

## PRIMARY STEPS IN THE PHOTOLYSIS OF 1,1,2,2-TETRACHLOROETHANE

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### Summary

The photolysis of 1,1,2,2-tetrachloroethane ( $\text{CHCl}_2\text{CHCl}_2$ ) was investigated at room temperature in the presence of  $\text{I}_2$ . The reaction products observed were *cis*- and *trans*-1,2- $\text{C}_2\text{H}_2\text{Cl}_2$ , 1,1- $\text{C}_2\text{H}_2\text{Cl}_2$ ,  $\text{C}_2\text{HCl}_3$ ,  $\text{C}_2\text{Cl}_4$  and  $\text{CHCl}_2\text{CHCl}$ . The formation of these products is discussed and is compared with the formation of photodecomposition products of other chlorinated ethanes and ethylenes. General conclusions are drawn about the relative importance of the  $\text{Cl}_2$ ,  $\text{HCl}$  and  $\text{H}_2$  elimination processes, and of the C—Cl bond rupture in the photolysis of chlorinated ethanes and ethylenes.

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### 1. Introduction

Over the past few years we have carried out considerable research on the primary processes in the photolysis of chlorinated ethanes and ethylenes. Some of the primary steps observed are the molecular eliminations of  $\text{Cl}_2$ ,  $\text{HCl}$  and  $\text{H}_2$ , and the rupture of the C—Cl bond. We have recently [1] investigated the photolysis of the totally unsymmetric  $\text{CH}_3\text{CCl}_3$  molecule. In order to gain information about the effects of the degree and the nature of the chlorine substituents on the occurrence and the relative importance of the various primary steps, we studied the photolysis of the totally symmetric ethane 1,1,2,2-tetrachloroethane ( $\text{CHCl}_2\text{CHCl}_2$ ).

### 2. Experimental

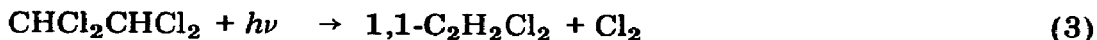
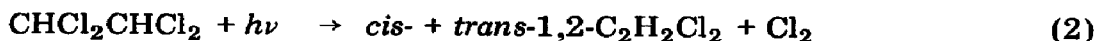
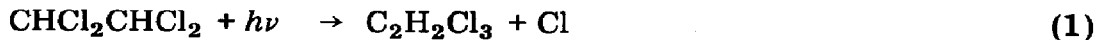
A conventional high vacuum apparatus, and a Hanovia medium pressure arc (type 16 A 13) as the light source were used. The UV light transmitted by this arc begins at a wavelength of about 2000 Å;  $\text{CHCl}_2\text{CHCl}_2$  starts to absorb extremely weakly at about 4000 Å. Below 4000 Å the absorption increases slowly towards shorter wavelengths, it becomes appreciable at

2500 Å and it becomes very intense at wavelengths shorter than 2200 Å. Most experiments were carried out either with unfiltered light, or with light of wavelength greater than 3000 Å by inserting a Corning filter 0-54 between the arc and the cell. Because of the aforementioned absorption characteristics, the experiments with unfiltered light cover mainly the range 2000 - 2200 Å. Exposure times of about 10 h were required to obtain sufficient products at wavelengths above 3000 Å, whereas the exposure times of the experiments with unfiltered light were measured in minutes. All experiments were carried out at room temperature and with a  $\text{CHCl}_2\text{CHCl}_2$  pressure of 5 Torr. The effect of pressure variations in the  $\text{CHCl}_2\text{CHCl}_2$  was not studied since the maximum vapor pressure of  $\text{CHCl}_2\text{CHCl}_2$  at room temperature is about 6 Torr. Some data were obtained in the presence of octafluorocyclobutane (OFCB) as an inert deactivator. In order to avoid complications by secondary reactions, time studies were performed to confirm that the product rate was independent of the exposure time. Even at the longest exposure time the conversion was less than 1% of the starting material.

All experiments reported in this work were carried out in the presence of  $\text{I}_2$  as a free radical scavenger. The reaction products were determined quantitatively by gas chromatography. By far the most abundant products were *cis*- and *trans*-1,2- $\text{C}_2\text{H}_2\text{Cl}_2$ , which together comprised about 70 - 80% of all products. In addition 1,1- $\text{C}_2\text{H}_2\text{Cl}_2$ ,  $\text{C}_2\text{HCl}_3$ ,  $\text{C}_2\text{Cl}_4$  and  $\text{CHCl}_2\text{CHClI}$  were formed. The quantitative relationship between reaction products with closely related retention times has been well established. Therefore it was possible to give quite accurate results for the ratios  $R_{\text{cis-1,2-C}_2\text{H}_2\text{Cl}_2} / R_{\text{trans-1,2-C}_2\text{H}_2\text{Cl}_2}$  ( $R_{\text{cis}}/R_{\text{trans}}$ ) and  $R_{1,1\text{-C}_2\text{H}_2\text{Cl}_2} / R_{\text{cis+trans}}$ . However, it was not always possible to obtain accurate data for the ratios  $R_{\text{C}_2\text{HCl}_3} / R_{\text{cis+trans}}$  and  $R_{\text{C}_2\text{Cl}_4} / R_{\text{cis+trans}}$ . This is not surprising since both  $\text{C}_2\text{HCl}_3$  and  $\text{C}_2\text{Cl}_4$  were formed in relatively small amounts.

### 3. Results and discussion

The primary products obtained by photolysing  $\text{CHCl}_2\text{CHCl}_2$  in the presence of  $\text{I}_2$  are *cis*- and *trans*-1,2- $\text{C}_2\text{H}_2\text{Cl}_2$ , 1,1- $\text{C}_2\text{H}_2\text{Cl}_2$ ,  $\text{C}_2\text{HCl}_3$ ,  $\text{C}_2\text{Cl}_4$  and  $\text{CHCl}_2\text{CHClI}$ . To explain the formation of these products we suggest that the following primary steps occur:



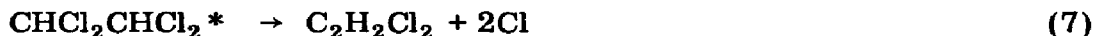
It is clear that  $\text{CHCl}_2\text{CHClI}$  is formed by C—Cl bond rupture and the subsequent reaction of the  $\text{C}_2\text{H}_2\text{Cl}_3$  radical with  $\text{I}_2$ . The amount of  $\text{CHCl}_2\text{CHClI}$  produced was generally so small that no accurate data can be given

about its production and about its behavior under various experimental conditions.

In principle, the dichloroethylenes might be produced by either of the following reactions:



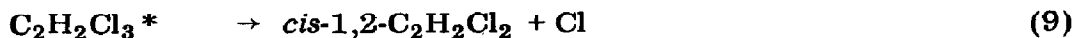
or



Energetically, step (6) requires approximately  $40 \text{ kcal mol}^{-1}$  and step (7) about  $100 \text{ kcal mol}^{-1}$ . Since the dichloroethylenes are observed at wavelengths above  $3000 \text{ \AA}$  (at energies smaller than  $95 \text{ kcal mol}^{-1}$ ), step (7) cannot occur in the longer wavelength region of this investigation. Similar considerations establish that, at wavelengths greater than  $3000 \text{ \AA}$ ,  $\text{C}_2\text{Cl}_4$  and  $\text{C}_2\text{HCl}_3$  must be produced by molecular elimination of  $\text{H}_2$  and  $\text{HCl}$ . Therefore, it could be suggested that all the ethylenes are produced from the same excited state of the  $\text{CHCl}_2\text{CHCl}_2$  molecule. If this is correct then the ratio  $R_{1,1-\text{C}_2\text{H}_2\text{Cl}_2}/R_{\text{cis}+\text{trans}}$  should be constant regardless of the energy of the incident light and of the presence or absence of inert deactivators; this was observed. We obtained a value for  $R_{1,1-\text{C}_2\text{H}_2\text{Cl}_2}/R_{\text{cis}+\text{trans}}$  of  $0.06 \pm 0.01$ . We believe that *cis*- and *trans*-1,2- $\text{C}_2\text{H}_2\text{Cl}_2$  are produced via  $\alpha,\beta$  elimination of  $\text{Cl}_2$  and that 1,1- $\text{C}_2\text{H}_2\text{Cl}_2$  is produced by  $\alpha,\alpha$  elimination of  $\text{Cl}_2$  and subsequent rearrangement of the  $\text{CHCl}_2\text{CH}$  radical to  $\text{CCl}_2\text{CH}_2$ . The ratio  $R_{1,1-\text{C}_2\text{H}_2\text{Cl}_2}/R_{\text{cis}+\text{trans}}$  is then a measure for the ratio of  $\alpha,\alpha/\alpha,\beta$  elimination of  $\text{Cl}_2$ . The value of 0.06 obtained indicates that  $\alpha,\alpha$  elimination of  $\text{Cl}_2$  is very unimportant relative to  $\alpha,\beta$  elimination of  $\text{Cl}_2$ . These data are consistent with results obtained previously for the photolysis of dichloroethylenes; molecular elimination of  $\text{Cl}_2$  is the most important step in the photolysis of symmetric dichloroethylenes [2, 3] and is a very unimportant step in the photolysis of 1,1- $\text{C}_2\text{H}_2\text{Cl}_2$  [4]. We obtained a value for the ratio  $R_{\text{C}_2\text{HCl}_3}/R_{\text{cis}+\text{trans}}$  of  $0.15 \pm 0.03$  both in the absence and in the presence of a Corning filter 0-54, confirming that  $\text{C}_2\text{HCl}_3$  originates from the same excited state as the dichloroethylenes. The ratio for  $\text{Cl}_2/\text{HCl}$  elimination has been reported to be 3.1 for *cis*-1,2- $\text{C}_2\text{H}_2\text{Cl}_2$  [2] and to be 2.1 for *trans*-1,2- $\text{C}_2\text{H}_2\text{Cl}_2$  [3]. The value of about 6.5 obtained in this work for  $\text{CHCl}_2\text{CHCl}_2$  might perhaps be expected because of the increase in the number of chlorine atoms present in the molecule. Our results for the production of  $\text{C}_2\text{Cl}_4$  were quite variable and, although in general the production of  $\text{C}_2\text{Cl}_4$  seemed to parallel that of  $\text{C}_2\text{HCl}_3$ , we hesitate to suggest that this compound originates from the same excited state as the other olefins.

Finally, it is interesting to study in somewhat greater detail the production of the most important compounds, *i.e.* *cis*- and *trans*-1,2- $\text{C}_2\text{H}_2\text{Cl}_2$ . Although initially results for the ratio  $R_{\text{cis}}/R_{\text{trans}}$  seemed inaccurate, an inspection of the data obtained in time studies indicated clearly that it varied with the exposure time. This ratio extrapolated to unity for zero exposure time and increased with increasing exposure time to a maximum

value of about  $2.2 \pm 0.2$ . These results may be explained by accepting that the *cis* and *trans* isomers are produced in a 1:1 ratio in the primary step and that deviations from this ratio are caused by the following isomerization process:



This isomerization mechanism was originally suggested by Wijnen [5] and by Ayscough *et al.* [6] and has recently been confirmed by Ausubel and Wijnen [7]. The chlorine atoms, which initiate the chain mechanism in reaction (8), are produced by reaction (1) or, to a minor extent, by secondary decomposition of the reaction products. If this mechanism is correct then it should be possible to prevent an increase in the ratio  $R_{\textit{cis}}/R_{\textit{trans}}$  by deactivating the excited  $\text{C}_2\text{H}_2\text{Cl}_3^*$  radical through reaction (11). Indeed, with increasing amounts of OFCB as an inert deactivator the ratio  $R_{\textit{cis}}/R_{\textit{trans}}$  decreased and approached unity even at long exposure times. The value obtained for  $R_{\textit{cis}}/R_{\textit{trans}}$  of  $2.2 \pm 0.2$  indicates that the excited  $\text{C}_2\text{H}_2\text{Cl}_3^*$  radical decomposes to yield  $69 \pm 2\%$  of the *cis* and  $31 \pm 2\%$  of the *trans* isomer. These results are in fair-to-excellent agreement with those reported by Ausubel and Wijnen [7] (62% and 38% respectively), by Ebert and Büll [8] (63% and 37%), by Ayscough *et al.* [9] (66% and 34%) and by Wai and Rowland [10] (67% and 33%).

By comparison of the data reported in this work with those obtained in previous investigations it is possible to draw some general conclusions about the relative importance of the various primary steps occurring in the photolysis of chlorinated ethanes and ethylenes. The molecular elimination of  $\text{Cl}_2$  from the  $\alpha, \beta$  position is the most important primary process in the compounds we have investigated ( $\text{CHCl}_2\text{CHCl}_2$ , *cis*- [2] and *trans*-1,2- $\text{C}_2\text{H}_2\text{Cl}_2$  [3]).  $\text{Cl}_2$  elimination from the  $\alpha, \alpha$  position either does not occur ( $\text{CH}_3\text{CCl}_3$  [1]) or occurs only to a minor extent ( $\text{CH}_2\text{CCl}_2$  [4],  $\text{CD}_3\text{CHCl}_2$  [11] and  $\text{CHCl}_2\text{CHCl}_2$ ). Molecular elimination of  $\text{HCl}$  is an important primary process observed in all the compounds we have investigated. It may occur exclusively from the  $\alpha, \beta$  position ( $\text{CD}_3\text{CHCl}_2$  [11]) or from both  $\alpha, \alpha$  and  $\alpha, \beta$  positions ( $\text{CH}_2\text{CDCl}$  [12]). We have observed molecular elimination of  $\text{H}_2$  only from chlorinated ethanes and exclusively from the  $\alpha, \beta$  positions ( $\text{CD}_3\text{CHCl}_2$  [11] and  $\text{CHCl}_2\text{CHCl}_2$ ). The primary step which produces C—Cl bond rupture is the most important step in the photolysis of  $\text{C}_2\text{H}_3\text{Cl}$  [13], it is almost non-existent for  $\text{CHCl}_2\text{CHCl}_2$  and it is not observed for  $\text{CH}_2\text{CCl}_2$ . In general increased chlorine substitution in the ethanes and ethylenes seems to favor both  $\text{Cl}_2$  and  $\text{HCl}$  elimination at the expense of C—Cl bond rupture.

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