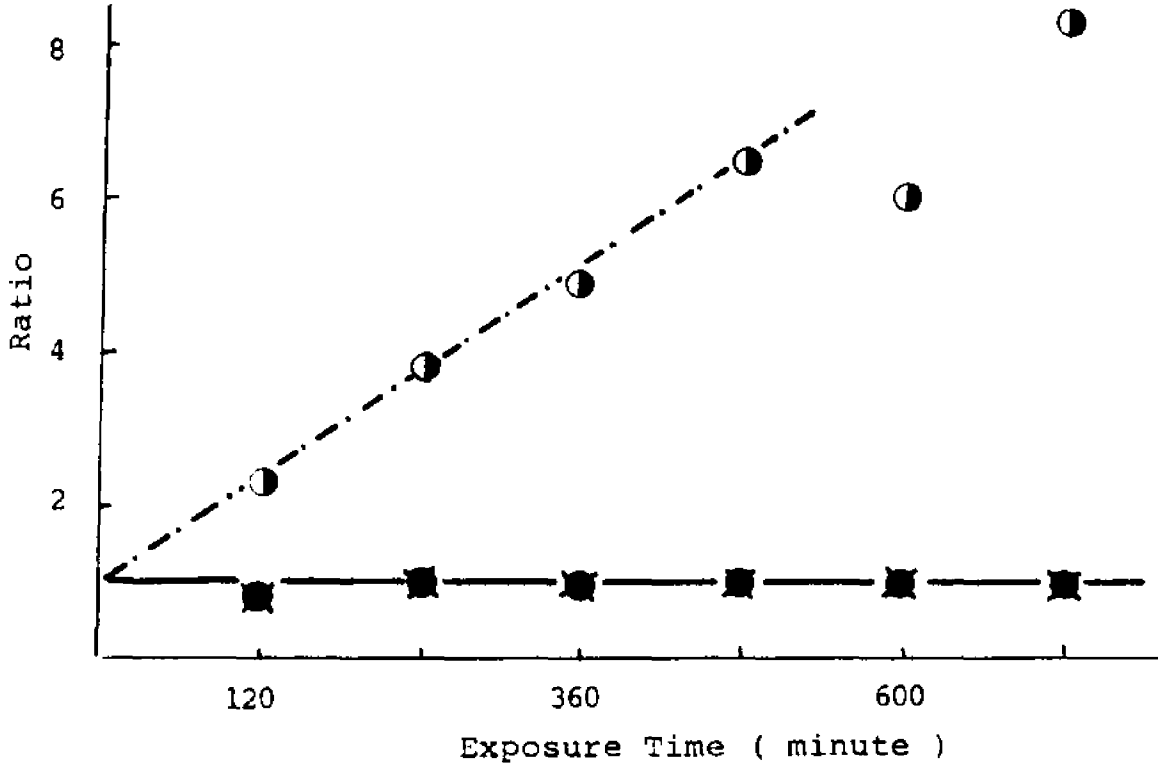


Fig. 13. Plot of product ratios in terms of without-H_2S/with-H_2S against exposure time at λ > 220 nm. -◑-; CH_2=$CHCH_3$, -■-; CH_2=$CClCH_3$

but not that of propene. The steep slope for $R_{CH_2=CHCH_3}/R_{CH_2=CClCH_3}$ proves that a radical process is active which involves 2-chloropropene but not propene. It is evident from the production of the cis-trans isomerization that we have been able to scavenge the chlorine atoms. We must, therefore, by the use of hydrogen sulfide, have introduced another radical into the system. No doubt this radical is the hydrogen atom produced in the primary step by photolysis of hydrogen sulfide.

$$H_2S + h\nu \longrightarrow HS^{\bullet} + H^{\bullet}$$

The increase of the ratio of 2-chloropropene in Table 24 with exposure time is mainly due to a relative decrease in production of the compound in the presence of hydrogen sulfide. This decrease can be explained by the reaction :

$$CH_2=CClCH_3 + H^{\bullet} \longrightarrow CH_3\dot{C}ClCH_3^{*}$$

It should be emphasized once more that at zero time, where this secondary reaction can not take place, the ratio, $R_{CH_2=CHCH_3}/R_{CH_2=CClCH_3}$, is identical to the ratio observed in the absence of hydrogen sulfide.

Secondly, the ratio, $R_{CHCl=CHCH_3}/R_{CH_2=CClCH_3}$, extrapolates to a value of 12.5 much larger than the value of 0.2 observed in the absence of hydrogen sulfide. The values, smaller than unity, for cis- and trans-1-chloropropene in Table 24 show clearly that 1-chloropropenes are produced in much larger quantities in the presence of hydrogen sulfide than in the absence of it. Furthermore, these differences are larger, the shorter

the exposure time. Or, in other words, the longer the exposure time —— this means the more hydrogen sulfide has been reduced by photolysis —— the closer the data approach those obtained in the absence of hydrogen sulfide. This implies the occurrence of some other process.

Hydrogen sulfide starts to absorb appreciably at about 270 nm and the absorption reaches a maximum at about 195 nm(105). Since it has a larger absorption coefficient, relative to 1,2-dichloropropane, hydrogen sulfide absorbs a large fraction of incident light even at 10 % concentration. The results at $\lambda > 220$ nm have so far been explained by the reaction sequence.

$$CH_2ClCHClCH_3 + h\nu \longrightarrow CH_2ClCHClCH_3^{**}$$

$$CH_2ClCHClCH_3^{**} \longrightarrow CH_2=CHCH_3 + Cl_2$$

$$CH_2ClCHClCH_3^{**} \longrightarrow CH_2=CClCH_3 + HCl$$

Table 25. Relative Quantum Yields of the Products in the Photolysis of 1,2 - Dichloropropane in the Presence of H_2S at $\lambda > 220$ nm.

Expt. No.	Time Min.	$CH_2=CHCH_3$	$CH_2=CClCH_3$	$CHCl=CHCH_3$ Cis	$CHCl=CHCH_3$ Trans
1	120	0.22	0.04	0.21	0.53
2	240	0.26	0.04	0.21	0.49
3	360	0.31	0.03	0.20	0.46
4	480	0.30	0.03	0.21	0.45
5	600	0.31	0.03	0.25	0.41
6	720	0.37	0.02	0.23	0.37

$$CH_2ClCHClCH_3^* \longrightarrow CHCl{=}CHCH_3 + HCl$$

As a first approximation one is tempted to assume that in the presence of hydrogen sulfide a large fraction of the light yielding the "two star" excited state is absorbed by the scavenger itself and thus, causes a variation of the product distribution. If this were so, less propene should be produced in the presence of hydrogen sulfide than in the absence. since after all propene is the main reaction product of the "two star" excited state. The results given in Table 24 and Figure 13, clearly show that this is not correct. We suggest, therefore, that hydrogen sulfide may not only decompose into H• and HS• radicals but may also play an important role in the following energy transfer process :

$$H_2S + h\nu \longrightarrow H_2S^*$$

$$H_2S^* + CH_2ClCHClCH_3 \longrightarrow H_2S + CH_2ClCHClCH_3^*$$

$$CH_2ClCHClCH_3^* \longrightarrow CHCl{=}CHCH_3 + HCl$$

This mechanism explains the large increase in 1-chloropropene production in the presence of hydrogen sulfide. Since, with increasing exposure time, the concentration of hydrogen sulfide decreases, this reaction sequence explains also why this observed increase in 1-chloropropene production decreases in importance with increasing exposure times.We should expect that at longer exposure time the concentration of the hydrogen sulfide has been reduced and thus the suggested energy transfer reaction has been also reduced.

(2) Photolysis in the Presence of H_2S at $\lambda > 200$ nm

We also carried out a series of experiments in the presence of hydrogen sulfide at $\lambda > 200$ nm. These data are given in Tables 26 and 27, and are graphically represented in Figure 14. Basically the data can be explained by the mechanism developed for the results in the presence of hydrogen sulfide at $\lambda > 220$ nm. At $\lambda > 200$ nm, chlorine

Table 26. Photolysis of 1,2 - Dichloropropane in the Presence of Hydrogen Suldide at $\lambda > 200$ nm. Products in molecules/ml X 10^{-15}

Expt.	Time	$CH_2=CHCH_3$	$CH_2=CClCH_3$	$CHCl=CHCH_3$	
No.	Min			Cis	Trans
1	5	1.63	0.223	0.652	1.14
2	10	4.19	0.583	0.927	3.89
3	15	5.34	0.731	1.71	4.30
4	20	7.77	0.809	2.29	5.24
5	25	10.3	0.867	2.99	7.08
6	30	11.3	0.896	3.39	8.28
7	35	12.7	0.924	3.75	9.32
8	40	15.0	0.983	4.10	9.54
9	50	18.8	1.12	5.77	11.4
10	60	22.7	1.27	7.37	13.2
11	70	26.2	1.29	7.97	13.4

*The photolysis was carried out at an initial 1,2-dichloropropane pressure of 20 torr in the presence of 2 torr of hydrogen sulfide.

atoms are introduced into the system directly by the primary process (reaction 4) and by the secondary photolysis of chlorine molecules. It is gratifying to observe that the presence of hydrogen sulfide has again suppressed the cis-trans isomerization of 1-chloropropene as is clearly shown by the low value of approximately 0.4 extrapolated for the ratio cis/trans of 1-chloropropene.

Table 27. Product Ratios in the Photolysis of 1,2 - Dichloropropane in the Presence of Hydrogen Sulfide at $\lambda > 200$ nm.

Expt.	Time	Cl_2 Elimination	$CH_2{=}CHCH_3$	$CHCl{=}CHCH_3$	c-$CHCl{=}CHCH_3$
No.	Min.	HCl Elimination	$CH_2{=}CClCH_3$	$CH_2{=}CClCH_3$	t-$CHCl{=}CHCH_3$
1	5	0.81	7.34	8.07	0.57
2	10	0.78	7.17	8.26	0.24
3	15	0.79	7.49	8.43	0.40
4	20	0.93	9.60	9.31	0.44
5	25	0.94	11.8	11.6	0.42
6	30	0.90	12.6	13.0	0.37
7	35	0.91	13.7	14.1	0.40
8	40	1.0	13.4	13.8	0.43
9	50	1.0	16.9	15.9	0.51
10	60	1.1	17.9	16.2	0.56
11	70	1.2	20.3	16.6	0.59

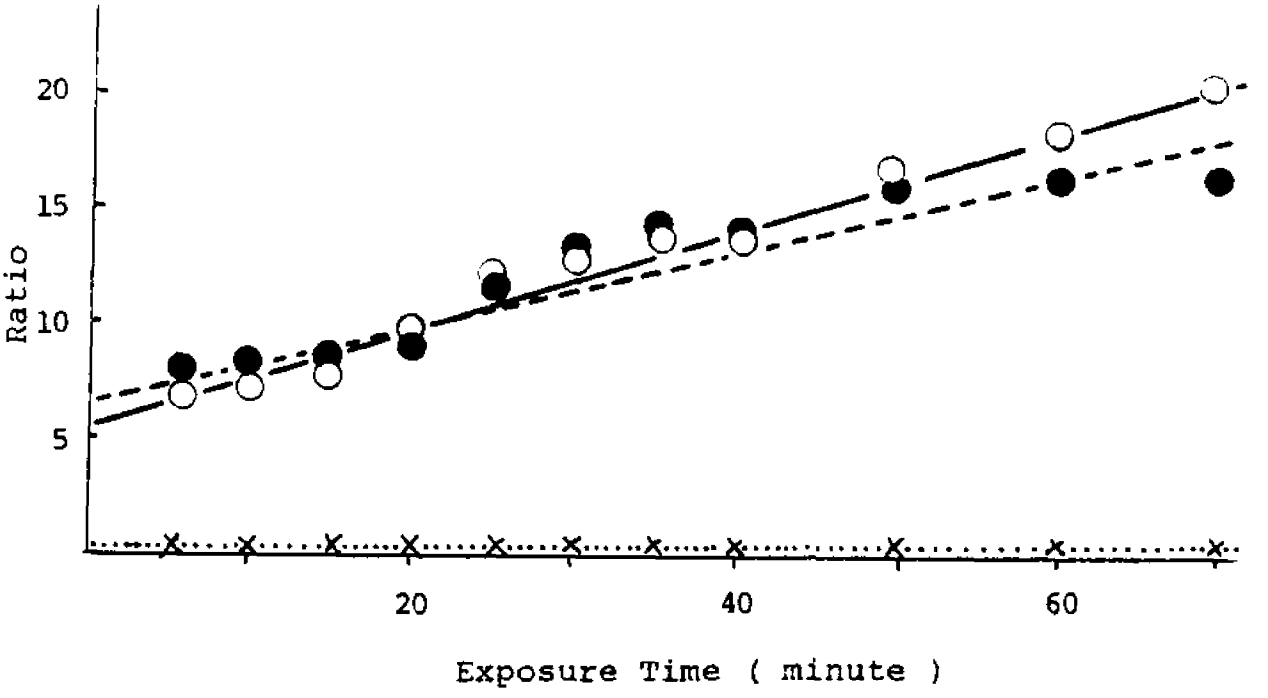


Fig. 14. Plot of product ratios against exposure time in the photolysis of 1,2-dichloropropane in the presence of H_2S at $\lambda > 200$ nm.
——○—— ; CH_2=$CHCH_3$/CH_2=$CClCH_3$, - - ● - - ; $CHCl$=$CHCH_3$/CH_2=$CClCH_3$
·····×····· ; c-$CHCl$=$CHCH_3$/t-$CHCl$=$CHCH_3$

6. Photolysis of 1,2 - Dichloropropane in the Presence of H_2O and SO_2

In the liquid phase, there are several examples where the photolysis of organic halides produced ionic intermediates(106 - 114). Although such intermediates are not likely to occur in the gas phase at the wavelength of this investigation, it seemed interesting to carry out the photolysis in the presence of additives other than water in order to possibly clarify the increased production of 1-chloropropenes in the presence of hydrogen sulfide. Experiments were, therefore, carried out with water and with sulfur dioxide. Water does not absorb, but sulfur dioxide does in the

wavelength region of this study. A comparison of the two results should allow us to decide whether possibly a variation in product distribution was caused due to partial absorption of the light by the additives such as hydrogen sulfide and/or sulfur dioxide. Water and sulfur dioxide also differ in the fact that water can form hydrogen bond while sulfur dioxide can not. Neither water nor sulfur dioxide is detected by the flame ionization detector of the gas chromatograph, thus facilitating the analysis of the products.

(1) Photolysis in the Presence of Water

The data on the photolysis of 1,2-dichloropropane in the presence of water are given in Tables 28 - 31. In addition the relative quantum yields of the reaction products are shown in Tables 32 and 33. It is quite clear that these data do not provide any evidence for cations. As a matter of fact, the relative quantum yields obtained in the presence of water are for all practical purpose identical to those obtained with water both at $\lambda > 220$ nm and at $\lambda > 200$ nm. This shows clearly that water vapor does not exert any effect except that of a third body.

Water seems to be a much more efficient deactivator than sulfur hexafluoride. Water vapor is completely transparent in the wavelength areas studied in this investigation, since it does not start to absorb until at about 180 nm. Thus the decrease in propene production at $\lambda > 220$ nm is not due to a partial light absorption by water vapor but exclusively to its deactivating effect. It is interesting to study this effect in

Table 28. Photolysis of 1,2 - Dichloropropane in the Presence of Water at $\lambda >$ 200 nm. Products in molecules/ml X 10^{-15}

Expt. No.	H_2O Pressure Torr	CH_2=$CHCH_3$	CH_2=$CClCH_3$	$CHCl$=$CHCH_3$ Cis	$CHCl$=$CHCH_3$ Trans
1	0	14.1	2.80	1.87	1.50
2	4	14.9	2.48	2.38	2.00
3	8	14.3	2.50	1.81	1.51
4	12	12.1	2.50	1.71	0.828
5	16	8.93	1.83	1.47	1.25
6	20	7.24	1.26	0.793	0.724

* The photolysis was carried out at an initial pressure 10 torr of 1,2-dichloropropane. The exposure time was 30 minutes.

Table 29. Product Ratios in the Photolysis of 1,2 - Dichloropropane in the Presence of Water at $\lambda >$ 200 nm.

Expt. No.	H_2O Pressure Torr	Cl_2 Elimination / HCl Elimination	CH_2=$CHCH_3$ / CH_2=$CClCH_3$	$CHCl$=$CHCH_3$ / CH_2=$CClCH_3$	c-$CHCl$=$CHCH_3$ / t-$CHCl$=$CHCH_3$
1	0	2.3	5.1	1.2	1.3
2	4	2.2	6.0	1.7	1.2
3	8	2.5	5.7	1.3	1.2
4	12	2.4	4.8	1.0	2.0
5	16	2.0	4.8	1.5	1.2
6	20	2.6	5.7	1.2	1.1

Table 30. Photolysis of 1,2 - Dichloropropane in the Presence of Water at $\lambda > 220$ nm. Products in molecules/ml X 10^{-15}

Expt. No.	H_2O Pressure Torr	$CH_2{=}CHCH_3$	$CH_2{=}CClCH_3$	$CHCl{=}CHCH_3$ Cis	$CHCl{=}CHCH_3$ Trans
1	0	11.2	4.97	2.34	1.42
2	4	10.0	4.26	3.42	3.43
3	8	8.20	4.42	3.04	2.38
4	12	6.97	3.22	2.60	3.09
5	16	5.61	3.41	2.10	1.23
6	20	5.10	2.80	1.84	1.61

* The photolysis was carried out an initial pressure 10 torr of 1,2-dichloropropane. The exposure time was 10 hours.

Table 31. Product Ratios in the Photolysis of 1,2 - Dichloropropane in the Presence of Water at $\lambda > 220$ nm.

Expt. No.	H_2O Pressure Torr	Cl_2 Elimination / HCl Elimination	$CH_2{=}CHCH_3$ / $CH_2{=}CClCH_3$	$CHCl{=}CHCH_3$ / $CH_2{=}CClCH_3$	c-$CHCl{=}CHCH_3$ / t-$CHCl{=}CHCH_3$
1	0	1.2	2.3	0.75	1.7
2	4	0.90	2.4	1.6	1.0
3	8	0.83	1.9	1.2	1.3
4	12	0.78	2.2	1.8	0.84
5	16	0.83	1.7	0.97	1.7
6	20	0.81	1.8	1.2	1.1

Table 32. Relative Quantum Yields of the Products as a Function of Water Pressure in the Photolysis of 1,2-Dichloropropane at $\lambda > 200$nm.

Expt. No.	H_2O Pressure Torr	$CH_2=CHCH_3$	$CH_2=CClCH_3$	$CHCl=CHCH_3$ Cis	$CHCl=CHCH_3$ Trans
1	0	0.70	0.14	0.09	0.07
2	4	0.69	0.11	0.11	0.09
3	8	0.71	0.12	0.09	0.08
4	12	0.70	0.15	0.10	0.05
5	16	0.66	0.14	0.11	0.09
6	20	0.72	0.13	0.08	0.07

Table 33. Relative Quantum Yields of the Products as a Function of Water Pressure in the Photolysis of 1,2-Dichloropropane at $\lambda > 220$nm.

Expt. No.	H_2O Pressure Torr	$CH_2=CHCH_3$	$CH_2=CClCH_3$	$CHCl=CHCH_3$ Cis	$CHCl=CHCH_3$ Trans
1	0	0.56	0.25	0.12	0.07
2	4	0.48	0.20	0.16	0.16
3	8	0.45	0.25	0.17	0.13
4	12	0.44	0.20	0.17	0.19
5	16	0.45	0.28	0.27	0.10
6	20	0.45	0.25	0.16	0.14

somewhat greater detail. According to the proposed mechanism, at $\lambda >$ 220 nm the processes involving the production of propene are

$$CH_2ClCHClCH_3 + h\nu \longrightarrow CH_2ClCHClCH_3^{**} \quad (2)$$

$$CH_2ClCHClCH_3^{**} \longrightarrow CH_2{=}CHCH_3 + Cl_2 \quad (5)$$

$$CH_2ClCHClCH_3^{**} \longrightarrow CH_2{=}CClCH_3 + HCl \quad (6)$$

$$CH_2ClCHClCH_3^{**} + M \longrightarrow CH_2ClCHClCH_3^{*} + M^{*} \quad (7)$$

From these the following equation may be derived.

$$R_{CH_2=CHCH_3} = k_5[CH_2ClCHClCH_3^{**}]$$

$$d[CH_2ClCHClCH_3^{**}]/dt = \alpha I_{abs.}$$

$$-d[CH_2ClCHClCH_3^{**}]/dt = [CH_2ClCHClCH_3^{**}]\{k_5 + k_6 + \hat{k_7}[CH_2ClCHClCH_3] + \tilde{k_7}[H_2O]\}$$

Assuming steady state consideration, we obtain

$$[CH_2ClCHClCH_3^{**}] = \frac{\alpha I_{abs.}}{k_5 + k_6 + \hat{k_7}[CH_2ClCHClCH_3] + \tilde{k_7}[H_2O]}$$

It has been assumed that deactivation may occur by water ($\tilde{k_7}$) and also by 1,2-dichloropropane (self-quenching, $\hat{k_7}$).

$$\frac{1}{R_{CH_2=CHCH_3}} = \frac{k_5 + k_6 + \hat{k_7}[CH_2ClCHClCH_3] + \tilde{k_7}[H_2O]}{k_5 \alpha I_{abs.}}$$

In the above equation $I_{abs.}$ is constant, since all experiments are carried out with the same light intensity and the same 1,2-dichloro-

propane pressure, thus

$$k_5 + k_6 + k_7\hat{}[CH_2ClCHClCH_3] = K_I$$

We obtained then :

$$\frac{1}{R_{CH_2=CHCH_3}} = \frac{K_I}{k_5 \alpha I_{abs.}} + \frac{k_7\tilde{}}{k_5 \alpha I_{abs.}} [H_2O]$$

In Figure 15 we have plotted $1 / R_{CH_2=CHCH_3}$ versus water pressure

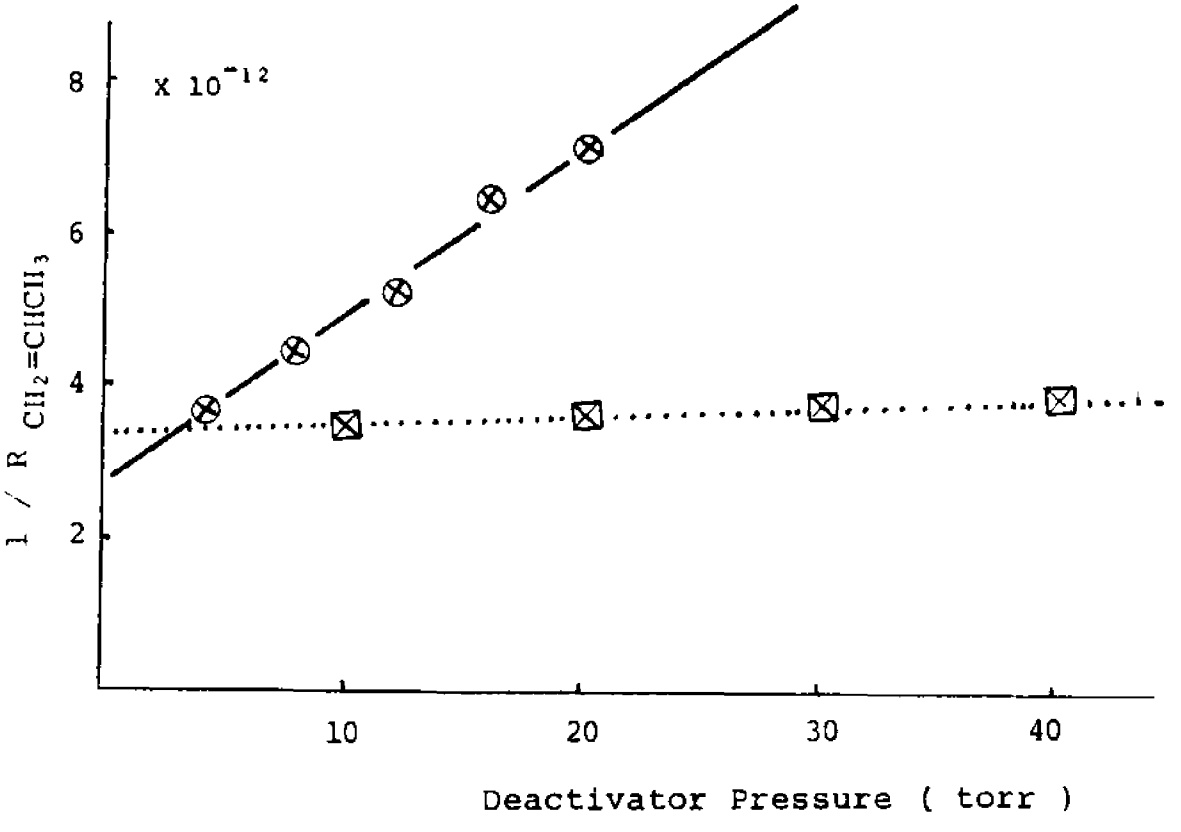


Fig. 15. Plot of $1 / R_{CH_2=CHCH_3}$ against deactivator pressure.

⊗ ; in the presence of H_2O, ⊠ ; in the presence of SF_6

and also $1 / R_{CH_2=CHCH_3}$ versus sulfur hexafluoride pressure. There is excellent agreement between the data and the equation. The data, furthermore indicate that water is a much more efficient deactivator for the excited state yielding propene than sulfur hexafluoride.

(2) Photolysis in the Presence of Sulfur Dioxide

Finally, some experiments were carried out in the presence of sulfur dioxide. Data obtained at $\lambda > 200$ nm and at $\lambda > 220$ nm are given in Tables 34 - 37. Even though sulfur dioxide absorbs ultraviolet light in the investigated region(116), the relative quantum yields both in the presence of sulfur dioxide and in the absence of any gas are almost identical. This proves sulfur dioxide is a poor deactivator relative to sulfur hexafluoride and particular so relative to water. There is no visible effect which might be attributed to sulfur dioxide as a free radical scavenger. This is perhaps not surprising since the SO_2Cl radical, possibly produced by the reaction of chlorine atom with sulfur dioxide, no doubt will readily decompose again to sulfur dioxide and chlorine atom.

The data at $\lambda > 220$ nm show a similar lack of any profound effect, caused by the presence of sulfur dioxide except for one important observation. The ratio, cis/trans 1-chloropropene, plotted in Figure 16, clearly increases with decreasing exposure time. This is the complete opposite of the behavior of the ratio observed in the all other experiments. In the absence of sulfur dioxide, initially the trans-1-chloropropene is

Table 34. Photolysis of 1,2 - Dichloropropane in the Presence of Sulfur Dioxide at $\lambda > 200$ nm. Products in molecules/ml X 10^{-15}

Expt. No.	Time Min.	$CH_2=CHCH_3$	$CH_2=CClCH_3$	$CHCl=CHCH_3$ Cis	$CHCl=CHCH_3$ Trans
1	5.0	5.77	1.85	0.602	0.324
2	7.5	8.85	2.32	1.22	0.758
3	10.0	11.5	2.72	1.73	1.06
4	12.5	13.9	2.73	1.91	1.27
5	15.0	15.2	2.76	2.10	1.65
6	20.0	21.1	3.51	2.63	2.46
7	30.0	31.7	4.58	4.52	3.79
8	40.0	40.6	4.84	5.73	5.72
9	60.0	44.7	4.26	7.41	5.82

Table 35. Photolysis of 1,2 - Dichloropropane in the Presence of Sulfur Dioxide at $\lambda > 220$ nm. Products in molecules/ml X 10^{-15}

Expt. No.	Time. Min.	$CH_2=CHCH_3$	$CH_2=CClCH_3$	$CHCl=CHCH_3$ Cis	$CHCl=CHCH_3$ Trans
1	120	3.22	2.32	1.07	0.262
2	240	6.35	4.02	2.47	1.20
3	360	10.2	5.42	4.16	3.15
4	480	12.8	6.79	5.81	5.22
4	600	15.9	7.74	7.29	6.03
6	720	19.4	8.41	7.92	6.35

* All the experiments were carried out at an initial pressure 20 torr of 1,2-dichloropropane in the presence of 2 torr of sulfur dioxide.

Table 36. Product Ratios in the Photolysis of 1,2 - Dichloropropane in the Presence of Sulfur Dioxide at $\lambda > 200$ nm.

Expt.	Time	Cl_2 Elimination	$CH_2=CHCH_3$	$CHCl=CHCH_3$	c-$CHCl=CHCH_3$
No.	Min.	HCl Elimination	$CH_2=CClCH_3$	$CH_2=CClCH_3$	t-$CHCl=CHCH_3$
1	5.0	2.1	3.1	0.49	1.9
2	7.5	2.1	3.8	0.85	1.6
3	10.0	2.1	4.2	1.0	1.6
4	12.5	2.4	5.1	1.2	1.5
5	15.0	2.3	5.5	1.4	1.3
6	20.0	2.5	6.0	1.5	1.1
7	30.0	2.5	6.9	1.8	1.2
8	40.0	2.5	8.4	2.4	1.0
9	60.0	2.6	11	3.1	1.3

Table 37. Product Ratios in the Photolysis of 1,2 - Dichloropropane in the Presence of Sulfur Dioxide at $\lambda > 220$ nm.

Expt.	Time	Cl_2 Elimination	$CH_2=CHCH_3$	$CHCl=CHCH_3$	c-$CHCl=CHCH_3$
No.	Min.	HCl Elimination	$CH_2=CClCH_3$	$CH_2=CClCH_3$	t-$CHCl=CHCH_3$
1	120	0.88	1.4	0.57	4.1
2	240	0.82	1.6	0.91	2.1
3	360	0.80	1.9	1.4	1.3
4	480	0.71	1.9	1.7	1.1
5	600	0.75	2.1	1.7	1.2
6	720	0.86	2.3	1.7	1.3

Table 38. Relative Quantum Yields of the Products in the Photolysis of 1,2-Dichloropropane in the Presence of Sulfur Dioxide at λ>200 nm.

Expt.	Time	CH_2=$CHCH_3$	CH_2=$CClCH_3$	$CHCl$=$CHCH_3$	
No.	Min.			Cis	Trans
1	5.0	0.67	0.22	0.07	0.04
2	7.5	0.67	0.18	0.09	0.06
3	10.0	0.68	0.16	0.10	0.06
4	12.5	0.70	0.14	0.10	0.06
5	15.0	0.70	0.13	0.10	0.07
6	20.0	0.71	0.12	0.09	0.08
7	30.0	0.71	0.10	0.10	0.09
8	40.0	0.71	0.09	0.10	0.10
9	60.0	0.72	0.07	0.12	0.09

Table 39. Relative Quantum Yields of the Products in the Photolysis of 1,2-Dichloropropane in the Presence of Sulfur Dioxide at λ>220 nm.

Expt.	Time	CH_2=$CHCH_3$	CH_2=$CClCH_3$	$CHCl$=$CHCH_3$	
No.	Min.			Cis	Trans
1	120	0.47	0.34	0.15	0.04
2	240	0.45	0.29	0.18	0.08
3	360	0.44	0.24	0.18	0.14
4	480	0.41	0.22	0.19	0.18
5	600	0.43	0.21	0.20	0.16
6	720	0.46	0.20	0.19	0.15

formed, after which there is a chlorine atom induced isomerization process, and finally with increased exposure time, the equilibrium ratio 1.5 is reached. In the presence of sulfur dioxide the isomer produced initially or at least favored to a large extent is the cis isomer. In the discussion we will compare the role of sulfur dioxide in this cis/ trans ratio to similar cases reported in the literature

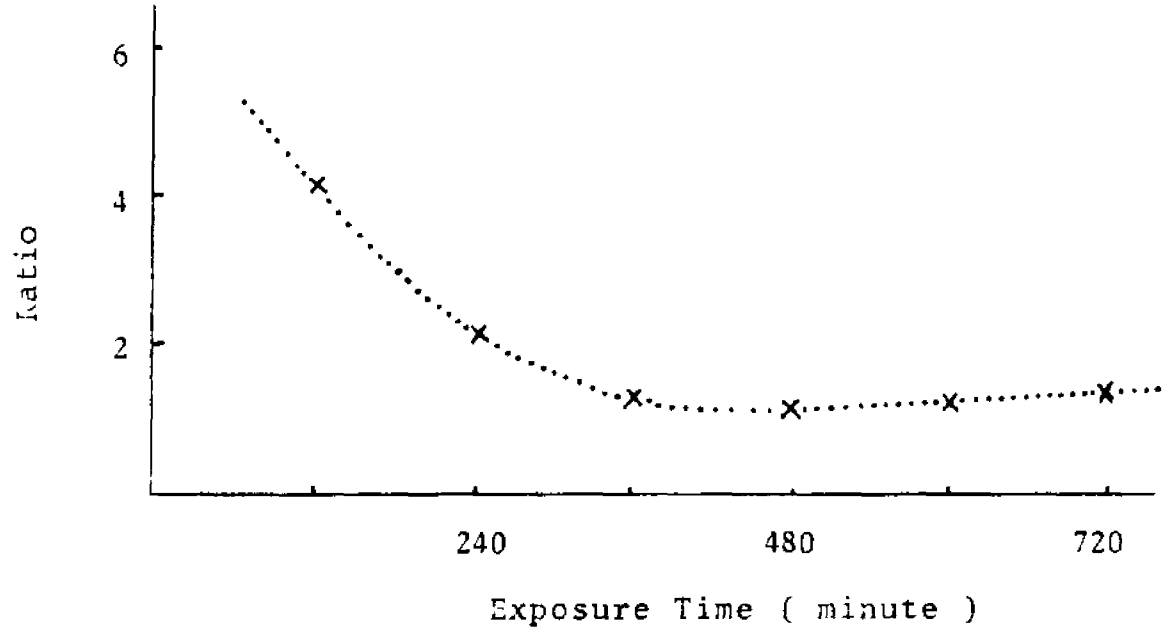


Fig. 16. Plot of cis/trans 1-chloropropene against reaction time in the photolysis of 1,2-dichloropropane in the presence of sulfur dioxide at $\lambda > 220$ nm.

7. Photolysis of 2,2 - Dichloropropane

Some experiments were carried out on the photolysis of 2,2-dichloropropane. It should, after all, be interesting to observe the difference

in the primary process between 1,2- and 2,2-dichloropropane. Only two reaction products were observed : 2-chloropropene and 2-chloropropane. The data obtained at $\lambda > 200$ nm are given in Table 40 for experiments carried out in the absence of hydrogen sulfide and in Table 41 for experiments in the presence of hydrogen sulfide. Similarly Tables 42 and 43 show the data obtained at $\lambda > 220$ nm.

There seems no doubt that the observed products must be explained by the following two primary steps.

Table 40. Photolysis of 2,2-Dichloropropane at $\lambda > 200$ nm.

$P_{CH_3CCl_2CH_3}$ = 20 torr, Products in molecules/ml X 19^{-15}

Expt. No.	Time Min.	$CH_2{=}CClCH_3$	$CH_3CHClCH_3$	$\frac{CH_2CHClCH_3}{CH_2{=}CClCH_3}$
1	2.5	3.40	1.50	0.44
2	5.0	5.01	3.43	0.68
3	7.5	6.91	5.14	0.74
4	10.0	7.61	7.00	0.92
5	12.5	8.19	8.61	1.0
6	15.0	9.79	10.5	1.1
7	20.0	10.3	13.7	1.3
8	30.0	11.7	18.1	1.5
9	40.0	11.3	20.4	1.8
10	50.0	10.8	21.4	2.0
11	60.0	10.6	31.1	2.9

$$CH_3CCl_2CH_3^{*} \longrightarrow CH_2{=}CClCH_3 + HCl$$
$$\longrightarrow CH_3\dot{C}ClCH_3 + \cdot Cl$$

Where the $CH_3\dot{C}ClCH_3$ radical in the absence of hydrogen sulfide forms $CH_3CHClCH_3$ to some extent by reaction with hydrogen chloride. Hydrogen chloride is a good hydrogen atom donor and has been used frequently as a free radical scavenger(62, 117). The molecular elimination of hydrogen chloride is, of course, completely analogous that from 1,2-dichloropropane, producing 2-chloropropene and cis- and trans-1-chloropropene.

Table 41. Photolysis of 2,2-Dichloropropane in the Presence of Hydrogen Sulfide at $\lambda > 200$ nm. Products in molecules/ml X 10^{-15}

Expt No.	Time Min.	$CH_2{=}CClCH_3$	$CH_3CHClCH_3$	$\frac{CH_3CHClCH_3}{CH_2{=}CClCH_3}$
1	2.5	0.806	4.75	5.9
2	5.0	1.37	8.82	6.4
3	7.5	2.01	12.5	6.2
4	10.0	2.39	15.7	6.6
5	12.5	3.04	20.2	6.7
6	15.0	3.56	24.5	6.9
7	20.0	4.58	31.4	6.9
8	25.0	4.61	36.8	8.0
9	30.0	4.89	39.6	8.1

* The photolysis was carried out at an initial pressure 20 torr of 2,2-dichloropropane and at 2 torr of hydrogen sulfide.

Table 42. Photolysis of 2,2 - Dichloropropane at $\lambda > 220$ nm.

$P_{CH_3CCl_2CH_3}$ = 20 torr, Products in molecules/ml X 10^{-15}

Expt. No.	Time Min.	$CH_2=CClCH_3$	$CH_3CHClCH_3$	$\frac{CH_3CHClCH_3}{CH_2=CClCH_3}$
1	120	5.12	1.02	0.20
2	240	9.38	3.26	0.35
3	360	12.1	6.13	0.51
4	480	12.0	7.92	0.66
5	600	12.2	10.0	0.83
6	720	12.4	13.2	1.1

Table 43. Photolysis of 2,2 -Dichloropropane in the Presence of Hydrogen Sulfide at $\lambda > 220$ nm. Products in molecules/ml X 10^{-15}

Expt. No.	Time Min.	$CH_2=CClCH_3$	$CH_3CHClCH_3$	$\frac{CH_3CHClCH_3}{CH_2=CClCH_3}$
1	120	1.73	14.0	8.1
2	240	1.89	25.7	13.6
3	360	1.64	37.2	22.6
4	480	1.92	49.3	25.7
5	600	1.85	62.8	34.0
6	720	1.94	72.0	37.1

* The photolysis was carried out at an initial pressure 20 torr of 2,2-dichloropropane and at 2 torr of hydrogen sulfide.

There is no evidence for C - Cl rupture in the photolysis of 1,2-dichloropropane. The absence of propene, here in the case of 2,2-dichloropropane, clearly indicates that molecular elimination of chlorine did not take place.

In Figures 17 and 18 we plotted the ratio $R_{CH_3CHClCH_3}/R_{CH_2=CClCH_3}$ for the data at $\lambda > 200$ nm and $\lambda > 220$ nm, respectively, against exposure time. Thus it is possible to extrapolate the data to zero exposure time as indeed was done in the photolysis of 1,2-dichloropropane. Data in the presence of hydrogen sulfide yield $R_{CH_3CHClCH_3}/R_{CH_2=CClCH_3}$ = 2 at $\lambda > 220$ nm and 5.8 at $\lambda > 200$ nm. The intercepts in the absence of hydrogen sulfide are considerably smaller and more difficult to determine. As approximate values the same ratio we suggest 0.04 at $\lambda > 220$ nm and 0.15 at $\lambda > 200$ nm. In the case it is clear that the ratio increases, both in the presence and in the absence of hydrogen sulfide, at shorter wavelengths.

We are, thus, dealing with two different excited states of which the lower energy state decomposes by hydrogen chloride elimination and the higher energy state by C - Cl rupture. The primary processes in the photolysis of 2,2-dichloropropane can now be given as :

$$CH_3CCl_2CH_3 + h\nu \longrightarrow CH_3CCl_2CH_3^{**}$$

$$CH_3CCl_2CH_3^{**} \longrightarrow CH_3CCl_2CH_3^{*}$$

$$CH_3CCl_2CH_3^{*} \longrightarrow CH_2=CClCH_3 + HCl$$

$$CH_3CCl_2CH_3^{**} \longrightarrow CH_3\dot{C}ClCH_3 + {}^{\bullet}Cl$$

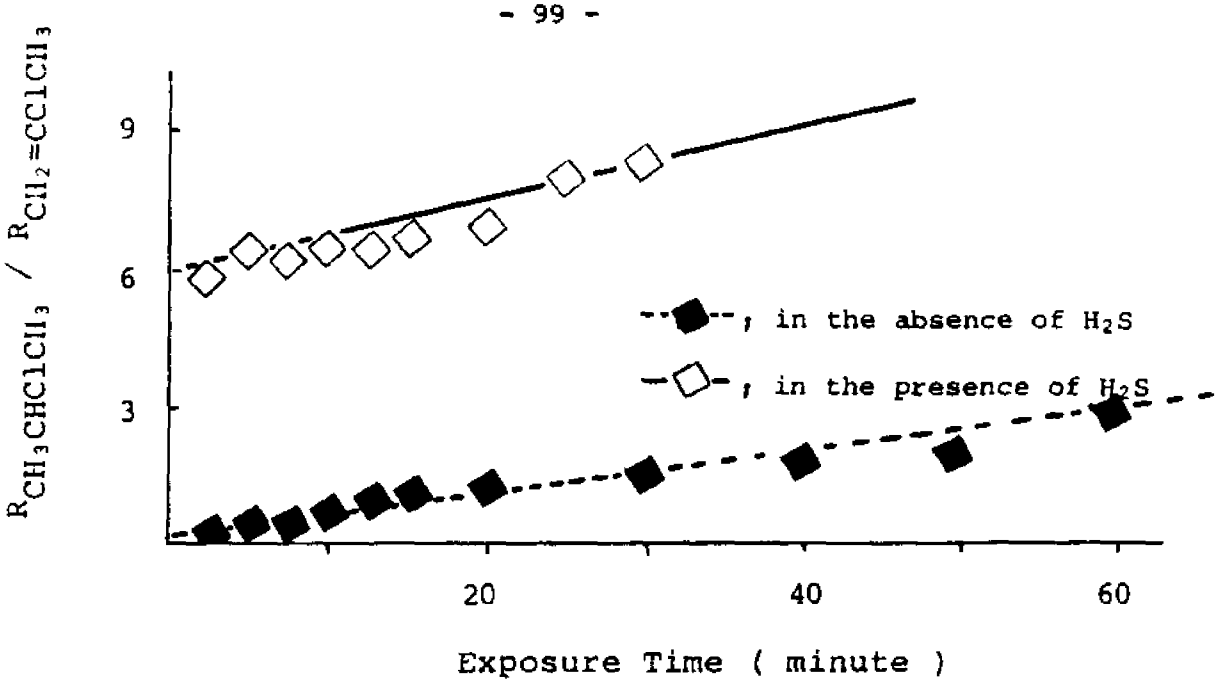


Fig. 17. Plot of the product ratio against exposure time in the photolysis of 2,2-dichloropropane at $\lambda > 200$ nm.

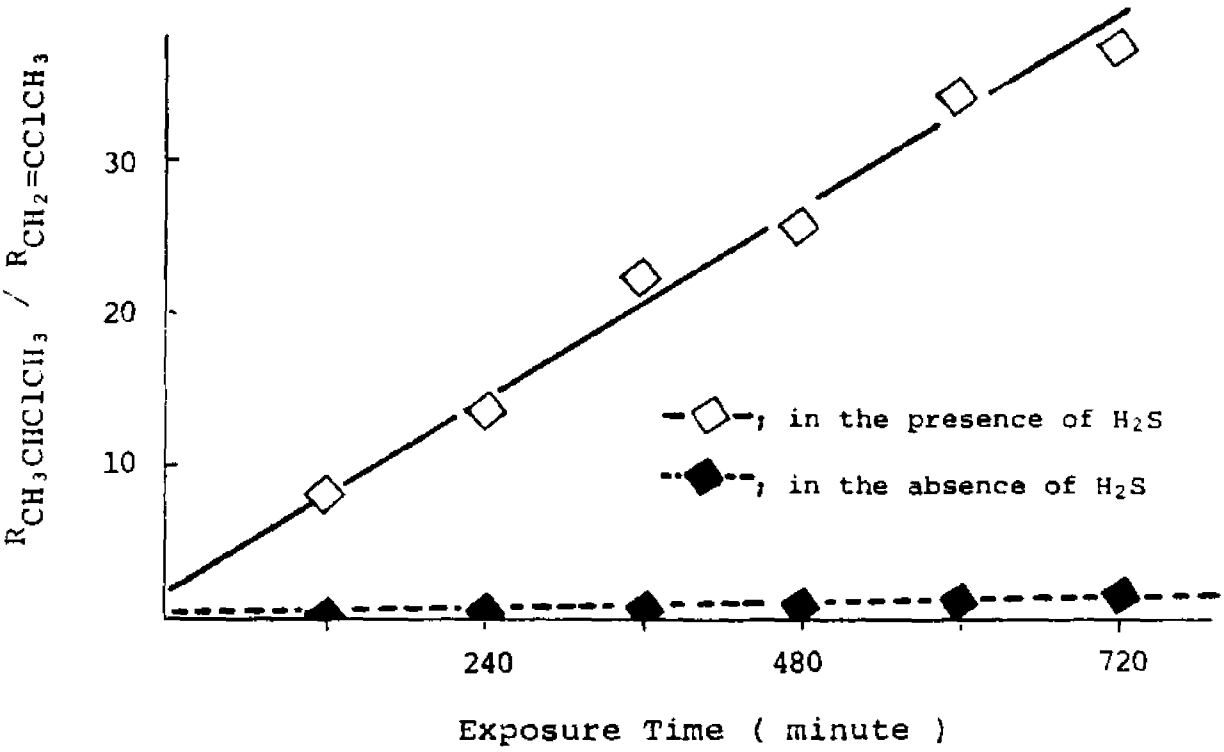


Fig. 18. Plot of the product ratio against exposure time in the photolysis of 2,2-dichloropropane at $\lambda > 220$ nm.

Here, as in case of 2,2-dichloropropane, the hydrogen chloride elimination occurs from the lowest lying excited state.

The data in Tables 40 to 44 clearly indicate that, at least initially, 2-chloropropane increases linearly with exposure time but 2-chloropropene does not. This is, no doubt, due to secondary reactions of chlorine atom and/or hydrogen atom (in the presence of hydrogen sulfide) with 2-chloropropene. These results confirm our earier observation that 2-chloropropene is extremely prone to free radical attack.

Finally we like to add that a few experiments were carried out on the photolysis of 1,3-dichloropropane. The results estabilished, clearly, that, at $\lambda > 200$ nm, hydrogen chloride elimination does occur, but molecular chlorine elimination does not.

IV. DISCUSSION

In order to discuss in detail the data obtained in this investigation, it is, perhaps, best to state once more the reaction mechanism which we propose to explain the observed results.

$CH_2ClCHClCH_3 + h\nu \longrightarrow CH_2ClCHClCH_3^{***}$ (1)

$\longrightarrow CH_2ClCHClCH_3^{**}$ (2)

$\longrightarrow CH_2ClCHClCH_3^{*}$ (3)

$CH_2ClCHClCH_3^{***} \longrightarrow CH_2{=}CHCH_3 + 2\ Cl\cdot$ (4)

$CH_2ClCHClCH_3^{**} \longrightarrow CH_2{=}CHCH_3 + Cl_2$ (5)

$\longrightarrow CH_2{=}CClCH_3 + HCl$ (6)

$CH_2ClCHClCH_3^{**} + M \longrightarrow CH_2ClCHClCH_3^{*} + M^*$ (7)

$CH_2ClCHClCH_3^{*} \longrightarrow CHCl{=}CHCH_3 + HCl$ (8)

$\cdot Cl + CH_2{=}CClCH_3 \longrightarrow CH_2Cl\dot{C}ClCH_3^{*}$ (9)

$CH_2Cl\dot{C}ClCH_3^{*} \longrightarrow CH_2{=}CClCH_3 + \cdot Cl$ (10)

$\longrightarrow CHCl{=}CHCH_3 + \cdot Cl$ (11)

$CH_2ClCClCH_3^{*} + M \longrightarrow CH_2Cl\dot{C}ClCH_3 + M^*$ (12)

$\cdot Cl + CHCl{=}CHCH_3 \longrightarrow \cdot CHClCHClCH_3^{*}$ (13)

$\cdot CHClCHClCH_3^{*} \longrightarrow$ cis-$CHCl{=}CHCH_3 + \cdot Cl$ (14)

$\longrightarrow$ trans-$CHCl{=}CHCH_3 + \cdot Cl$ (15)

$\cdot CHClCHClCH_3^{*} + M \longrightarrow \cdot CHClCHClCH_3 + M^*$ (16)

To our knowledge there are no previous pubilcations, dealing with the photolysis of 1,2- dichloropropane or indeed any other dichloropropane.As

pointed out in the introduction, a considerable amount of work has, however, been carried out on the photolysis of chlorinated ethanes and ethylenes and, we believe, some valid comparisons may be drawn.

1. Molecular Detachment.

In order to explain the formation of the reaction products the existence of three excited states is proposed. The two lower excited states decompose by molecular elimination processes producing propylenes, hydrogen chloride and chlorine molecules. Hydrogen chloride elimination was first reported by Wijnen(14) but has, since then, been observed in many chlorine-containing compounds. For example, the vibrational energy content of hydrogen chloride formed by molecular elimination of dichloroethylenes has been discussed by Berry and Pimentel(118) and again by Berry(119). Extensive studies on hydrogen chloride eliminations from vibrationally excited chloroethanes have been carried out by Setser and coworkers(71, 120 - 121).

Our data do not allow us to distinguish between a 1,1- or 1,2-elimination process. Although both types of hydrogen chloride elimination have been observed in the past, the 1,2-process seems to occur preferentially(57) and sometimes, even exclusively(63). We are assuming that in the photolysis of 1,2-dichloropropane the elimination processes given by reaction 6 and 8 occur predominantly, if not exclusively, via 1,2-elimination of hydrogen chloride.

$$CH_2ClCHClCH_3^{**} \longrightarrow CH_2{=}CClCH_3 + HCl \qquad (6)$$

$$CH_2ClCHClCH_3^{*} \longrightarrow CHCl{=}CHCH_3 + HCl \qquad (8)$$

It is interesting to note that the formation of 3-chloropropene was not observed even though the analytical technique was such that it could be detected, had it been formed. Sandorfy(38) suggests that the elimination occurs from an excited Rydberg state, where the chlorine atom with the help of the large Rydberg orbital will pull out a hydrogen atom to form hydrogen chloride. If so, the chlorine atom seems to be extremely regiospecific, abstracting hydrogen atoms from chloromethyl, and not from the unsubstituted methyl group in the 1,2-dichloropropane molecule. Although this step is energetically favored(141), the total one-sidedness is somewhat surprising.

Our data furthermore suggest that 1-chloropropene and 2-chloropropene originate from two different excited states. If we apply Sandorfy's theory to our system, those excited states might be the 4s and 4p Rydberg state. Accepting in this instance that the primary initiation is the excitation or weakening of the C — Cl bond, it may even be understood that reaction 8 where a secondary C — Cl bond is to be broken may occur from a lower excited state, since it is energetically favored over reaction 6. where a primary C — Cl bond is involved

In general the primary process in the photolysis of 1,2-dichloropropane is very much similar to that reported for the cis- and trans-1-dichloroethylenes by Ausubel and Wijnen(58, 59). They have shown the

existance of two excited states for the trans compound and obtained the following reaction for lower excited state.

$$trans\text{-}CHCl{=}CHCl^{*} \longrightarrow CH{\equiv}CH + Cl_2$$
$$\longrightarrow CH{\equiv}CCl + HCl$$
$$\longrightarrow {\cdot}C_2H_2Cl + {\cdot}Cl$$

with rate constants in the proportions 8 : 3.8 : 1 in the order given above. For the higher excited state they reported :

$$trans\text{-}CHCl{=}CHCl^{**} \longrightarrow {\cdot}C_2H_2Cl + {\cdot}Cl$$

Similarly the lower excited state of the cis compound gave :

$$cis\text{-}CHCl{=}CHCl^{*} \longrightarrow CH{\equiv}CH + Cl_2$$
$$\longrightarrow CH{\equiv}CCl + HCl$$
$$\longrightarrow {\cdot}C_2H_2Cl + {\cdot}Cl$$

with ratios 3.1 : 1 :0.28.

The higher excited state of cis compound produced :

$$cis\text{-}CHCl{=}CHCl^{**} \longrightarrow CH{\equiv}CH + 2\ {\cdot}Cl$$
$$\longrightarrow {\cdot}C_2H_2Cl^{*} + {\cdot}Cl$$

Where $\dot{C}_2H_2Cl^{*}$ is a vibrationally excited radical.

These data were discussed extensively by Sandorfy(122) who stated "It is rather tempting to argue that the higher excited state which yields chlorine atom is the V (n^{*}) valence shell state and the lower

excited state which yields mainly chlorine molecule and hydrogen chloride is the 4s Rydberg state." It is clear that the two excited states reported for cis- and trans-1,2-dichloroethylene correspond to the "two" and "three star" excited state reported here. The comparison can be driven even further if it is realized that Ausubel and Wijnen mentioned the possibility of an excited state in the case of cis-1,2-dichloroethylene of even lower energy (comparable to the "one star" excited state here) which produced only acetylene and chlorine molecules. Since the 4s and 4p Rydberg states are relatively close together(122), it may be that in the case of cis-1,2-dichloroethylene and 1,2-dichloropropane the two lower excited states are 4s and 4p states while the higher excited state producing C — Cl rupture is a valence shell state.

2. Cis - Trans Isomerization

Returning to step 8 which produces cis- and trans-1-chloropropene by elimination of hydrogen chloride, it is interesting to take a closer look at the initial cis/trans ratio. The data of the photolysis in the absence of a scavenger in the low wavelength region(λ > 200 nm) clearly indicate that the ratio, cis/trans extrapolates at zero exposure time to a value considerably smaller than unity (see Figure 8). This result is also confirmed by experiments in the presence of hydrogen sulfide as a free radical scavenger. Both sets of data with hydrogen sulfide at λ > 220 nm and at λ > 200 nm show that, initially, the trans compound is formed in

larger quantities than the cis compound. Data obtained with hydrogen sulfide (see Figure 12) at $\lambda >$ 220 nm allow an extrapolation to $R_{cis}/R_{trans} \simeq 0.33$ at zero exposure time, a Figure quite consistent with the data in the absence of a free radical scavenger. This implies that cis-trans isomerizations do not proceed rapidly compared to the photoelimination process as indeed, observed before by Berry(119). This exclusive or preferential production of trans isomer was explained earlier by consideration of the conformational isomers. when the hydrogen chloride elimination takes place via a four-centered transition state, syn elimination which leads to cis isomer experiences a steric congestion between the chlorine atom and the methyl group in the 1,2-dichloropropane molecule, thus favoring production of the trans isomer.

With increase in exposure time, the ratio, cis/trans increases at $\lambda >$ 200 nm to a constant value of 1.5. This value represents the thermodynamic equilibrium for the cis-trans isomerization and agrees with the value reported by Shevt-Sova and Andreevskii(123). This equilibrium is reached by a chlorine atom free radical induced isomerization represented by reactions 13 to 16 :

$$\cdot Cl + CHCl{=}CHCH_3 \longrightarrow \cdot CHClCHClCH_3^* \qquad (13)$$

$$\cdot CHClCHClCH_3^* \longrightarrow cis\text{-}CHCl{=}CHCH_3 + \cdot Cl \qquad (14)$$

$$\cdot CHClCHClCH_3^* \longrightarrow trans\text{-}CHCl{=}CHCH_3 + \cdot Cl \qquad (15)$$

$$\cdot CHClCHClCH_3^* + M \longrightarrow \cdot CHClCHClCH_3 + M^* \qquad (16)$$

The production of vibrationally excited radicals by addition of a radical

to an olefin is well established. Numerous examples are reported in the literature such as the hydrogen atom addition to C_2H_4, C_2H_3Cl, C_2H_3F (124 -126) and a chlorine atom to C_2H_4 and substituted ethylenes in general (127).

The mechanism of cis-trans isomerization, given above, is completely analogous to the chlorine atom induced isomerization of cis- and trans-1,2-dichloroethylene reported by Wijnen (14) and by Dainton, et al. (95) and extensively discussed by Ausubel and Wijnen (96). It is interesting to report that the equilibrium value for R_{cis}/R_{trans} in the case of dichloroethylene reported in the literature varies from about 2.0 to 1.6 (95, 96, 128, 129). These data are in good agreement with the observed value of about 1.5 for cis/trans of 1-chloropropene, if we consider 1-chloropropene as a substituted dichloroethylene where a chlorine atom has been replaced by a methyl group. The equilibrium value of 1.5 for cis/trans is also shown by the data at $\lambda > 340$ nm (see Figure 4). Due to the long exposure time the equilibrium already reached within the first three hours of exposure. In this case the chlorine atom, initiating the isomerization, must have been produced by secondary photolysis of chlorine molecules produced by step 5 of the primary process. This is confirmed by experiments with hydrogen sulfide. In the presence of hydrogen sulfide the equilibrium was not reached due to the fact that the chlorine atoms to be reponsible for the isomerization were intercepted by the hydrogen sulfide.

In reaction 13, we have not expressed an opinion whether the chlorine atom adds on to the primary or to the secondary carbon of the

1-chloropropene molecule. Free radical addition to propylene occurs preferentially to the end carbon(90 %) rather than to the middle carbon (10 %)(130, 131). This ratio is, however, change for substituted propylenes as is shown for example, by $CHF=CHCF_3$ where free radical addition to the CHF group occurs three times as fast as addition to the middle carbon(132). There are also differences in regioselectivity depending on the electrophilic character of the free radical. For example, in addition to $CHF=CF_2$, the electrophilic $\cdot CCl_3$ radical attacked the CHF carbon, while the essentially nonpolar $\cdot CH_3$ radical preferred the CF_2 carbon(133). Steric influences also play an important role. A bulky radical shows a greater preference than a smaller radical(134) for a less hindered side. It was observed that the relative reactivity of the radical $\cdot R'$ in addition reaction with olefins leading to copolymerization systems, depends on the nature of R as follows : -COR > CN > Cl > COOR > OR > CH_3 > H

$$\cdot R' + CH_2=CHR \longrightarrow R'-CH_2-\dot{C}HR$$

This ratio again indicates that addition reactions occur much faster with chlorine substituted olefins than with nonsubstituted olefins. It also explains why propene is not involved in free radical addition reaction in our system. For our mechanism it is actually irrelevant where the chlorine atom adds the chloropropene molecule. The important factor is the replacement of the double bond to single bond, thus allowing free rotation, and production of either the cis or the trans compound upon

decomposition.

The correctness of the cis-trans isomerization is also emphasized by the addition of sulfur hexafluoride. Increased pressure of sulfur hexafluoride causes an increased deactivation of the vibrationally excited $\dot{C}HClCHClCH_3^*$ radical preventing it from decomposing and thus stopping the isomerization. As can be seen in Table 15, the ratio cis/trans decreases with increasing sulfur hexafluoride pressure.

Perhaps unexpected was the relatively high value $R_{cis} / R_{trans} = 4$ obtained in the presence of sulfur dioxide (see Figure 16). There are, however, examples in the literature where rather high cis/trans ratios are reported. Hammond, Turro and Leermakers(135) observed cis / trans ratio of 4.0 to 4.1 and 4.5 in the photosensitized isomerization of trans-1,2-dichloroethylene using benzophenone and benzil, respectively. as sensitizers.

3. Regioisomerization

As we have seen, cis- and trans-1-chloropropene are produced in the primary process from the lowest excited state of 1,2-dichloropropane. A state, somewhat higher in energy, produces simultaneously propene by molecular chlorine elimination and 2-chloropropene by hydrogen chloride elimination. All our data show that 2-chloropropene is extremely reactive toward free radical attack. This is in complete agreement with literature data. Walling(136), for example, reports that styrene

radicals add 380 times faster to 2-chloropropene than to vinyl chloride.

We also observed that a decrease in 2 - chloropropene production with exposure time caused an increase in the production of cis- and trans- 1-chloropropene. In order to explain this, the following reaction sequence is proposed.

$$\cdot Cl + CH_2{=}CClCH_3 \longrightarrow CH_2Cl\dot{C}ClCH_3^{*} \quad (9)$$

$$CH_2Cl\dot{C}ClCH_3^{*} \longrightarrow CH_2{=}CClCH_3 + \cdot Cl \quad (10)$$

$$\longrightarrow CHCl{=}CHCH_3 + \cdot ClCl \quad (11)$$

$$CH_2Cl\dot{C}ClCH_3^{*} + M \longrightarrow CH_2Cl\dot{C}ClCH_3 + M^{*} \quad (12)$$

The chlorine atom addition to 2-chloropene given in reaction 9 may proceed either by reaction 9a or by 9b.

$$\cdot Cl + CH_2{=}CClCH_3 \longrightarrow CH_2Cl\dot{C}ClCH_3^{*} \quad (9a)$$

$$\longrightarrow \cdot CH_2CCl_2CH_3^{*} \quad (9b)$$

But orientation in free radical additions to unsymmetrical olefins is determined at the addition step, which occurs so as to leave the most stable radical. Thus hydrogen atom addition to propylene occurs preferentially to the terminal carbon(130, 131). Bromine atoms also attack the terminal carbon(137). The preference for addition to primary carbons is even more enhanced by chlorine atom subsitution in the 2-chloropropene molecule. Reaction 9b is, thus not likely to occur to any great extent. However, even if it did occur, the $\dot{C}H_2CCl_2CH_3^{*}$ radical would upon decomposition produce again the starting materials, 2-chloropropene and

chlorine atoms. Reaction 9b is, thus, not expected to have any noticable impact upon the results.

Reaction 9a produces vibrationally excited $CH_2Cl\dot{C}ClCH_3^*$ radicals which may decompose according to reaction 10 and 11. Although, to our knowledge, reaction 11 has not been reported in the literature, it is extremely reasonable, since, energetically speaking, the breaking of a secondary C - Cl bond (reaction 11) is favored over the breaking of a primary C - Cl bond (reaction 10). According to the mechanism the production of cis- and trans-1-chloropropene via reaction 11 should be reduced or prevented by addition of an inert deactivator(reaction 12). This was confirmed by experiments with added sulfur hexafluoride. These data clearly show the continuous decrease in 2-chloropropene, but this time, without formation of cis- and trans-1-chloropropene, since the vibrationally excited $CH_2Cl\dot{C}ClCH_3^*$ radical was prevented from decomposing by deactivational collision with sulfur hexafluoride.

4. Partial Deactivation of the Excited State

At this stage we should perhaps recall once more that the chloropropenes and propene are produced from two different excited states.

$$CH_2ClCHClCH_3^{**} \longrightarrow \begin{cases} CH_2{=}CClCH_3 + HCl & (5) \\ CH_2{=}CHCH_3 + Cl_2 & \end{cases}$$

$$CH_2ClCHClCH_3^{**} \longrightarrow CH_2{=}CClCH_3 + HCl \qquad (6)$$

$$CH_2ClCHClCH_3^{*} \longrightarrow CHCl{=}CHCH_3 + HCl \qquad (8)$$

Experiments with sulfur hexafluoride at $\lambda > 220$ nm provide strong evidence for a partial deactivation of the "two star" excited state to the"one star" excited state as shown by reaction 7.

$$CH_2ClCHClCH_3^{**} + SF_6 \longrightarrow CH_2ClCHClCH_3^{*} + SF_6^{*} \quad (7)$$

Similarly the data in the presence of water show that water is an extremely efficient deactivator of the excited state producing propene and 2-chloropropene. It might, therefore, be concluded that the two excited states leading to molecular elimination of Cl_2 and HCl are vibrationally excited ground states. However,this is contradicted by the fact that Setser and coworker(71, 120 - 121) have made extensive studies of the reactions of many vibrationally excited chloroethanes and chlorofluoroethanes. Molecular elimination of hydrogen chloride was always observed, but that of molecular chlorine was not. We are, therefore, suggesting with Tschuikow - Roux and coworkers(68) that the decomposition occurs directly from the excited Rydberg states and that the life times of such excited states might be commensurate with their degree of vibrational excitation. As pointed out earlier in this discussion, Sandorfy(138, 139) has drawn similar conclusions in his recent reviews. These suggestions are supported by life time calculations obtained from our deactivation studies with sulfur hexafluoride and water.

In Figure 15 we plotted $1 / R_{CH_2=CHCH_3}$ versus X, where X is the pressure of the deactivator, in our case, the pressure of water or that of sulfur hexafluoride.

$$\frac{1}{R_{CH_2=CHCH_3}} = \frac{k_5 + k_6 + k_7\hat{}\,[CH_2ClCHClCH_3\tilde{}]}{k_5\,\alpha\,I_{abs.}} + \frac{k_7\tilde{}\,[X]}{k_5\,\alpha\,I_{abs.}}$$

It is clear from the above equation that these plots should yield straight lines with identical intercepts since identical 1,2-dichloropropane pressures were used in both series of experiments. As Figure 15 shows, the intercepts are, although not identical, of the same order of magnitude. As a matter of fact, there difference may be explained by a difference in light transmission of the quartz windows, since different cells were used for these experiments.

The data obtained from Figure 15 may be used to carry out life time calculation. If we assume that for more effective deactivator, water, deactivation occurs at every collision an approximate life time of 0.6×10^{-8} sec.$^{-1}$ may be calculate for the excited state $CH_2ClCHClCH_3^{**}$ yielding propene and 2-chloropropene via elimination of molecular chlorine and hydrogen chloride, respectively.

A similar life time of 0.24×10^{-8} sec.$^{-1}$ was obtained by Ausubel and Wijnen(58, 59) for the excited state of cis-1,2-dichloroethylene yielding mainly acetylene and chloroacetylene via molecular elimination of chlorine and hydrogen chloride, respectively. It was precisely this state of the 1,2-dichloroethylene molecule for which Sandorfy(122, 138, 139) proposed an excited Rydberg state. Further confirmation may be derived from similar life times obtained for the excited chloroethane molecule decomposing by HCl elimination. Again decomposition is

suggested to occur from an excited 4s or 4p Rydberg state(46, 140).

In the presence of sulfur hexafluoride we observed at $\lambda > 220$ nm a collisional deactivation of the "two star" excited state to the "one star" excited state. It is interesting that in the photolysis of CH_2FCH_3Cl the excited state yielding ethylene and ClF (comparable to our "two star" excited state) also experienced partial deactivation. Tschuikow - Roux and coworkers(93) observed in the photolysis of CH_2FCH_2Cl at 147 nm a pressure dependence which they "attributed to a collisional modification of an excited state CH_2FCH_2Cl to another state decomposing by carbon - halogen bond fission, a process seen to increase with increase pressure".

5. Final Review

To our knowledge, the photolysis of dichloropropane has not been reported in the literature. The photolysis of 1-chloropropane(99) and 2-chloropropane(98) has, however, been investigated, and hydrogen chloride elimination and C - Cl bond rupture were observed in the primary process. The longest wavelength used in these studies was 184.9 nm(99). Most experiments were carried out at 147 nm and lower wavelength. It is, thus, not surprising that in addition to the step mentioned, fragnentation of the chloropropane molecule occurred.

The photolysis of a series of chloro-, fluoro- and chlorofluoro-ethanes has been investigated by Tschuikow - Roux and coworkers(64 -

68, 90 - 94) at 147 nm and 123.6 nm. They reported that even at these short wavelengths, the main primary processes are molecular eliminations such as those of HCl, Cl_2, ClF, HF, F_2, and H_2. The following for example, reported in the photolysis of CH_2FCH_2Cl at 147 nm as a result of molecular elimination ; ethylene, fluoroethylene, cis- and trans-1-fluoroethylene and vinyl chloride.

Most directly related to this work are the investigations by Wijnen and coworkers in the photolysis of chlorinated ethanes and ethylenes such as C_2H_3Cl(14), cis-$C_2H_2Cl_2$(59, 60), trans-$C_2H_2Cl_2$(59, 60), $CH_2=CCl_2$ (96), CD_3CHCl_2(62),CH_3CCl_3(61), and $CHCl_2CHCl_2$(89), since they were carried out at wavelengths comparable to those used in this investigation. Yuan and Wijnen drew the following general conclusion about the relative importance of the various primary steps occurring in the photolysis of chlorinated ethylenes and ethanes : primary process in compounds with chlorine atoms in 1,2-position ($CHCl_2CHCl_2$, CHCl=CHCl). Molecular chlorine elimination from the 1,1-positions either does not occur (CH_3CCl_3) or occurs only to a minor extent ($CH_2=CCl_2$, CD_3CHCl_2, $CHCl_2CHCl_2$). Molecular elimination of hydrogen chloride is an important primary process observed in all the compounds they investigated. It may occur exclusively from the 1,2-position (CD_3CHCl_2) or from both the 1,1- and 1,2-position ($CH_2=CDCl$). The primary step, producing C - Cl rupture, is the most important step in the photolysis of vinyl chloride(57), it is almost non-existent in $CHCl_2CHCl_2$, and it is not observed in the photolysis of $CH_2=CCl_2$. They concluded that

increased chlorine substitution in the ethanes and ethenes seems to favor both molecular chlorine and hydrogen chloride eliminations at the expense of C - Cl fissions.

The data in this investigation confirm those conclusions in all respects. Molecular chlorine elimination was the most important step in the photolysis of 1,2-dichloropropane (1,2-elimination) and completely abscence in the photolysis of 2,2-dichloropropane (1,1-elimination). Hydrogen chloride eliminations were important steps in both compounds. C - Cl fission was observed in 2,2-dichloropropane but not in 1,2-dichloropropane, probably because the configuration of the last compound offers more modes of decomposition (chlorine elimination + two different hydrogen chloride eliminations) than the first which has only one mode of hydrogen chloride elimination. Thus, this discussion has shown that our results are not only consistent within themselves but also with data reported in the literature regarding similar systems.

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