

THE PRIMARY PROCESS IN THE PHOTOLYSIS OF *TRANS*-1,2-C₂H₂Cl₂

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Summary

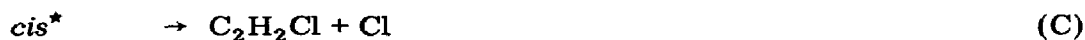
The primary process in the photolysis of *trans*-1,2-C₂H₂Cl₂ has been investigated in the wavelength range 2000 to 2400 Å as a function of initial *trans* pressure. The results indicate that the primary process in this region may be given by:



The ratio of rate constants $k_2:k_3:k_4$ is 8:3.8:1. Comparisons with previously reported data on the photolysis of the *cis*-isomer clearly establish that the products do not originate from an excited state common to both isomers. Differences in behaviour of the excited states of the *cis*- and *trans*-isomers are discussed.

Introduction

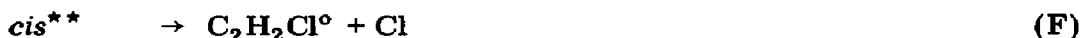
Recently [1] we have reported that the primary process in the photolysis of *cis*-1,2-C₂H₂Cl₂ may be given by the following reactions for the wavelength region 2200 to 2400 Å:





The data, furthermore, indicated that $k_A:k_B:k_C$ is 3.1:1:0.28.

In the wavelength region 2000 to 2200 Å another excited state was observed which produced the following additional reactions:



where $C_2H_2Cl^\circ$ represents a vibrationally excited radical.

In the present study we have examined the primary process of *trans*- $C_2H_2Cl_2$ in the wavelength range 2000 to 2400 Å. Interesting comparisons in photochemical behaviour of these compounds may be made from these studies.

Experimental

Essentially the same technique was used as described in the photolysis of *cis*- $C_2H_2Cl_2$ [1]. The light absorption by *trans*- $C_2H_2Cl_2$ (henceforth indicated by *Trans*) in the near u.v. has a maximum at about 2000 Å [2 - 4] and decreases rapidly towards 2400 Å. A minute but definite absorption could, however, be observed up to 4000 Å. Most irradiations were carried out with the full light of a Hanovia medium pressure mercury arc, Type 16A 13. Such experiments cover for all practical purposes the wavelength range 2000 to 2400 Å. As will be mentioned later, some irradiations were carried out with light of $\lambda > 2400$. We will report extensively on two series of experiments in which the product rates were determined as a function of initial *Trans* pressure. One series was carried out in the presence of I_2 as a scavenger, the other in the presence of HCl as a scavenger. The reaction products in the presence of I_2 were C_2H_2 , C_2HCl , *cis*- $C_2H_2Cl_2$, *trans*- $CHClCHI$ and *cis*- $CHClCHI$. The ratio of *trans/cis* for $CHClCHI$ production was always observed to be 4, regardless of experimental conditions. Since the isomerization process of *cis*- and *trans*- $C_2H_2Cl_2$ will be discussed in a separate paper, data regarding the formation of the *cis*-isomer are not included in this paper. Identical products were found if HCl (present in 5% concentration) was used as a scavenger, except for the fact that *trans*- and *cis*- $CHClCHI$ were now observed as C_2H_3Cl . Under exactly identical conditions except for the nature of the scavenger, the total amount of C_2H_2ClI produced in the presence of I_2 was equal to the amount of C_2H_3Cl formed in the presence of HCl.

The *trans*-1,2-dichloroethylene was obtained from the Aldrich Chemical Company and was purified by gas chromatography to better than 99.98% purity. The impurities were *cis*-1,2- $C_2H_2Cl_2$ and 1,1- $C_2H_2Cl_2$ in a ratio of about 10 to 1 respectively.

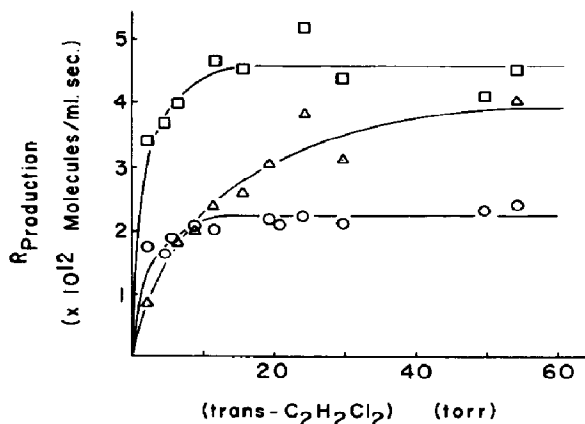


Fig. 1. Rate of product formation in the photolysis of *trans*-C₂H₂Cl₂ (2000 to 2400 Å). □, R_{C₂H₂}; ○, R_{C₂HCl}; △, R_{C₂H₂Cl}.

Results and Interpretation

In Fig. 1 we present the rates of product formation as a function of initial *Trans* pressure for experiments carried out in the presence of I₂ and for an effective wavelength range 2000 to 2400 Å. The CHClCHI rate represents the sum of the *cis* and *trans* isomers of this compound. Figure 1 clearly shows that R_{C₂H₂} and R_{C₂HCl} follow a similar pattern. The rates of production of these compounds increase rapidly with increasing *Trans* pressure until a maximum is reached at about 10 Torr. The rate of CHClCHI production does not reach a maximum until the initial *Trans* pressure is about 40 Torr. Thus, there is here a first indication that we are dealing with more than one excited state. A similar series of experiments was carried out in which HCl was used as a scavenger. In Table 1 we give the ratios R_{C₂H₂}/R_{C₂HCl}, R_{C₂H₂}/R_{C₂H₂Cl} and R_{C₂HCl}/R_{C₂H₂Cl} as a function of initial *Trans* pressure for the two series. The ratio R_{C₂H₂}/R_{C₂HCl} is equal to 2.0 ± 0.1 for each series regardless of the initial *Trans* pressure. This proves that C₂H₂ and C₂HCl must originate from the same excited state. The ratios R_{C₂H₂}/R_{C₂H₂Cl} and R_{C₂HCl}/R_{C₂H₂Cl} show a clear pressure effect, they decrease with increasing *Trans* pressure. It may, therefore, be concluded that the C₂H₂Cl radicals must at least in part originate from an excited state different from the one yielding acetylene and chloroacetylene. It should be noted that these two series were carried out under similar but not identical experimental conditions since it was necessary to dismantle the system after the I₂ experiments in order to remove excess I₂ and mercury iodides which had been formed. We believe that the differences observed between the two series for the ratios R_{C₂H₂}/R_{C₂H₂Cl} and R_{C₂HCl}/R_{C₂H₂Cl} are due to variations in the energy distribution of the incident light, especially since, as mentioned in the experimental section, identical experiments with I₂ and HCl gave identical results. To confirm this some experiments were carried out in which, with the aid of Corning filters, the effective wavelength range was

TABLE 1

Product ratios in the photolysis of *trans*-C₂H₂Cl₂ as a function of initial pressure.

Pressure (Torr)	$R_{C_2H_2}/R_{C_2HCl}$	$R_{C_2H_2}/R_{C_2H_2Cl}$	$R_{C_2HCl}/R_{C_2H_2Cl}$
Scavenger: I ₂			
10	2.0	1.9	0.94
15	2.0	1.7	0.82
30	2.0	1.3	0.65
50	2.0	1.2	0.61
Scavenger: HCl			
10	2.1	1.3	0.64
15	2.0	1.1	0.56
30	2.0	1.1	0.55
50	2.2	1.1	0.51

limited from 2600 to 4000 Å and from 3000 to 4000 Å. There was no appreciable difference between the data obtained in the range 2600 to 4000 Å and those obtained in the range 3000 to 4000 Å. Furthermore, the ratio $R_{C_2H_2}/R_{C_2HCl}$ in this range was equal to 2 as obtained with the full arc of the mercury lamp. The ratios $R_{C_2H_2}/R_{C_2H_2Cl}$ and $R_{C_2HCl}/R_{C_2H_2Cl}$ were, however, larger by a factor of two compared to the data reported in Table 1. Thus, there is an increase in C₂H₂Cl radical production relative to the formation of C₂H₂ and C₂HCl with decreasing wavelength. It is extremely important to emphasize that all reaction products were observed even at $\lambda > 3000$ Å. As discussed extensively in an earlier publication [1], this means that at least in this long wavelength range C₂H₂ and C₂HCl must be produced by molecular detachment of Cl₂ and HCl respectively. The following primary steps are given to explain the data:



Reactions (2) and (3) explain why the ratio $R_{C_2H_2}/R_{C_2HCl}$ is independent of initial *Trans* pressure and of the wavelength of the incident light as observed in the limited range of this investigation. Accepting that the excited state

produced in reaction (1b) is more energetic than the one formed in (1a), the increase in C_2H_2Cl radical production with decreasing wavelength is explained by reaction (6). In the mechanism we have included the possibility that some C_2H_2Cl radicals may be produced from the lower excited state (reaction 4). In doing so the reactions of the lower excited state are similar to those previously suggested for *cis*- $C_2H_2Cl_2$ (see introduction). Differences in reactivity of the higher excited state between *cis*- and *trans*- $C_2H_2Cl_2$ will be discussed later. Accepting temporarily, that C_2H_2Cl radicals are produced by reactions (4) and (6) we obtain: $R_{C_2H_2Cl} = k_4(C_2H_2Cl_2^*) + k_6(C_2H_2Cl_2^{*\star})$. Since $R_{C_2H_2} = k_2(C_2H_2Cl_2^*)$, substitution for $(C_2H_2Cl_2^*)$ yields: $R_{C_2H_2Cl} = k_4/k_2 R_{C_2H_2} + k_6(C_2H_2Cl_2^{*\star})$. Although the exact value for k_4/k_2 is not known its outer limits are available. From the experiment with I_2 we have as extreme values for k_4/k_2 : (a) $k_4/k_2 = 0$ (meaning reaction (4) does not occur); and (b) $k_4/k_2 = 0.25$ (C_2H_2Cl radicals are produced exclusively by reaction (4)). Since the ratio $R_{C_2H_2Cl}/R_{C_2H_2}$ is pressure and wavelength dependent it is clear that at least some C_2H_2Cl radicals must be produced by reaction (6). Accepting steady state treatment and that the light absorption is proportional to the initial *Trans* pressure we obtain:

$$1/R_{C_2H_2Cl}^{*\star} = k_7/(\alpha k_6) + 1/(\alpha Trans) \quad (I)$$

In eqn. (I), α is the proportionality factor between initial *Trans* pressure and light absorbed. $R_{C_2H_2Cl}^{*\star}$ is the rate of C_2H_2Cl radical production *via* reaction (6) only and has been calculated by assigning various values for k_4/k_2 (within the limits 0 and 0.25) in the equation: $R_{C_2H_2Cl}^{*\star} = R_{C_2H_2Cl} \text{ total} - k_4/k_2 R_{C_2H_2}$. The data obtained in the presence of I_2 are plotted in Fig. 2 for three values of k_4/k_2 . The upper curve represents the data assuming $k_4/k_2 = 0$, the lower curve those for $k_4/k_2 = 0.25$, and the straight line was obtained from $k_4/k_2 = 0.13$. The value $k_4/k_2 = 0.13$ gives an equally excellent fit for the data obtained with HCl as a scavenger. Accepting, therefore, $k_4/k_2 = 0.13$, eqn. (I) yields $k_7/k_6 = 2.3 \times 10^{-18} \text{ (molecule/cm}^3\text{)}^{-1}$ for the I_2 data. A similar plot for the HCl data (not represented) produced $k_7/k_6 = 2.5 \times 10^{-18} \text{ (molecule/cm}^3\text{)}^{-1}$ in excellent agreement with the data where I_2 was used as a scavenger. The results thus indicate that C_2H_2Cl radicals are produced from two different excited states as also observed in the photolysis of the *cis* isomer and that the product ratios of the lower excited state are given by $R_{C_2H_2} : R_{C_2HCl} : R_{C_2H_2Cl} = 8 : 3.8 : 1$.

Discussion

Although this study has by no means been as extensive as the one carried out on the photolysis of the *cis* isomer, some extremely interesting data are obtained. Both isomers yield two excited states if irradiations are carried out with light covering the range 2000 to 2400 Å. The lower excited state of each isomer yields all three products: C_2H_2 , C_2HCl and C_2H_2Cl radicals. The behaviour of the higher excited *cis* state is different from that of the higher excited *trans* state. The higher excited state formed

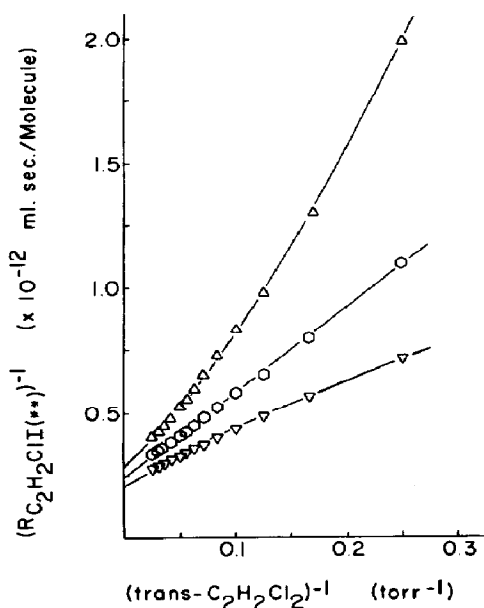
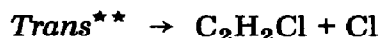


Fig. 2. Plots of $1/R_{C_2H_2ClI(***)}$ vs. $1/trans$ according to eqn. (I). The upper curve was obtained by assuming $k_4/k_2 = 0$, the lower curve by assuming $k_4/k_2 = 0.25$. The middle line represents the data assuming $k_4/k_2 = 0.13$.

in the photolysis of *cis* produced the following reactions:



In the above reaction sequence $C_2H_2Cl^\circ$ represents a vibrationally excited C_2H_2Cl radical. Reaction (E) may or may not occur *via* an excited C_2H_2Cl radical as intermediate. The higher excited state of the *trans* isomer produced, however, only the following reaction:



The similarity between these two excited states is clear since they both yield vinyl radicals. It is, however, extremely interesting that irradiations with apparently identical wavelength regions yield thermal C_2H_2Cl radicals from the *trans* and vibrationally excited C_2H_2Cl radicals from the *cis* isomer. These observations are paralleled by laser experiments carried out by Berry. He reports [4] that at $\lambda > 1550 \text{ \AA}$ the vibronic population ratios N_3/N_2 , N_2/N_1 and N_1/N_0 are consistently larger for the *cis* isomer than for the *trans* isomer. Perhaps some explanation for these observations may be gained by studying the absorption spectra of the isomers. The *cis* isomer has an absorption maximum at about 1900 \AA , the *trans* isomer at about 2000 \AA [2 - 4]. It may, therefore, be expected that the excited state of the *cis*

TABLE 2

Product ratios originating from the low excited state of *cis*- and of *trans*-C₂H₂Cl₂.

	<i>Cis</i> [*]	<i>Trans</i> [*]
$R_{C_2H_2}/R_{C_2HCl}$	3.1	2.1
$R_{C_2H_2}/R_{C_2H_2Cl}$	11.1	8.0
$R_{C_2HCl}/R_{C_2H_2Cl}$	3.5	3.8

isomer may carry about 7 kcal more energy than the excited state of the *trans* isomer. If it is assumed that the C₂H₂Cl radicals produced in the *trans* compound have an energy just below the threshold energy of a vibrationally excited radical, then these 7 kcal of excess energy might well explain the observations. Although the wavelength range of our experiments covered a relatively narrow band from 2000 to 2400 Å, our results indicate that experiments with monochromatic light may yield extremely interesting data regarding the energy distributions of the excited states and their products.

As mentioned earlier the lower excited state of *cis*- and of *trans*-C₂H₂Cl₂ yield C₂H₂, C₂HCl and C₂H₂Cl radicals. Table 2 gives the product ratios obtained from the excited *cis* and *trans* isomers. It should be mentioned that for both isomers the C₂H₂Cl radical production is less than 10% of the total products. Thus, the $R_{C_2H_2Cl}$ data are not as accurate as those for $R_{C_2H_2}$ and R_{C_2HCl} . For this reason we hesitate to state that the observed differences for $R_{C_2H_2}/R_{C_2H_2Cl}$ and for $R_{C_2HCl}/R_{C_2H_2Cl}$ are real. There is, however, no such doubt regarding the ratio $R_{C_2H_2}/R_{C_2HCl}$. The large difference observed for $R_{C_2H_2}/R_{C_2HCl}$ clearly established that the products do not originate from an excited state common to both isomers. This ratio $R_{C_2H_2}/R_{C_2HCl}$ represents the rate of molecular Cl₂ elimination over the rate of molecular HCl elimination. It is clear that the molecular elimination of Cl₂ must be an α,β -process. Both α,α - and α,β -eliminations of HCl have been observed from chlorinated ethanes [5] and ethylenes [4, 6]. It is expected that both processes also occur here. The fact that $R_{C_2H_2}/R_{C_2HCl}$ is larger for the *cis* isomer than the *trans* isomer is perhaps not surprising. The geometry of the *cis* molecule favors Cl₂ elimination (the Cl atoms are adjacent to each other) and hinders α,β -elimination of HCl (owing to the *trans* position of these atoms). The *trans* molecule favors α,β -elimination of HCl but reduces the possibility of Cl₂ elimination. For both isomers the Cl₂ elimination is larger than the HCl elimination in spite of the fact that there are four possibilities for HCl elimination compared to only one possibility for Cl₂ elimination. This may reflect the bulkiness of the Cl atoms thus bringing them close together and favoring Cl₂ elimination over HCl elimination.

Finally, we would like to mention that shortly we hope to present data on the primary process in CH₂CCl₂. Since the molecular elimination processes in this molecule are limited to α,β for HCl and α,α for Cl₂ a com-

parison with the data given here for *cis*- and *trans*-C₂H₂Cl₂ should be interesting.

Acknowledgement

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