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Abstract

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MECHANISM AND ISOTOPE EFFECT OF THE PRIMARY ACT IN THE THERMAL DECOMPOSITION OF CHLOROFORM

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In recent works devoted to the thermal decomposition of organic halogen derivatives, one of two mechanisms is usually assumed for the elementary act of decomposition of the molecules of these compounds: a radical mechanism with rupture of the C–Hal bond (R—X $\rightarrow$ R $\cdot$ +X$\cdot$), or a molecular mechanism of direct elimination of H–Hal through a four-membered transition complex (for example,

$$C_2H_5Br \rightarrow \begin{array}{c} H\text{—}Br \\ \vdots \\ H\text{—}C\text{—}C\text{—}H \\ \\ H \end{array} \rightarrow \begin{array}{c} \vdots \\ C_2H_4 \\ H \end{array} + HBr,$$

In principle, one can also imagine a third mechanism of molecular decomposition: cleavage of H–Hal from one carbon atom with the primary formation of a derivative of divalent C:

$$\begin{array}{cc} R_1 & H \\ \backslash & / \\ C & \\ / & \backslash \\ R_2 & X \end{array} \rightarrow \begin{array}{c} R_1 \\ \backslash \\ C + HX \\ / \\ R_2 \end{array}$$

We shall call this mechanism biradical* mechanism. A biradical mechanism of decomposition has been proposed at different times for some compounds, but has not been sufficiently substantiated in any one case.

Studying the thermal decomposition of methane chloroderivatives, we came to the conclusion that such a mechanism, the mechanism of direct elimination of a hydrogen halide, takes place in the case of chloroform and methylene chloride.

In the present work, data are given on the decomposition of chloroform, and also of deuterochloroform $CDCl_3$.

The reaction was studied in a jet vacuum apparatus similar to that used for investigating the decomposition of C_3H_5Cl ([1]). Chloroform at low pressures was passed through a heated reaction vessel in an excess of toluene vapor or without a carrier gas. The reaction products, together with undecomposed chloroform, entered a system of traps, where they were subjected to analysis. As is known ([2]), the products of the thermal decomposition of chloroform are HCl and C_2Cl_4, as well as small amounts of C_2Cl_6, C_2HCl_5, etc. In our work, HCl and C_2Cl_6 were determined quantitatively. Hydrogen chloride was determined by titration with alkali and by Folgard microtitration. In experiments with $CDCl_3$, in order to determine DCl in the hydrogen chloride, the latter was converted by reaction with CH_3MgJ into methane, which was analyzed on a mass spectrometer for CH_3D content**. Special experiments with a previously prepared mixture

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* This name is to a considerable extent conventional, since the particle formed may not be a biradical in the strict sense of the word (for example, CO).

** Mass-spectrometric analysis of the mixture of HCl and DCl itself proved extremely difficult.

HCl and DCl showed that the isotopic composition of methane coincides, to an accuracy of 1%, with the composition of the hydrogen chloride taken. In this way it was possible to analyze less than $1 \cdot 10^{-4}$ mole of DCl. C_2Cl_6 was frozen out in a U-shaped tube cooled to $-40°$——$50°$ and was determined by weighing.

Deuterochloroform was synthesized from chloral by treating it with a solution of K_2CO_3 in heavy water (b.p. 61°, $n_D^{20} = 1.4452$).

In the experiments on the isotope effect, ordinary chloroform was synthesized according to the same scheme. Toluene was obtained by hydrolysis of pure *p*-toluenesulfonic acid, followed by distillation on a column (b.p. 110.5°, $n_D^{20} = 1.4968$).

The decomposition of chloroform was studied in the interval 485–660°. Table 1 gives the results of experiments at 584°. It may be seen that the decomposition of chloroform follows a monomolecular law.

In experiments without carrier gas, the first-order rate constant (the constants were calculated from HCl) is retained at pressures of 16–36 mm, but decreases at lower pressures. In a stream of toluene, no decrease of the rate constant at low pressures of $CHCl_3$ is observed, and the reaction rates in toluene and without carrier gas are equal. This, on the one hand, shows that the decrease of the constant at low pressures is associated with energetic rather than chemical factors, and, on the other hand, demonstrates the absence of an inhibiting action of toluene in the decomposition reaction. It is important to note that in experiments in a stream of toluene, dibenzyl is almost completely absent from the reaction products (less than 2–3% of HCl). The amount of hexachloroethane in the reaction products without carrier gas was approximately 10% of HCl.

Table 1

No.	P_{CHCl_3}, mm	$P_{C_6H_5CH_3}$, mm	τ_k, sec	k, sec^{-1}
1	35.9	–	0.324	0.294
2	29.3	–	0.354	0.279
3	29.0	–	0.354	0.266
4	23.1	–	–	0.300
5	19.0	–	0.456	0.249
6	17.3	–	0.426	0.281
7	10.6	–	0.78	0.182
8	9.6	–	1.01	0.203
9	7.66	10.1	0.288	0.266
10	6.40	–	1.24	0.143
11	2.03	11	0.294	0.250
12	1.84	13.8	0.416	0.272
13	1.18	15.2	0.366	0.282

Packing the reaction vessel with glass wool or quartz glass was not accompanied by any noticeable change in the reaction rate. The temperature dependence of the rate constant in the coordinates $\lg k$, $\frac{1}{T}$ (Fig. 1, straight line 1) is expressed by the formula:

$$k = 2.63 \cdot 10^{11} e^{-\frac{47000}{RT}} \text{ sec}^{-1}$$

These data are already in sharp contradiction with the radical mechanism of decomposition of $CHCl_3$, proposed in the recent work of Samelyuk and Bernstein ([2]):

$$CHCl_3 \rightarrow Cl\cdot + \cdot CHCl_2$$

$$Cl + CHCl_3 \rightarrow HCl + \cdot CCl_3$$

$$\cdot CHCl_2 + CHCl_3 \rightarrow CH_2Cl_2 + \cdot CCl_3.$$

Indeed, the decomposition rate constant is too large (the activation energy too small) for homogeneous radical decomposition at the C–Cl bond, which should proceed with an activation energy equal to $D(C—Cl)$ in $CHCl_3$ ($\sim$ 70 kcal). A radical mechanism, when the reaction is carried out in toluene, should have led to the formation of dibenzyl in amounts comparable with the amount of HCl (cf. decomposition of bromine derivatives of methane ([3,4])), since of the

Fig. 1. Dependence of the reaction rate constant k on temperature: a–$CHCl_3$ in a stream of toluene, b–$CDCl_3$ in a stream of toluene, v–$CHCl_3$ without carrier gas

Figure 1: Fig. 1. Dependence of the reaction rate constant k on temperature: a–$CHCl_3$ in a stream of toluene, b–$CDCl_3$ in a stream of toluene, v–$CHCl_3$ without carrier gas

two particles formed ($Cl\cdot$ and $\cdot CHCl_2$) the chlorine atom in any case should have reacted with toluene with formation of the benzyl radical. We also cannot accept any chain scheme of decomposition

$CHCl_3$, since the absence of inhibition of the reaction by toluene indicates the absence of chains.

Table 2

Decomposition of $CHCl_3$ and $CDCl_3$ in toluene ($t = 57^\circ$)

Nos. of experiments	P_{CHCl_3}, mm	P_{CDCl_3}, mm	P_{total}, mm	τ_k, sec	k_{CHCl_3}	k_{CDCl_3}
1	0.758	–	19.4	0.684	0.222	–
2	0.856	–	19.1	0.656	0.233	–
3	–	1.295	17.4	0.700	–	0.135
4	–	2.51	17.0	0.706	–	0.145
5	–	2.69	19.6	0.672	–	0.143
6	–	2.85	19.1	0.709	–	0.138
7	3.89	–	23.5	0.687	0.258	–
8	4.16	–	22.3	0.720	0.209	–
9	4.17	–	22.7	0.687	0.234	–
Average					$0.231 \pm$	$0.140 \pm$
. . .					0.008	0.003

It is interesting to compare the data on the decomposition of chloroform and deuterochloroform. From Table 2 it follows that the decomposition proceeds with a noticeable isotope effect. The ratio of the decomposition rates of light and heavy chloroform at 574° is 1.65. In Fig. 1 (straight line 2) the temperature dependence of the decomposition rate of $CDCl_3$ is given. The slope of the straight line, as for $CHCl_3$, gives for the activation energy a value of 47 ± 2 kcal. The accuracy of the experiment, however, is insufficient to determine separately the contribution of the isotope effect to the value of the activation energy and to the pre-exponential factor.

Fig. 1. Dependence of the reaction rate constant k on temperature: a–$CHCl_3$ in a stream of toluene, b–$CDCl_3$ in a stream of toluene, v–$CHCl_3$ without

carrier gas.

Table 3 gives the data of some experiments for determining the isotopic composition of hydrogen chloride in the reaction products of $CDCl_3$. As can be seen from the table, the hydrogen chloride formed during the decomposition of $CDCl_3$ in an excess of toluene contains about 35% DCl. It is noteworthy that this relative DCl content depends neither on the ratio of $CDCl_3$ to toluene, nor on the temperature, nor on the contact time. The isotope effect in the decomposition of chloroform indicates that, in the rate-determining stage, there participates

hydrogen atom. The formation of considerable amounts of DCl in the decomposition of $CDCl_3$ in toluene and the first order of the reaction indicate that this rate-determining step is a biradical decomposition:

$$CHCl_3 \rightarrow HCl + CCl_2 \tag{1}$$

Indeed, in the case of primary formation of atomic chlorine, it would have had to react with toluene (which is always present in excess) with the formation only of light HCl. To prove this, experiments were carried out in which molecular chlorine was added to a stream of $CDCl_3$ in toluene (under conditions of slight decomposition of $CDCl_3$). The hydrogen chloride formed proved to be light. Moreover, if the isotopic composition of the hydrogen chloride formed were a consequence of competition between the reaction of the Cl atom with light toluene and with heavy chloroform, then the amount of DCl in the products would depend on the ratio of chloroform to toluene in the stream. In fact, this is not observed. The considerable amounts of light HCl in the hydrogen chloride among the products of the reaction of CDCl in toluene indicate, however, that part of the hydrogen chloride (approximately half—as shown by experiments without toluene) is formed not by reaction (1), but by some reaction with toluene. This cannot simply be an exchange reaction of DCl with toluene. Special experiments carried out at temperatures up to 700° and contact times up to 0.4 sec showed that DCl does not exchange appreciably with toluene under these conditions. Moreover, if exchange of the primarily formed DCl with toluene occurred, then the isotopic composition of the hydrogen chloride would depend on the contact time.

Taking into account the equality of the reaction rates in toluene and without a carrier gas, we assume that in both cases a secondary reaction takes place with formation of HCl. The following reactions may be assumed.

Without a carrier gas:

$$CCl_2 + CHCl_3 \rightarrow HCl + C_2Cl_4;$$

In toluene:

$$CCl_2 + C_6H_5CH_3 \rightarrow HCl + C_6H_5CH{=}CHCl.$$

Table 3

No.	t, °C	P_{CDCl_3}, mm	$P_{C_6H_5CH_3}$, mm	τ_k, sec	DCl, %
1	587	7.01	–	1.48	84
2	582	3.36	15.9	0.490	36
3	622	0.764	14.0	0.216	33.4
4	652	0.286	16.8	0.178	39
5	652	1.88	16.9	0.362	35
6	652	0.507	18.9	0.107	30
7	652	0.570	15.9	0.338	38

The formation of C_2Cl_6 is apparently a consequence of dimerization of the CCl_3 radicals, possibly formed by the reaction

$$2CCl_2 \rightarrow CCl + CCl_3.$$

Of course, such a mechanism of the secondary reactions is purely hypothetical. However, independently of this, the primary decomposition of chloroform by a biradical mechanism seems to us proven.

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