Chemistry

Corresponding Member of the Academy of Sciences of the USSR G. A. Razuvaev, N. S. Vasileiskaya,

1960

SovietRxiv

Abstract

Full Text

Chemistry

Corresponding Member of the Academy of Sciences of the USSR G. A. Razuvaev,
N. S. Vasileiskaya,
and E. P. Oleinik

PATHWAYS OF HEXACHLOROETHANE FORMATION IN PHOTOREACTIONS OF CARBON TETRACHLORIDE WITH ALCOHOLS

The radical decomposition of CCl_4 into CCl_3 radicals and Cl under irradiation with ultraviolet light ([1]), upon heating ([2]), and under the catalytic action of metals ([3]) has long been known. The reaction of CCl_4 with alcohols, described by us ([4]), proceeds upon heating and under the action of light through the intermediate formation of the CCl_3 radical, according to the overall equations:

$$2CCl_4 + CH_3OH \xrightarrow{200\text{–}210^\circ} 2CHCl_3 + CH_2O + 2HCl, \qquad (1)$$

$$2CCl_4 + CH_3OH \xrightarrow{h\nu} C_2Cl_6 + CH_2O + 2HCl. \qquad (2)$$

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, $CHCl_3$ is formed, whereas under irradiation with ultraviolet light only hexachloroethane is formed. Upon heating a mixture of CCl_4 with alcohols in the presence of initiators, both compounds are formed: $CHCl_3$ and hexachloroethane ([5]).

Pford ([6]), repeating the reaction between alcohols and CCl_4 (the reaction was carried out in excess alcohol), irradiated CCl_4 with methyl and ethyl alcohols using ultraviolet light. As a result of the reaction he detected hexachloroethane, the corresponding aldehyde, HCl, and traces of $CHCl_3$. On this basis, Pford gives the following scheme of the process:

$$\begin{array}{ccccccc} CCl_4 & \xrightarrow{h\nu} & CCl_3\cdot & & & & +Cl\cdot \\ & \swarrow +CCl_3\cdot & & \searrow +CH_3OH & & & \searrow \\ C_2Cl_6 & & & CHCl_3 + \cdot CH_3OH & \nearrow & HCl + CH_2O & \end{array} \qquad (3)$$

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

$$CHCl_3 + CCl_4 \xrightarrow{\{h\nu\}} C_2Cl_6 + HCl. \quad (4)$$

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:

$$CCl_3 \cdot + C^*HCl_3 \rightarrow C^*Cl_3 \cdot + CHCl_3. \quad (5)$$

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

$$C^*Cl_3 \cdot + CCl_4 \rightarrow C^*Cl_4 + CCl_3, \quad (6)$$

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° 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:

$$CCl_4 + \frac{1}{2}Ni \rightarrow CCl_3 \cdot + - \frac{1}{2}NiCl_2. \quad (7)$$

If the CCl_3-radicals formed then reacted according to equation (5), the resulting C_2Cl_6 would be active. The C_2Cl_6 (6 imp/min) and 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 C_2Cl_6 from an admixture of active C^*HCl_3, it was treated several times with unlabeled $CHCl_3$ and sublimed. Unlabeled $CHCl_3$ and C_2Cl_6 were added to the CCl_4 fraction after the experiment, and 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 CCl_4 and 5.0 ml of $CHCl_3$ (activity 772 imp/min) was irradiated under nitrogen with ultraviolet light for 130 h. If the CCl_4 distilled off after the photoreaction acquired activity, then, consequently, exchange between the CCl_3-radical and CCl_4 according to reaction (6) takes place. As a result of the reaction, $CHCl_3$, CCl_4, C_2Cl_6, and HCl were isolated. The extent of reaction was determined from the amount of HCl evolved. The isolated CCl_4 proved inactive (7 imp/min), which shows the absence of "chain transfer" of CCl_3-radicals. The C_2Cl_6 obtained had an activity of 565 imp/min.

Thus, reactions (5) and (6), which could interfere with the use of labeled $CHCl_3$ to explain the mechanism of formation of C_2Cl_6 in the photoreaction of CCl_4 with $CHCl_3$, do not occur. For further investigation of the mechanism of formation of C_2Cl_6 we irradiated with ultraviolet light under nitrogen for 110 h a mixture of 15.5 ml of CCl_4, 2.2 ml of C^*HCl_3 (900 imp/min), and 15.0 ml of CH_3OH. From the reaction mixture were isolated $CHCl_3$, HCl, CCl_4, and C_2Cl_6, which were not active (activities: CCl_4–7 imp/min, C_2Cl_6–17 imp/min). Hence it is evident that the CCl_3-radical does not abstract H from the alcohol, i.e., in reaction (3) $CHCl_3$ is not formed.

Consequently, C_2Cl_6 is obtained only through dimerization of CCl_3-radicals formed during photolysis of CCl_4.

The impossibility, in photoreactions, of abstraction of hydrogen by the 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.

Gorky State University
named after N. I. Lobachevsky

Received
15 IX 1959

REFERENCES

[1] H. J. Schumacher, *Zs. ang. Chem.*, **49**, 631 (1936); **51**, 763 (1938); **53**, 501 (1940).
C. S. Marvell, E. J. Prill, D. H. de Tar, *J. Am. Chem. Soc.*, **69**, 52 (1947);
M. S. Kharasch, K. Jensen, W. Urry, *J. Am. Chem. Soc.*, **69**, 110 (1947).
[2] K. Kolbe, *Ann.*, **54**, 147 (1845).
[3] S. Radziszewski, *Ber.*, **17**, 834 (1884).
[4] G. A. Razuvaev, N. S. Vasil' eiskaya, *DAN*, **80**, 69 (1951).
[5] B. N. Moryganov, *ZhOKh*, **25**, 493 (1955).
[6] K. Pfodte, *J. Pract. Chem.*, **5**, 3–4, 196 (1957).
[7] H. J. Schumacher, K. Wolf, *Zs. phys. Chem.*, **25**, 161 (1934).
[8] A. A. Miller, J. E. Willard, *J. Chem. Phys.*, **17**, 168 (1949).

Note: Figure translations are in progress. See original paper for figures.