[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Photochemical Studies. XXII. The Effect of Radiation of Wave Length 1980–1860 Å. on *Cis* and *Trans* Dichloroethylenes

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In a recent article[2] a study was presented of the absorption spectra of the *cis* and *trans* dichloroethylenes. These spectra may be divided roughly into three regions: (1) a continuous absorption with maximum about 1950 Å. in the *cis* and 1850 Å. in the *trans* form. This absorption extends at least to wave lengths as long as 2500 Å. at room temperature and resembles that found in all compounds containing a carbon–chlorine bond; (2) a banded region beginning about 1540 Å. and extending to shorter wave lengths (somewhat shorter for the *cis* than the *trans* dichloroethylene); (3) another region of continuous absorption at shorter wave lengths and extending down to at least 750 Å., the limit of the observations made.

Two types of theory for the photochemical *cis–trans* isomerization have been advanced: (1) a theory virtually involving free rotation in the upper electronic state;[3] (2) a theory involving the addition of an atom or free group to the face of the carbon tetrahedron, followed by the simultaneous ejection of another group accompanied by isomerization.[4]

The mechanism of the photochemical isomerization of the *cis* and *trans* dichloroethylenes has not been investigated. Olson and Maroney[5] have studied the photochemical steady state in a mixture of the two dichloroethylenes at elevated temperatures. Maroney[6] has also studied the thermal equilibrium between the two forms at still higher temperatures and finds that it approaches a 1:1 mixture with a heat of isomerization of 500–725 calories.

The present investigation was undertaken with the object of determining the primary action of radiation in the first absorption region upon the two dichloroethylenes.

I. Experimental Procedure and Results

(a) Since the first region of continuous absorption may lead to the production of chlorine atoms which may furnish the free atoms necessary to produce isomerization by the second theory, attempts were first made to detect the production of such atoms.

The two dichloroethylenes were first illuminated by radiation from an aluminum spark (air path 2 cm.) in the presence of a silver surface. The silver was attacked, a purplish brown coating being formed which turned black in a developing bath. Since chlorine molecules do not readily attack silver under these conditions,[7] these experiments may be taken to indicate the presence of chlorine atoms. Pressures of 220 mm. of *cis* and 300 mm. of *trans* dichloroethylene were used and the unilluminated vapors had no effect on the silver.

During illumination a brownish solid substance was formed on the window both with the *cis* and *trans* forms.

(b) The *cis*-dichloroethylene was next illuminated in a quartz cell by radiation from the aluminum spark. Mercury vapor was removed by liquid air prior to admitting the dichloroethylene through a stopcock. The pressure was 100–106 mm. After illumination the cell was cut off and various reagents were sucked into the cell through the stopcock. A precipitate was produced with silver nitrate, but no test was obtained for free chlorine with potassium iodide–starch solution. When a dilute solution of ammonium hydroxide was introduced, the solution was found to be acid to methyl orange after removal.

These results indicate that some hydrogen chloride is formed upon illumination of *cis*-dichloroethylene.

(c) In the next experiments a flow system was used and the *cis*-dichloroethylene was passed through the cell and bubbled through a solution of sodium hydroxide. Three runs were made of the same duration (two hours) and 6.3 g. of the dichloroethylene passed through the cell in each case. The light intensity was constant to 2 or 3%. The following results were obtained: (I) Without illumination no precipitate with silver

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[1] Jesse Metcalf Fellow, 1934–1936.

[2] Mahncke and Noyes, *J. Chem. Phys.*, **3**, 536 (1935).

[3] Olson, *Trans. Faraday Soc.*, **27**, 69 (1931); Mulliken, *Phys. Rev.*, **41**, 751 (1932).

[4] Olson, *J. Chem. Phys.*, **1**, 418 (1933).

[5] Olson and Maroney, THIS JOURNAL, **56**, 1320 (1934).

[6] Maroney, *ibid.*, **57**, 2397 (1935).

[7] Rodebush and Klingelhoefer, *ibid.*, **55**, 130 (1933).

nitrate was obtained after acidifying with nitric acid. (II) With illumination 2.2 mg. of chlorine were precipitated as silver chloride. (III) In the third run a volume of hydrogen equal to the volume of the dichloroethylene was passed through the cell. 94.2 mg. of chlorine (as silver chloride) were obtained.

No test for free chlorine could be obtained with starch–potassium iodide solution in the flowing system.

The large increase in hydrogen chloride formation when hydrogen was mixed with the dichloroethylene is probably the best proof that an active form of chlorine is produced upon illumination.

(d) A further investigation was made of the solid product produced during illumination. In order to obtain more of this product, a stream of nitrogen containing *cis*-dichloroethylene was passed through the cell and then through a trap cooled with an ice–calcium chloride mixture. In this way about 6 mg. of a product with a quite sharp melting point (103.5–104° uncorrected) was obtained. The per cent. chlorine in this product was obtained by microanalysis[8] and was found to be 72.5. The percentage of chlorine in dichloroethylene is 73.2. It seems probable, therefore, that the polymerization product has the same empirical formula as the original material, although the tetrachlorobutanes would have 72.4% chlorine.

II. Discussion of Results

The appearance of a polymerization product would make an exact determination of the rate of isomerization of the dichloroethylenes extremely difficult. The presence of the polymer would invalidate rate measurements based on dielectric constant or vapor pressure and in addition the optical difficulties would be increased due to the solid product on the window.

Definite proof that dissociation into a free radical (probably C_2H_2Cl) and a chlorine atom is the *main* primary process is lacking. The reasons for believing that this is the main process, however, are the following: (1) the spectrum is continuous, indicating definitely that a primary dissociation of some sort is involved; (2) the number of dissociated (or *activated*) molecules which polymerize eventually is of the order of 1% of those which react with hydrogen to form hydrogen chloride, providing a dimer is produced. If a higher polymer is formed this fraction is even less. It is believed that theory number (2) is to be preferred to theory number (1) for any photochemical isomerization which might be produced in this region of the spectrum. This further supports the contention in the previous paper[2] that this region of absorption resembles those obtained in all compounds having carbon chlorine bonds.

The polymerization might take place either by a free radical mechanism or by an activation of the carbon–carbon bond without dissociation. In the latter event there would be two primary processes occurring in this spectral region. It is true that ethylene absorbs slightly in this region, but the evidence indicates that the products are acetylene and hydrogen in a flowing system.[9]

Summary

1. Evidence has been brought forward tending to show that chlorine atoms are produced when *cis* and *trans* dichloroethylene are illuminated with radiation from an aluminum spark through air.

2. A small amount of polymerization product is produced which has nearly the same per cent. chlorine as the dichloroethylene from which it is formed.

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[9] Mooney and Ludlam, *Trans. Faraday Soc.*, **25**, 442 (1929).