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Figure 1

Figure 1: Figure 1

Abstract

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KINETICS OF THE THERMAL DECOMPOSITION OF N,N-DIMETHYLNITROAMINE

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The mechanism of the thermal decomposition of nitro compounds has long attracted interest. A detailed analysis of reactions of this type, which proceed, as a rule, in the condensed phase, is complicated by the influence of a number of factors, such as phase transitions, catalysis by reaction products, the forces of the crystal lattice, etc. Therefore it is necessary to study the thermal decomposition of the simplest nitro compounds in the gas phase, where the various complicating factors are reduced to a minimum.

Fig. 1. Kinetics of the thermal decomposition of dimethylnitroamine at 200° C. 1—the dependence of the gas pressure on time; 2—the same dependence in semilogarithmic coordinates

We selected for investigation the simplest representative of the class of nitroamines—N,N-dimethylnitroamine (DMNA). The kinetics of its thermal decomposition was studied in the temperature range 180-260° by the manometric method, using a glass membrane manometer whose design has been described previously ([1]).

The data obtained show that the reaction proceeds in two stages, each stage being described by a first-order equation. Indeed, from Fig. 1 it is seen that in the coordinates $\lg(P_\infty - P) - t$ (P is the gas pressure at time t, P_∞ is the final pressure) a curve is obtained which, in two different regions, can be approximated by straight lines.

To determine whether the rate constants of these stages, k' and k'', depend on the initial gas pressure, experiments were carried out at a temperature of 240°, in which the initial pressure P_0 was varied from 64 to 400 mm Hg. The results obtained (Table 1) show that, within the experimental error, the constant k' does not change, while k'' increases somewhat with increasing P_0.

Additions of nitrogen dioxide have a noticeable effect on the kinetics of DMNA decomposition. Figure 2 gives kinetic curves for the decomposition of DMNA in the absence and in the presence of various amounts of NO_2. The DMNA sample in these experiments was chosen so that its partial pressure at the beginning of the experiment was ~50 mm Hg. As can be seen from the figure, in the presence of NO_2 the reaction is accelerated and has kinetics different from that of pure DMNA.

The main product of the thermal decomposition of DMNA is N,N-dimethylnitrosoamine (^{2}). Several experiments were carried out with this substance. As can be seen from Fig. 3, at 240° dimethylnitrosoamine itself does not decompose, but is capable of reacting with NO_2. The thermal decomposition of DMNA in the presence of dimethylnitrosoamine was also studied: at 240° and an equimolecular ratio of the components ($P_2 = 480$ mm Hg), the reaction proceeds in the same way as in the case of pure DMNA. The rate constants are, respectively: $k = 5.8 \cdot 10^{-4}$ sec^{-1}, $k'' = 8.8 \cdot 10^{-4}$ sec^{-1}. Figure 4 and Table 2 present the temperature dependence of the rate constants. The Arrhenius dependence obtained from these data by the method of least squares has the form: $k = 10^{14.1} \exp(-40800 \pm 1800/RT)$ sec^{-1}. As for the quantity k'', it does not obey the Arrhenius equation (see Fig. 4).

The thermal decomposition of DMNA in the temperature range 165-200° was studied by Flournoy (^{2}), who proposed the following reaction scheme:

$$(CH_3)_2NNO_2 \xrightarrow{k_1} (CH_3)_2N\cdot + NO_2, \tag{I}$$

$$(CH_3)_2NNO_2 + NO_2 \xrightarrow{k_2} NO + \text{oxidation products}, \tag{II}$$

$$(CH_3)_2N\cdot + NO \xrightarrow{k_3} (CH_3)_2NNO, \tag{III}$$

and in reaction (II) one molecule of DMNA reduces at least 4 molecules of NO_2. Flournoy did not carry out a detailed kinetic analysis of the process.

If it is assumed that only one molecule of NO_2 participates in the limiting act of reaction (II), then the rate constant k_2 will not be a true one: it will include a coefficient taking into account the number of NO_2 molecules participating in reaction (II). Denoting the concentration of DMNA by x, and the concentration of NO_2 by y, for reactions (I) and (II) we obtain the following system of differential equations:

$$\frac{dx}{dt} = -k_1 x - k_2 xy, \tag{1}$$

$$\frac{dy}{dt} = -k_1 x - k_2 xy. \tag{2}$$

Fig. 2. Effect of NO_2 on the kinetics of the thermal decomposition of dimethylnitroamine (the DMNA charge was the same in all experiments). 1 — in the absence of NO_2. 2, 3, 4 —in the presence of NO_2 at different initial gas pressures (P_0): 2 —$P_0 = 165$, 3 —$P_0 = 345$, 4 —$P_0 = 590$ mm Hg; 5 — dependence $\lg(P_\infty - P) - t$ for curve 2.

Figure 2: Fig. 2. Effect of NO_2 on the kinetics of the thermal decomposition of dimethylnitroamine (the DMNA charge was the same in all experiments). 1 — in the absence of NO_2. 2, 3, 4 —in the presence of NO_2 at different initial gas pressures (P_0): 2 —$P_0 = 165$, 3 —$P_0 = 345$, 4 —$P_0 = 590$ mm Hg; 5 —dependence $\lg(P_\infty - P) - t$ for curve 2.

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At small degrees of conversion, y is negligibly small. Therefore, setting $y = 0$, we obtain from (1):

$$-\frac{dx}{dt} = k_1 x. \tag{3}$$

Applying the method of stationary concentrations, let us set

$$\frac{dy}{dt} = 0.$$

Then from (1) and (2) we shall have:

$$y = \frac{k_1}{k_2}; \tag{4}$$

$$-\frac{dx}{dt} = 2k_1 x. \tag{5}$$

Thus, in the initial stage the thermal decomposition of DMNA should be described by equation (3), and then, if the stationarity condition is fulfilled, by equation (5). As is seen from Fig. 1, in complete agreement with (1), (3), and (5), the thermal decomposition of DMNA proceeds in two stages, and at each stage the reaction is first order. Establishing the relation between the data of Fig. 1 and equations (1), (3), and (5), we naturally assume that

$$-\frac{dx}{dt} = \frac{dP}{dt}.$$

On the basis of what has been said, one may take $k' = k_1$, $k'' = 2k_1$, so that the relation $k''/k' = 2$ should hold. From the data of Table 2 it is seen that $k''/k' = 2.0 \pm 0.8$. Taking into account that comparatively small errors in the quantities k' and k'' lead to significant errors in the value k''/k', it must be recognized that the agreement of the experimental value with the calculated one is quite good. Let us also note that the observed influence of NO_2 on the kinetics of the thermal decomposition of DMNA is also consistent with reaction scheme (I)–(III). The fact that the numerical values of the first-order rate constants obtained by Flournoy lie between the values k' and k'' (see Fig. 4) shows that he was unable to distinguish the two stages and, in processing the data, obtained average values.

The consideration carried out above is based on the application of the method of stationary concentrations. However, this method cannot always be applied (^{3}), and at present we do not have data that would make it possible to decide the question of the correctness of its application to the reaction under study. Therefore it is of interest to consider the exact solution of the system of equations (1), (2).

Fig. 3. Kinetics of the interaction of N,N-dimethylnitrosoamine with NO_2 (the charge of dimethylnitrosoamine is the same in all experiments). 1—in the absence of NO_2. 2, 3, 4—in the presence of NO_2 at P_0: 2—$P_0 = 165$, 3—$P_0 = 265$, 4—$P_0 = 405$ mm Hg.

Fig. 4. Temperature dependence of the rate constants k' (a) and k'' (b). The vertical dashes mark the data of Flournoy (^{2}).

Under the initial conditions $t = 0$, $x = x_0$, $y = 0$, this solution has the form

$$y + 2\frac{k_1}{k_2}\ln\left(1 - \frac{k_2}{k_1}y\right) = x - x_0,$$

$$t = \int_0^y \frac{dz}{\left[x_0 + z + 2\frac{k_1}{k_2}\ln\left(1 - \frac{k_2}{k_2}z\right)\right](k_1 - k_2 z)}. \tag{6}$$

It, of course, can no longer be interpreted as simply as was done in the approximate treatment. On the other hand, the system of equations (6) was obtained without any assumptions, so that its experimental verification (which can be carried out if the quantities k_1 and k_2 are known at the given temperature) should serve as one of the criteria for the correctness of the reaction scheme (I)–(III).

The second equation of system (6) can be written in the equivalent form:

$$y = \frac{k_1}{k_2}\left(1 - \exp\left[-k_2\int_0^t x(t)\,dt\right]\right). \tag{7}$$

From this equality it follows, first, that $y < k_1/k_2$. Secondly, since at any moment of time $x(t) \geqslant 0$, we obtain from (7) that y is a nondecreasing function of time, i.e., at no stage of the reaction should the concentration of NO_2 decrease. The derived inequality $y < k_1/k_2$ by no means discredits the possibility of applying the method of stationary concentrations in our case. It only shows that this method, and consequently inequalities (4) and (5), are fulfilled only in the first approximation. Therefore, by virtue of (1), the equality $k'' = 2k_1$ (which agrees well with the experimental data) should be replaced by the more rigorous $k'' = k_1 + k_2 y$, and at sufficiently high degrees of conversion $y = \text{const}$.

Since $k' = k_1$, it is quite natural that k' does not depend on the initial gas pressure and obeys the Arrhenius equation. As is evident from of the second equation of system (6), an increase in the initial gas pressure should lead to an increase in y. Therefore, by virtue of (8), k'' should also increase, which is indeed observed experimentally (see Table 1).

Table 1

Effect of the initial pressure on the kinetics of the thermal decomposition of DMNA at 220°

P_0, mm Hg	$k' \cdot 10^4$, sec^{-1}	$k'' \cdot 10^4$, sec^{-1}	P_0, mm Hg	$k' \cdot 10^4$, sec^{-1}	$k'' \cdot 10^4$, sec^{-1}
64	4.8	6.8	270	5.0	9.1
80	4.5	6.6	272	3.8	7.0
80	5.2	7.1	279	5.8	9.7
average	4.8 ± 0.3	6.9 ± 0.2	average	5.1 ± 1.3	8.4 ± 1.5
214	6.4	8.8	365	4.5	9.8
226	5.7	8.8	380	4.9	10.4
230	5.1	8.9	390	6.7	11.9
241	4.5	7.5	398	5.8	10.8
260	4.8	8.2	400	4.6	10.4
262	5.4	7.5	average	5.3 ± 1.0	$10.7\pm, 10$
268	4.1	8.7			

Thus, the scheme considered describes the course of the process satisfactorily in general outline, although a number of unclear points remain. Not knowing the value of k_2, it is difficult to say how justified the assumption made is,

$$-dP_x/dt = dP/dt.$$

It is also not entirely clear why inhibition of the reaction is absent upon introduction of dimethylnitrosoamine (as a result of the interaction of the latter with NO_2). Finally, for better agreement with experiment, the reaction scheme (I)–(III) should be supplemented by the reaction

$$(CH_3)_2NNO + NO_2 \rightarrow \text{products.} \qquad \text{(IV)}$$

Table 2

Temperature dependence of the rate constants of the thermal decomposition of DMNA

Temp., °C	$k' \cdot 10^4$, sec^{-1}	$k'' \cdot 10^4$, sec^{-1}	k''/k'
180	$2.2 \cdot 10^{-2}$	$4.8 \cdot 10^{-2}$	2.2
200.5	$1.5 \cdot 10^{-1}$	$4.3 \cdot 10^{-1}$	2.9
210	$4.5 \cdot 10^{-1}$	1.1	2.4
215.5	$6.4 \cdot 10^{-1}$	1.6	2.5
220	$9.0 \cdot 10^{-1}$	2.3	2.6
225	1.5	3.9	2.6
230	2.0	4.7	2.4
234.5	4.6	6.0	1.3
235	3.9	8.0	2.0
240	5.1	8.4	1.7
250	8.5	15.1	1.8
260*	–	24.5	–
260*	–	31.0	–

* At 260° the second stage begins so rapidly that k' cannot be determined.

If scheme (I)–(IV) is adopted, then the activation energy 40.8 ± 1.8 kcal/mole refers to the reaction of rupture of the N–N bond in DMNA. The N–N bond energy in DMNA was recently determined (4) by the electron-impact method and was found to be 47-48 kcal/mole. This value is somewhat higher than the activation energy determined by us. Nevertheless, it should be taken into account that the electron-impact method often gives insufficiently accurate results. The value of 55 kcal/mole obtained for the N–N bond in DMNA by a thermochemical calculation (5) essentially represents an average bond energy and in no way can be identified with the energy of the N–N bond in DMNA.

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