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# Chemistry

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## Abstract

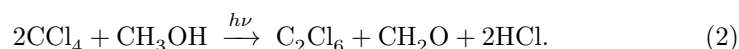
## Full Text

### Chemistry

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# PATHWAYS OF HEXACHLOROETHANE FORMATION IN PHOTOREACTIONS OF CARBON TETRACHLORIDE WITH ALCOHOLS

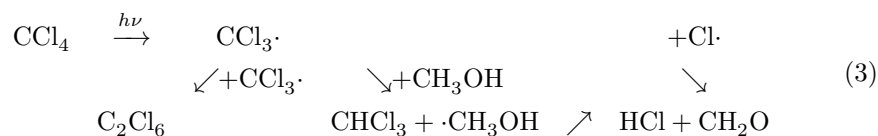
The radical decomposition of  $\text{CCl}_4$  into  $\text{CCl}_3$  radicals and  $\text{Cl}$  under irradiation with ultraviolet light <sup>(1)</sup>, upon heating <sup>(2)</sup>, and under the catalytic action of metals <sup>(3)</sup> has long been known. The reaction of  $\text{CCl}_4$  with alcohols, described by us <sup>(4)</sup>, proceeds upon heating and under the action of light through the intermediate formation of the  $\text{CCl}_3$  radical, according to the overall equations:



Reaction (1) is complicated by a number of secondary processes (formation of methyl chloride, methylal).

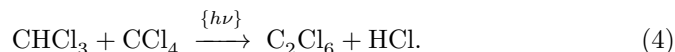
The fundamental difference between the thermo- and photoreactions consists in the fact that, in the thermal process,  $\text{CHCl}_3$  is formed, whereas under irradiation with ultraviolet light only hexachloroethane is formed. Upon heating a mixture of  $\text{CCl}_4$  with alcohols in the presence of initiators, both compounds are formed:  $\text{CHCl}_3$  and hexachloroethane <sup>(5)</sup>.

Pford <sup>(6)</sup>, repeating the reaction between alcohols and  $\text{CCl}_4$  (the reaction was carried out in excess alcohol), irradiated  $\text{CCl}_4$  with methyl and ethyl alcohols using ultraviolet light. As a result of the reaction he detected hexachloroethane, the corresponding aldehyde,  $\text{HCl}$ , and traces of  $\text{CHCl}_3$ . On this basis, Pford gives the following scheme of the process:



In this scheme, the formation of  $C_2Cl_6$  is assumed to occur as a result of dimerization of  $CCl_3$  radicals.

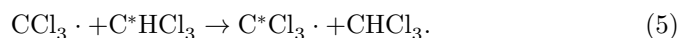
However, another pathway for the formation of  $C_2Cl_6$  may be admitted. In the photoreaction, the same process as under thermal action may occur at first (equation 1), and then  $CHCl_3$  reacts with  $CCl_4$  according to the equation



Indeed, upon irradiation with a mercury quartz lamp PRK-2 of a mixture of 46.5 g of  $CCl_4$  and 17.9 g of  $CHCl_3$  for 1 month, 4.0 g of  $C_2Cl_6$  is formed.

To test the interaction scheme, it seemed convenient to us to apply the method of labeled  $C^{14}$  atoms. To prove one process or the other, labeled  $C^{14}$  chloroform may be added to the reaction mixture of  $CCl_4$  and alcohol. If formation of  $C_2Cl_6$  proceeds according to equation (4), then forma-

the resulting  $C_2Cl_6$  must contain a label. In the case of dimerization of  $CCl_3$ -radicals obtained in the photolysis of  $CCl_4$ , hexachloroethane should be inactive. However, the following difficulties may be encountered. First, the  $CCl_3$ -radical formed during photolysis may react with  $CHCl_3$  according to the equation:

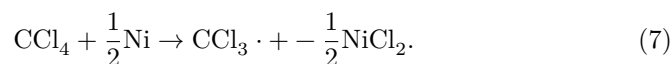


Second, the secondary  $C^*Cl_3$ -radical may react with  $CCl_4$  according to the equation:



i.e., a "chain transfer" of the  $CCl_3$ -radical may take place. Therefore we began with an investigation of the photoreaction of  $CCl_4$  and labeled  $C^*HCl_3$ . Reaction (5) is difficult to prove, since the inactive  $CHCl_3$  formed according to equation (5) will dilute the reacting active  $C^*HCl_3$  to an insignificant extent, i.e., within the error of determination.

To investigate this reaction we used another method: we used the reaction of  $CCl_4$  with metals, which proceeds with formation of  $C_2Cl_6$  (3). For this purpose we heated, to  $80^\circ$  for 10 h under nitrogen, 12.2 ml of  $CCl_4$ , 5.0 ml of  $C^*HCl_3$  (activity 900 imp/min), in the presence of skeletal Ni. In this case the primary reaction of formation of  $CCl_3$ -radicals can only be the interaction of  $CCl_4$  with Ni according to the scheme:



If the  $\text{CCl}_3$ -radicals formed then reacted according to equation (5), the resulting  $\text{C}_2\text{Cl}_6$  would be active. The  $\text{C}_2\text{Cl}_6$  (6 imp/min) and  $\text{CCl}_4$  (3 imp/min) isolated from the reaction mixture were not active, which indicates the absence of reactions (5) and (6).

The main attention in this experiment, as in all subsequent ones, was directed to purification of the isolated reaction products, and the quantitative aspect was not taken into account. To purify  $\text{C}_2\text{Cl}_6$  from an admixture of active  $\text{C}^*\text{HCl}_3$ , it was treated several times with unlabeled  $\text{CHCl}_3$  and sublimed. Unlabeled  $\text{CHCl}_3$  and  $\text{C}_2\text{Cl}_6$  were added to the  $\text{CCl}_4$  fraction after the experiment, and  $\text{CCl}_4$  was isolated by rectification. This purification method was used for all experiments.

Reaction (6) was investigated as follows. A mixture of 12.2 ml of  $\text{CCl}_4$  and 5.0 ml of  $\text{CHCl}_3$  (activity 772 imp/min) was irradiated under nitrogen with ultraviolet light for 130 h. If the  $\text{CCl}_4$  distilled off after the photoreaction acquired activity, then, consequently, exchange between the  $\text{CCl}_3$ -radical and  $\text{CCl}_4$  according to reaction (6) takes place. As a result of the reaction,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ,  $\text{C}_2\text{Cl}_6$ , and  $\text{HCl}$  were isolated. The extent of reaction was determined from the amount of  $\text{HCl}$  evolved. The isolated  $\text{CCl}_4$  proved inactive (7 imp/min), which shows the absence of "chain transfer" of  $\text{CCl}_3$ -radicals. The  $\text{C}_2\text{Cl}_6$  obtained had an activity of 565 imp/min.

Thus, reactions (5) and (6), which could interfere with the use of labeled  $\text{CHCl}_3$  to explain the mechanism of formation of  $\text{C}_2\text{Cl}_6$  in the photoreaction of  $\text{CCl}_4$  with  $\text{CHCl}_3$ , do not occur. For further investigation of the mechanism of formation of  $\text{C}_2\text{Cl}_6$  we irradiated with ultraviolet light under nitrogen for 110 h a mixture of 15.5 ml of  $\text{CCl}_4$ , 2.2 ml of  $\text{C}^*\text{HCl}_3$  (900 imp/min), and 15.0 ml of  $\text{CH}_3\text{OH}$ . From the reaction mixture were isolated  $\text{CHCl}_3$ ,  $\text{HCl}$ ,  $\text{CCl}_4$ , and  $\text{C}_2\text{Cl}_6$ , which were not active (activities:  $\text{CCl}_4$ —7 imp/min,  $\text{C}_2\text{Cl}_6$ —17 imp/min). Hence it is evident that the  $\text{CCl}_3$ -radical does not abstract H from the alcohol, i.e., in reaction (3)  $\text{CHCl}_3$  is not formed.

Consequently,  $\text{C}_2\text{Cl}_6$  is obtained only through dimerization of  $\text{CCl}_3$ -radicals formed during photolysis of  $\text{CCl}_4$ .

The impossibility, in photoreactions, of abstraction of hydrogen by the  $\text{CCl}_3$ -radical from alcohol and chloroform, and the absence of "chain transfer," in our opinion,

can be explained by a rather considerable stabilization energy, equal to 12 kcal/mole (7)—19 kcal/mole (8). In thermal processes, reactions involving the abstraction of H from alcohols proceed at comparatively high temperatures.

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