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Abstract

Full Text

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THERMAL DECOMPOSITION OF CERTAIN ORGANIC COMPOUNDS IN THE PRESENCE OF DEUTERIUM

(Presented by Academician N. N. Semenov, 14 VII 1960)

The study of the photolysis of organic compounds, carried out under various conditions, has made it possible to develop a method for determining the ratios of rate constants and the differences in activation energies of competing elementary radical reactions (¹).

Fig. 1. Temperature dependence of the distribution of various deuteromethanes formed during the pyrolysis of acetone

Fig. 2. Temperature dependence of the ratio CH_3D/CH_4 in pyrolysis experiments:
I—di-tert-butyl peroxide, *II*—acetone, *III*—dimethylmercury, *IV*—acetaldehyde

If the rate constant and activation energy of one of the elementary steps are known, then it appears possible to determine the corresponding quantities for other elementary reactions as well. One of the best-known elementary processes most frequently used for this purpose is the reaction of radicals with molecular deuterium.

In this case the rates of two processes are compared, for example:

$$\dot{R} + R_1H \rightarrow RH + \dot{R}; \tag{1}$$

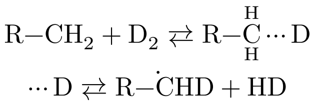
$$R + D_2 \rightarrow RD + \dot{D}. \tag{2}$$

By determining the value of the ratio of the amounts of the products RH and RD formed at different temperatures, and knowing the activation energy of process (2) (for methyl radicals $E_2 = 11.7 \pm 0.1$ kcal ([2])), one can find the activation energy of elementary reaction (1).

It should be noted, however, that this method has been developed exclusively for photochemical reactions, since when it is applied to other types of reactions, in particular to thermal ones, considerable experimental difficulties arise. These difficulties are due mainly to the possibility of secondary processes taking place, leading to the same products as those obtained in reactions (1) and (2).

In connection with the study of the pyrolysis mechanism of certain organic compounds, we have investigated the question of the applicability of deuterium to determine the constants of the elementary processes in these reactions. At the same time, carrying out this study was stimulated by the need for experimental verification of the conclusions of Voevodskii, Lavrovskaya, and Mardaleishvili ([3]) concerning the possibility of isotopic exchange of free radicals with molecular deuterium.

According to these authors, the exchange reaction



$$R{-}CH_2 + D_2 \rightleftarrows R{-}\overset{H}{\underset{H}{C}}\cdots D \cdots D \rightleftarrows R{-}\dot{C}HD + HD \tag{3}$$

proceeds at a high rate and, in an excess of deuterium, leads to complete exchange for deuterium of the hydrogen atoms at the valence-unsaturated carbon atom.

Table 1

Pyrolysis of acetone, 508°C

Run No.	τ, sec	CH_3D/CH_4	Run No.	P, mm Hg	CH_3D/CH_4
Reactor without packing	**Reactor without packing**	**Reactor without packing**	**Reactor without packing**	**Reactor without packing**	**Reactor without packing**
$P = 0.8$ mm Hg	$P = 0.8$ mm Hg	$P = 0.8$ mm Hg	$\tau = 1.60$ sec	$\tau = 1.60$ sec	$\tau = 1.60$ sec
266	0.34	3.61	271	6.0	3.60
267	0.45	3.58	272	5.0	3.61

Run No.	τ, sec	CH_3D/CH_4	Run No.	P, mm Hg	CH_3D/CH_4
268	0.77	3.63	273	4.0	3.59
269	1.48	3.59	274	2.0	3.61
270	1.72	3.60	275	1.0	3.60
Reactor with packing $P = 1.0$ mm Hg	**Reactor with packing** $P = 1.0$ mm Hg	**Reactor with packing** $P = 1.0$ mm Hg	**Reactor with packing** $\tau = 1.46$ sec	**Reactor with packing** $\tau = 1.46$ sec	**Reactor with packing** $\tau = 1.46$ sec
279	0.24	2.98	296	6.0	3.60
280	0.35	2.97	297	5.0	3.61
281	0.65	2.99	298	4.0	3.54
282	1.17	2.98	299	2.0	3.30
823	1.70	2.99	300	1.0	2.98
			301	0.5	2.44

In the present work we studied the reaction of abstraction of a hydrogen atom by methyl radicals formed during the pyrolysis of acetaldehyde, acetone, dimethylmercury, and di-tert-butyl peroxide, from the molecule of the starting substance in the presence of D_2. The experiments were carried out in a high-vacuum flow apparatus, at various contact times (0.1-4 sec), total pressure of 0.6-5 mm Hg, and in the temperature interval 130-850°C, measured with an accuracy of $\pm 1^{\circ}$. The thermal decomposition reaction of the compounds studied by us was carried out in a quartz vessel ($V = 130$ cm^3) to a conversion depth of 0.001-10%, with a 10-15-fold excess of deuterium.

In a number of experiments the reactor was filled with quartz tubes, which led to a change in S/V by a factor of 15.

The isotope composition of methane, formed as the main product in the pyrolysis of each of the substances studied by us under various conditions, was studied in greatest detail. Measurements of the ratio of the various deuteromethanes were carried out on an MS-4 mass spectrometer.

Figure 1 gives the temperature dependence of the distribution of the various deuteromethanes formed in the pyrolysis of acetone. The distribution of deuteromethanes formed from the other substances investigated by us has an analogous character. Up to a temperature of 500-600°, the depth of reaction at various contact times is 0.01-5%. Under these conditions methane consists exclusively of CH_3D and CH_4 molecules. Their ratio at a given temperature does not depend on the total pressure or the contact time, which may serve as an indication of the absence of secondary processes under these conditions. At temperatures above approximately 600°, the reaction proceeds to a greater depth, up to 10-30%, and poly-substituted methanes, up to CD_4, are formed as products. The latter circumstance is due to secondary processes, apparently mainly at the expense of an increase in the concentration of deuterium atoms in the reaction zone. In experiments on the thermal decomposition of acetone at 500°, in which the reactor was filled with quartz tubes, it was observed that at pressures above approximately 4-5 mm Hg the ratio CH_3D/CH_4 is the same as in the case of a reactor without packing. However, in the first

case, in contrast to the second, a decrease in the total pressure of the mixture leads to a decrease in the ratio CH_3D/CH_4 (Table 1).

As in the case of the reactor without packing, in the packed reactor the ratio CH_3D/CH_4 does not depend on the contact time.

These facts indicate a heterogeneous influence of the surface of the reactor and of the packing on the reaction rate and, in particular, on the increase in the fraction of the yield of CH_4, which is manifested only at low pressures ($P < 4$ mm Hg).

On the basis of the data obtained, it may be asserted that under the experimental conditions we selected ($P > 1$ mm Hg and in the absence of packing), the results of which are given below, there is no appreciable fraction of secondary processes or noticeable influence of the reactor wall on the reaction.

Table 2

Substance	ΔE	E_1	E_1 lit.
$CH_3—CO—CH_3$	2.5 ± 0.2	9.2 ± 0.3	9.6 ± 0.4 (6)9.7 ± 0.1 (7)9.5 ± 1.0 (8)
CH_3CHO	3.8 ± 0.4	7.9 ± 0.5	7.5 ± 0.4 (9)
$(CH_3)_3CO_2$	2.2 ± 0.2	9.5 ± 0.3	11.7 ± 0.3 (4)
$Hg(CH_3)_2$	1.9 ± 0.4	9.8 ± 0.5	10.8 ± 0.5 (10)

In Fig. 2 are presented experimental data obtained in studying the temperature dependence of the ratio CH_3D/CH_4 in experiments on the pyrolysis of the compounds investigated. The values calculated from them for the difference in the activation energies of processes (1) and (2), and the absolute values of the activation energy for the abstraction by methyl radicals of hydrogen atoms from the corresponding compounds, given in Table 2, are in satisfactory agreement with the literature data. The noticeable discrepancy in the value of E_1 for the reaction of hydrogen-atom abstraction from di-tert-butyl peroxide is apparently due to an overestimated value of the activation energy in the work of Pritchard and Trotman-Dickenson (4), since such a large value of the activation energy was found only for the abstraction by a methyl radical of a hydrogen atom from methane ($E_1 = 12.8$ kcal) (1).

The experimental data we have obtained may serve as an indication that measurements of the rate constants of elementary radical reactions by the method of comparing the rates of reactions (1) and (2) are not complicated by secondary processes only up to temperatures of approximately 500—550°.

From the agreement of the values of the activation energies for the abstraction by methyl radicals of hydrogen atoms from the corresponding organic compounds in experiments on their photochemical and thermal decomposition it follows that, in the photolysis of the substances we investigated, the "hot" radicals discussed in the literature (^{5}) are not formed.

Together with these conclusions one may infer that the mechanism proposed by Voevodsky and co-workers for the exchange of radicals with molecular deuterium under conditions of a thermal reaction does not occur, since polysubstituted molecules of the final products appear only at temperatures above 600° as a result of secondary substitution processes.

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