

PRIMARY REACTIONS IN THE PHOTOLYSIS OF 1,1-DICHLOROETHYLENE

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Summary

The photolysis of 1,1-C₂H₂Cl₂ has been investigated in the presence of I₂. The results indicate that at $\lambda > 2000 \text{ \AA}$ two excited states are produced. The lower excited state produces C₂H₂ and C₂HCl in a ratio of 0.3 to 1; the higher excited state produces C₂H₂Cl radicals. The results of this investigation are compared with data from the photolysis of *cis*- and *trans*-1,2-C₂H₂Cl₂.

Introduction

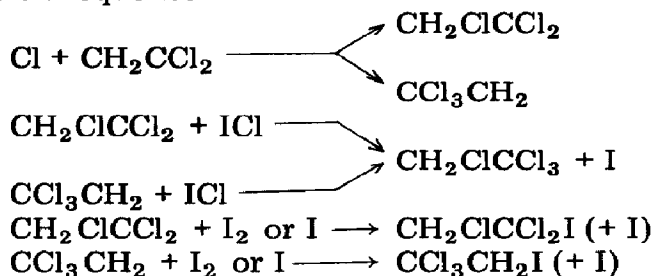
Recently [1, 2] we have reported on the primary process in the photolysis of *cis*- and of *trans*-1,2-C₂H₂Cl₂. It was observed that at $\lambda > 2000 \text{ \AA}$ two excited states were produced from each isomer. The higher excited state was associated primarily with the production of vibrationally excited C₂H₂Cl radicals. The lower excited state produced mainly C₂H₂ and C₂HCl via molecular elimination of Cl₂ and HCl respectively. It seemed of great interest to us to study in particular these elimination processes in 1,1-C₂H₂Cl₂ where, because of the configuration of this compound the elimination processes are limited to α , α -elimination of Cl₂ and α , β -elimination of HCl.

Experimental

The experimental technique was similar to the one used in studying the photolysis of *cis*- [1] and of *trans*-1,2-C₂H₂Cl₂ [2]. The u.v. absorption spectrum of 1,1-C₂H₂Cl₂ has a maximum at about 1900 Å and tails off towards 2400 Å [3, 4]. We observed, however, minute absorption up to about 3000 Å. Most irradiations were carried out with

the full arc of the 16 A 13 Hanovia medium pressure mercury arc. The effective incident light in these experiments covered for all practical purposes the wavelength range 2000 to 2400 Å. In some experiments Corning filters 9-54 (transmitting above 2200 Å) and 0-53 (transmitting above 2600 Å) were inserted between arc and cell.

Qualitative and quantitative determination of the reaction products was carried out by gas chromatography. A 6 ft. column packed with 25% (by weight) of silicon grease on Celite was used for analysis. The main reaction products obtained by photolyzing CH_2CCl_2 in the presence of I_2 were: CH_2CClI , C_2HCl and C_2H_2 . Small to trace amounts of $\text{CH}_2\text{ClCCl}_2\text{I}$ and of $\text{CCl}_3\text{CH}_2\text{I}$ were also observed. Since the iodo compounds were not commercially available identification was carried out as follows. Under identical gas chromatographic conditions the retention time of the peak ascribed to 1,1- $\text{C}_2\text{H}_2\text{ClI}$ was slightly shorter than the retention time of *trans*-1,2- $\text{C}_2\text{H}_2\text{ClI}$ produced by photolyzing *cis*- or *trans*-1,2- $\text{C}_2\text{H}_2\text{Cl}_2$ in the presence of I_2 [1, 2]. The peaks attributed to CH_2CClI , $\text{CH}_2\text{ClCCl}_2\text{I}$ and to CH_2ICCl_3 were absent if 1, 1- $\text{C}_2\text{H}_2\text{Cl}_2$ was photolyzed in the presence of HBr and in their place we observed $\text{C}_2\text{H}_3\text{Cl}$ and $\text{CH}_2\text{ClCCl}_3$. Further confirmation was obtained by the gas phase reaction of ICl with excess CH_2CCl_2 . In addition to $\text{CH}_2\text{ClCCl}_3$ two compounds were observed whose retention times coincided with the peaks attributed by us to $\text{CH}_2\text{ClCCl}_2\text{I}$ and to CH_2ICCl_3 . The formation of these compounds is a direct result of the addition of Cl atoms to CH_2CCl_2 and subsequent reactions of the radicals thus produced with ICl and/or I_2 as given by reaction sequence:



In our photolysis experiments of 1,1- $\text{C}_2\text{H}_2\text{Cl}_2$ in the presence of I_2 the amount of $\text{CH}_2\text{ClCCl}_2\text{I}$ formed was about 10% of the amount of 1,1- $\text{C}_2\text{H}_2\text{ClI}$ produced. The production of CH_2ICCl_3 was too small to allow quantitative determination of this product. Although experiments were carried out at 18°, 28° and at 45°C no temperature effect could be observed. For this reason the discussion will be limited to the data obtained at 28 °C.

The 1,1-dichloroethylene was obtained from the Eastman Chemical Company. It was purified by repeated distillation to about 99.9% purity. The impurity remaining in the sample was *trans*-1,2- $\text{C}_2\text{H}_2\text{Cl}_2$. It should be pointed out that the purified compound had a tendency to polymerize spontaneously. This could be prevented by storing the compound at dry ice temperature.

Time studies were performed to confirm that the product rates reported in this paper were independent of exposure time. Conversions were limited to less than 1% of the starting material.

Results and Discussion

The primary products obtained by photolyzing 1,1- $C_2H_2Cl_2$ in the presence of I_2 are CH_2CClI , C_2HCl and C_2H_2 . The formation of CH_2CClI is explained by C-Cl rupture and subsequent scavenging of the $CH_2=CCl$ radical by I_2 . It is interesting to point out that we observed CH_2CClI but not *cis*- and *trans*- $CHClCHI$. This proves that a structural isomerization involving H atom shift is absent in the CH_2CCl radical. Observations regarding the absence of an F atom shift in the Hg photosensitized photolysis of difluoroethylenes have previously been reported [5].

1, 1-Dichloroethylene is a good free radical scavenger and it was, therefore, necessary to establish that I_2 was capable of scavenging all CH_2CCl radicals. The experiments with I_2 as scavenger were carried out by saturating the cell with I_2 vapor. By carrying out experiments at 18° and at 45 °C the I_2 vapor pressure in the cell was varied from 0.2 Torr at 18 °C to 1.1 Torr at 45 °C. The rate of CH_2CClI production was not altered by this change in I_2 pressure proving that all CH_2CCl radicals were scavenged by I_2 even at the lowest temperature. These data are completely analogous to previous observations that C_2H_3 radicals produced in the photolysis of C_2H_3Cl [6] and $CHClCH$ radicals produced by photolysis of *cis*- and *trans*- $CHClCHCl$ can be scavenged quantitatively by I_2 .

A priori, the formation of C_2HCl might be explained by either of the following reactions:



Energetically, step (A) requires approximately 15 kcal/mol and step (B) about 125 kcal/mol where this last value corresponds to a wavelength of ~ 2300 Å. The fact that C_2HCl is observed as a reaction product even at $\lambda > 2600$ Å (as will be pointed out later) establishes that at least in part C_2HCl is produced by reaction (A). Even at $\lambda > 2000$ Å step (B) is energetically speaking only barely possible. If step (B) would occur we would expect to observe $C_2H_3Cl_2I$ produced by H atom addition to CH_2CCl_2 and subsequent scavenging of the $C_2H_3Cl_2$ radical by I_2 . In the presence of C_2H_4 and I_2 we would expect to observe C_2H_5I . None of these products were observed. This is particularly important since the addition products of Cl atoms (produced by C-Cl rupture) are observed as CH_2ClCCl_2I and CH_2ICCl_3 . In the presence of C_2H_4 the presence of Cl atoms in the system was observed in the form of C_2H_4ClI . We suggest, therefore, that C_2HCl is produced mainly, if not exclusively, by molecular

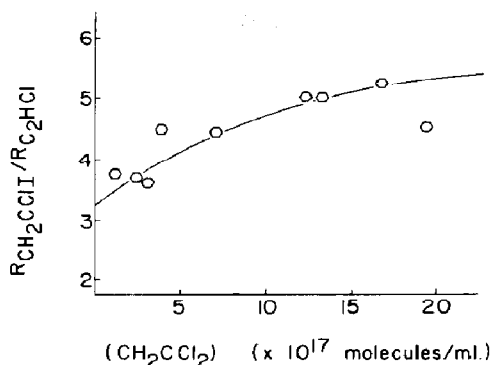


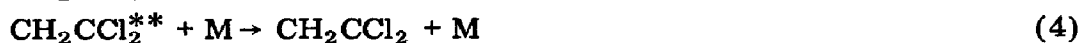
Fig. 1. Plot of $R_{\text{CH}_2\text{CClI}}/R_{\text{C}_2\text{HCl}}$ as a function of initial CH_2CCl_2 pressure.

detachment of HCl. This conclusion is completely analogous to previous reports that the simultaneous production of H and Cl atoms from $\text{C}_2\text{H}_3\text{Cl}$ [7] and from symmetrical dichloroethylenes [1, 2] does not occur at $\lambda > 2000 \text{ \AA}$.

Acetylene is a definite but minor product in the photolysis of 1, 1- $\text{C}_2\text{H}_2\text{Cl}_2$. In experiments with the full light of the mercury arc (effective range 2000 to 2400 \AA) C_2H_2 comprised less than 4% of the total primary process. It should, therefore, not be surprising that our data regarding acetylene are limited and subject to greater uncertainties. The ratio $R_{\text{C}_2\text{HCl}}/R_{\text{C}_2\text{H}_2}$ was determined as a function of initial 1, 1- $\text{C}_2\text{H}_2\text{Cl}_2$ pressure. The pressure range extended from 3.6 to 60.0 Torr, the ratio $R_{\text{C}_2\text{HCl}}/R_{\text{C}_2\text{H}_2}$ remained constant at 3.5 ± 0.5 indicating that C_2H_2 and C_2HCl originate from the same excited state.

A different relationship exists between C_2HCl and the CH_2CCl radical. Figure 1 clearly shows that the ratio $R_{\text{CH}_2\text{CClI}}/R_{\text{C}_2\text{HCl}}$ increases with increasing CH_2CCl_2 pressure. We also investigated the variation of the ratio $R_{\text{CH}_2\text{CClI}}/R_{\text{C}_2\text{HCl}}$ as a function of the energy of the incident light. For an initial CH_2CCl_2 pressure of about 50 Torr we obtained the following values for $R_{\text{CH}_2\text{CClI}}/R_{\text{C}_2\text{HCl}}$: 5 at $\lambda > 2000 \text{ \AA}$; 3.5 at $\lambda > 2200 \text{ \AA}$; and 0.6 at $\lambda > 2600 \text{ \AA}$. Clearly two different excited states are involved in the formation of the reaction products. There is no doubt that the higher excited state should be associated primarily with the production of CH_2CClI since the removal of higher energy light drastically reduces the production of this compound. Chloroacetylene, then, must originate mainly from the lower excited state. The question remains as to whether either of these products is produced by both excited states. Data in the presence of up to 73 Torr of SF_6 as inert deactivator showed a marked decrease in C_2HCl production without any apparent reduction in the rate of CH_2CClI formation. If chlorovinyl radicals were produced to any appreciable extent from the lower excited state then the addition of SF_6 should have produced also a reduction in the rate of CH_2CClI . Most of the C_2HCl must be produced by the lower excited state. It cannot, however, be established whether all of the chloroacetylene comes from that excited

state. Earlier we have pointed out that the ratio $R_{C_2HCl}/R_{C_2H_2}$ was equal to about 3.5 and independent of initial CH_2CCl_2 pressure. If both excited states were to produce C_2HCl they both would have to produce C_2H_2 as well, and in the same ratio. This seems unlikely. It is probable that the acetylenes are produced only by the lower excited state. The following may now be proposed to explain the observations:



In the above mechanism the lower excited state produces C_2H_2 and C_2HCl via molecular detachment of Cl_2 and HCl respectively. Identical reactions were observed in the photolysis of *cis*- [1] and of *trans*-1,2- $C_2H_2Cl_2$ [2]. The following equations may be derived from this mechanism:

$$(CH_2CCl_2)/R_{CH_2CClI} = 1/\alpha + (k_4/\alpha k_3)(CH_2CCl_2) \quad (I)$$

$$(CH_2CCl_2)/R_{C_2HCl} = (k_5 + k_6)/\beta k_5 + (k_7/\beta k_5)(CH_2CCl_2) \quad (II)$$

In eqns. (I) and (II), α and β are proportionality factors between pressure and amount of light absorbed for the higher and lower excited states of CH_2CCl_2 . The agreement between experimental data and eqns. (I) and (II) is excellent as may be seen in Fig. 2. From the plot of eqns. (I) and (II) we obtain: $k_4/k_3 \simeq 4.5 \times 10^{-18}$ and $k_7/(k_5 + k_6) \simeq 7.5 \times 10^{-18}$ (molecule/cm³)⁻¹. No other data are available in the literature for a direct comparison with the values of the rate constants obtained by us. However, as mentioned earlier, the ratio R_{CH_2CClI}/R_{C_2HCl} varies with pressure. The following equation may be derived for this ratio from the proposed mechanism:

$$\frac{R_{CH_2CClI}}{R_{C_2HCl}} = \frac{\alpha k_3}{\beta k_5} \left\{ \frac{(k_5 + k_6) + k_7(CH_2CCl_2)}{k_3 + k_4(CH_2CCl_2)} \right\} \quad (III)$$

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

$$R_{CH_2CClI}/R_{C_2HCl} = \alpha(k_5 + k_6)/\beta k_5$$

At high pressures, as $k_5 + k_6$ becomes negligible compared to $k_7(CH_2CCl_2)$ and k_3 compared to $k_4(CH_2CCl_2)$, the equation predicts that an asymptote

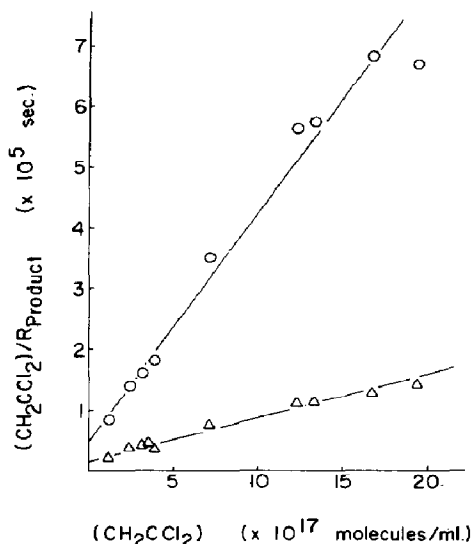


Fig. 2. Plots of $\text{CH}_2\text{CCl}_2/R_{\text{C}_2\text{HCl}}$ (O) and of $\text{CH}_2\text{CCl}_2/R_{\text{C}_2\text{H}_2\text{Cl}}$ (Δ) as a function of initial CH_2CCl_2 pressure.

TABLE 1

Product distributions from the lower excited states of dichloroethylenes*

	<i>cis</i> -1,2- $\text{C}_2\text{H}_2\text{Cl}_2$	<i>trans</i> -1,2- $\text{C}_2\text{H}_2\text{Cl}_2$	1,1- $\text{C}_2\text{H}_2\text{Cl}_2$
C_2H_2	3.1	2.1	0.3
C_2HCl	1	1	1
$\text{C}_2\text{H}_2\text{Cl}$	0.3	0.3	not obs.

*Relative to a production of C_2HCl equal to unity.

should be approached. At the asymptote:

$$R_{\text{CH}_2\text{CCl}_2}/R_{\text{C}_2\text{HCl}} = \alpha k_3 k_7 / \beta k_4 k_5$$

The plot of $R_{\text{C}_2\text{H}_2\text{Cl}_2}/R_{\text{C}_2\text{HCl}}$ in Fig. 1 clearly shows that this ratio approaches a maximum with increasing dichloroethylene pressure. Thus we obtain from Fig. 1 $(k_5 + k_6)/(k_5) = 3.2$ and $(k_3 k_7)/(k_4 k_5) \simeq 5.5$ which yields $k_4(k_5 + k_6)/k_3 k_7 \simeq 0.6$, a value in excellent agreement with the data obtained from eqns. (I) and (II).

Finally, it is interesting to compare the data from this investigation with those available for *cis*- and *trans*-1,2- $\text{C}_2\text{H}_2\text{Cl}_2$. In all three compounds, two different excited states were observed if photolysed at $\lambda > 2000 \text{ \AA}$. The higher excited state is the main source of chlorovinyl radicals in each of the dichloroethylenes. In Table 1 we show a comparison of the product yields from the lower excited state. All three compounds have in common that the production of $\text{C}_2\text{H}_2\text{Cl}$ radicals is of minor importance — as a matter

of fact this step seems to be absent with 1,1-C₂H₂Cl₂. The important feature is that with the symmetrical dichloroethylenes the molecular detachment of Cl is the most important step while with 1,1-C₂H₂Cl the elimination of HCl predominates. This is even more noteworthy since in 1,1-C₂H₂Cl₂ only α , β -elimination of HCl can occur while the HCl eliminations from the 1,2-dichloroethylenes probably occur via α , β - and α , α -eliminations as indeed observed in the photolysis of CH₂CCl [7]. Thus the relatively large acetylene yields in the photolysis of *cis*- and *trans*-C₂H₂Cl₂ must have been produced mainly from α , β -elimination of Cl₂ since our present investigation indicates that α , α -elimination of Cl₂ does not seem to be an important process in this type of compound. Finally, although of no direct relationship to the primary process, it is interesting to point out that we observed both CCl₃CH₂I and CH₂ClCCl₂I. No doubt, these products are formed by addition of Cl to the CCl₂ and to the CH₂ side of the CH₂CCl₂ molecule and through subsequent scavenging of the radicals, thus formed, by I₂. The fact that we observed mainly CH₂ClCCl₂I and only trace amounts of CCl₃CH₂I indicates that Cl atoms add predominantly, but not exclusively, to the CH₂ side of the CH₂CCl₂ molecule.

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