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ON THE THERMAL DECOMPOSITION OF NITROCELLULOSE IN VACUUM

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It is known that the thermal decomposition of nitrocellulose, which, if the gaseous decomposition products are not removed, proceeds with strong acceleration (see, for example, ([1])), takes place with a constant absolute rate of elimination of gaseous nitrogen compounds if it is carried out in a stream of inert gas ([2]). However, constancy of the absolute rate over a considerable portion of the decomposition means a substantial increase in the relative rate. It could be assumed that the reason for this increase is incomplete removal of the decomposition products during decomposition in a stream of inert gas. To test this assumption, A. D. Lebedev (1954) studied the decomposition of nitrocellulose with continuous pumping-off of the gases formed; the pressure in this case did not exceed $5 \cdot 10^{-4}$ mm Hg. To determine the rate of gas evolution, the pumps were disconnected for a short time; the increase in pressure, measured with a McLeod manometer, served as a measure of the rate of gas evolution. Between the decomposition vessel and the manometer there was a trap with liquid nitrogen, so that only the formation of gases that were difficult to condense and not retained by it was measured. Contrary to expectation, Lebedev' s experiments showed that the absolute rate of gas evolution under the indicated conditions does not decrease as decomposition proceeds, but increases strongly, severalfold (up to 8 times).

In connection with these results, the decomposition of nitrocellulose (13.35% N) in vacuum was investigated in greater detail. In addition to determining the quantity of difficultly condensing gases, the rate of formation of gases condensing in the trap was simultaneously determined. This was achieved by using two parallel, alternately switched traps. After operating for a certain time, one of the traps was switched off; the pressure of the decomposition products, after it had been warmed to room temperature, was measured with a membrane manometer, and the volume of gases was calculated (according to Clapeyron' s law). Along with this, the loss in weight of the specimen was determined with a McBain balance. The experiments were carried out at different temperatures (160–135°).

The graphs in Fig. 1 show that at 160° the rate of formation of gases condensing in the trap, greatest at the initial moment, continuously decreases; the rate of

Figure 1

Figure 1: Figure 1

formation of gases not captured by the trap, on the contrary, in agreement with Lebedev' s data, increases: relatively small at first, at the maximum it increases 7-8 times and approaches the rate of formation of the condensing gases. After passing through the maximum, the rate of formation of the difficultly condensing gases decreases. The volume of difficultly condensing gases amounts to from 1/4 to 1/3 of the total volume of gaseous decomposition products. In accordance with the described course of the curves for both rates, the total rate of gas evolution remains approximately constant for some time—until the maximum of the curve for the formation of difficultly condensing gases is reached—and then decreases sharply. The same picture of the course of decomposition is confirmed by the curves of loss in weight.

The graph of the dependence of the rates of gas evolution on temperature (Fig. 2) makes it possible to calculate (Table 1) the kinetic coefficients of the Arrhenius equation. The values of E and B for the rates of loss in weight and formation of condensing gases are practically identical. Here E is close to the activation energy of the primary process in the decomposition of alkyl nitrates, presumably consisting in the detachment of the NO_2 group ([3]). In turn, they are very close to the data of Will ([2]), obtained in the decomposition of nitrocellulose in a stream of inert gas $\left(k = 10^{17.5} \cdot e^{-43700/RT}\right)$. In decomposition

Fig. 1. Curves of the change of rates with time in the decomposition of nitrocellulose at temperatures 160, 150, and 145°: **1** —gases difficult to condense; **2** —condensing gases; **3** —sum of difficult-to-condense and condensing gases; **4** —loss in weight; **5** —gas evolution without evacuation of gases (at 160° $m/v = 15.8 \cdot 10^{-4}$ g/cm^3; at 145° $m/v = 13.9 \cdot 10^{-4}$ g/cm^3); **6** —gas evolution at quasi-constant pressure.

without removal of gases, the rate of gas evolution is noticeably greater, and its temperature dependence smaller; correspondingly, B is also smaller.

From the graphs of Fig. 1 it is seen that the dependence of the rate of gas evolution on time during the decomposition of nitrocellulose in vacuum is different for condensing and difficult-to-condense gases. This difference is difficult to explain without resorting to the assumption that, during decomposition, at least two consecutive reactions take place. Judging by the character of the curves, the formation of condensing products should be regarded as the result of primary processes. The simultaneous formation, in addition to condensing gases, of an intermediate non-gaseous product of limited stability, whose subsequent transformation is accompanied by the formation of difficult-to-condense* gases, would give the general picture of the course of decomposition that is observed experimentally.

However, the formation of condensing gases also cannot be regarded as a simple

monomolecular reaction. If at 160° there is observed a non-

* It should not be thought that, in this assumed reaction, only difficult-to-condense gases can be formed—simultaneous formation of condensing gases is possible; then the rate of formation of the latter represents the sum of two reactions.

a continuous decrease of this rate with time according to a law close to that of a first-order reaction, then at lower temperatures there is a substantial deviation from this regularity, as though this reaction in turn were a combination of two consecutive (or parallel) reactions. Thus, at 150 and 145° (Fig. 1) the rate of formation of condensing products at first decreases slowly; over a considerable interval of time this rate remains constant. As a result, the total rate of gas formation increases noticeably.

From the facts described it follows that such integral characteristics of decomposition as the total rate of gas formation or the loss in weight are, in the case of nitrocellulose, the result of a combination of a number of reactions and cannot be directly used for calculating the kinetic parameters of individual reactions.

Table 1

Kinetic coefficients of reaction rates in the thermal decomposition of nitrocellulose in vacuum at 135-160°

Reaction characteristic from which the rate constant was calculated	Initial values of rate constants, $K \cdot \sec^{-1} \cdot 10^5$	Initial values of rate constants, $K \cdot \sec^{-1} \cdot 10^5$	Initial values of rate constants, $K \cdot \sec^{-1} \cdot 10^5$	Initial values of rate constants, $K \cdot \sec^{-1} \cdot 10^5$	E, kcal/mol	$\lg B$	Method of calculating E
	135°	145°	150°	160°			

Reaction characteristic from which the rate constant was calculated	Initial values of rate constants, $K \cdot \sec^{-1} \cdot 10^5$	Initial values of rate constants, $K \cdot \sec^{-1} \cdot 10^5$	Initial values of rate constants, $K \cdot \sec^{-1} \cdot 10^5$	Initial values of rate constants, $K \cdot \sec^{-1} \cdot 10^5$	E, kcal/mol	$\lg B$	Method of calculating E
Loss in weight*	0.090	0.33	0.65	2.4	44600	17.8	By superposition of weight-loss curves over time
Formation of gases	0.18	0.60	1.1	3.3	43400	17.5	From initial rates of gas formation
Formation of condensing gases	0.24	0.77	1.5	4.9	42100	16.9	Same

Reaction characteristic from which the rate constant was calculated	Initial values of rate constants, $K \cdot \sec^{-1} \cdot 10^5$	Initial values of rate constants, $K \cdot \sec^{-1} \cdot 10^5$	Initial values of rate constants, $K \cdot \sec^{-1} \cdot 10^5$	Initial values of rate constants, $K \cdot \sec^{-1} \cdot 10^5$	E, kcal/mol	$\lg B$	Method of calculating E
Formation of difficultly condensing gases	0.019	0.084	0.16	0.50	45700	17.8	By superposition of curves in coordinates $\Delta v/\Delta\tau = f(\tau)$
Gas evolution without evacuation of gases**	0.10	0.40	—	1.9	39200	15.0	By superposition of curves $p = f(\tau)$

* The rate constant of loss in weight was calculated relative to the loss in weight at τ_∞, and for gas formation relative to the volumes of gases evolved at τ_∞.

** The experiments were carried out at 100–170°.

The experiments described above refer to decomposition in vacuum. The decomposition of nitrocellulose in a closed volume and the influence of certain impurities on this decomposition were also studied by measuring the pressure with a membrane manometer ([4]). It was confirmed, in agreement with earlier studies ([1]), that gas formation under these conditions proceeds with considerable acceleration. In this case much more gas is formed than during decomposition

Fig. 2

Figure 2: Fig. 2

in vacuum, and the weight of the solid residue is smaller.

The acceleration of gas formation is the greater, the more nitrocellulose there is per unit volume of the vessel, i.e., the higher the pressure of the decomposition products. However, acceleration of gas formation was also observed in experiments at quasi-constant pressure, when the pressure was allowed to rise only to a certain small value (20 mm Hg), after which the gases were rapidly pumped out. In this case as well, the rate increased considerably (by about a factor of 2) with time; hence it follows, in agreement with the experiments in vacuum, that the acceleration of gas formation during nitrocellulose decomposition is caused not only by an increase in the concentration of gaseous decomposition products.

The initial rates of gas formation in vacuum and without removal of gases are practically identical; the rate at the maximum in the latter case $\left(\frac{m}{v} = 10 \div 20 \cdot 10^{-4}\ \text{g/cm}^2\right)$ is only 3-4 times greater than at $5 \cdot 10^{-4}$ mm, i.e., in

a million times lower pressure. In other words, the accelerating action of the gaseous decomposition products on its course is so small that there is hardly any basis for considering it catalytic. It also depends only weakly on pressure in the low-pressure region. The transition from experiments at quasi-constant pressure, where the average pressure is 10 mm, to experiments without removal of gases, where $P_{\max} = 500$ mm, increases the rate of gas evolution only by a factor of 2. With a further increase in pressure, at the maximum $\left(\frac{\Delta v}{\Delta \tau}\right)_{\max}$ increases approximately in proportion to this pressure.

In light of the data obtained, it is probable that the influence of the gaseous decomposition products consists mainly in the interaction of their reactive components with one another and with the solid substance, leading to the formation of additional volumes of gases.

Fig. 2. Dependence of rate constants on temperature: 1 —formation of gases that are difficult to condense; 2 —formation of condensable gases; 3 —total gas evolution; 4 —loss in weight; 5 —gas evolution without removal of gases. The constants are plotted on the graph in different arbitrary units; for their absolute values see Table 1.

Experiments on the decomposition of nitrocellulose in the presence of oxygen showed that, while slowing gas evolution at the beginning of the experiment, it subsequently leads to a sharp acceleration of decomposition. The presence of water vapor by itself only weakly accelerates gas evolution during decomposition; however, when water and oxygen are present together, after an induction period during which the pressure changes hardly at all, there occurs a sudden drop in pressure and then a sharp acceleration of gas evolution. Thus, the picture of

decomposition described in the literature (see, e.g., [5]), which was considered to be due to the influence of water, is in fact determined by the combined action of water and atmospheric oxygen, in the atmosphere of which the experiments were usually begun. The difference between nitrocellulose and nitroglycerin, whose decomposition is accelerated by water even in the absence of oxygen [6], is apparently due primarily to the fact that the nitrogen dioxide split off in the case of nitrocellulose is rapidly reduced to nitric oxide, no acid is formed, and hydrolysis in their absence proceeds slowly. Oxygen, by oxidizing NO, ensures a sufficient concentration of NO_2 and acids. True, according to our experiments, nitric oxide also causes an acceleration of the decomposition of nitrocellulose, but its action is much weaker than that of nitrogen dioxide or of acids—nitric acid and especially sulfuric acid. We add that the action of nitric acid was studied both in the absence of water and in its presence. In the latter case the acceleration is considerably stronger. It should also be pointed out that, during the decomposition of nitrocellulose in the presence of NO_2 or nitric acid, the curves of the rate change with time have two characteristic maxima; the magnitude and the time of their occurrence depend on the amount of nitrogen dioxide or acid.

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REFERENCES CITED

1. A. V. Sapozhnikov, ZhRFKhO, **36**, 836 (1904); **37**, 822 (1905); **38**, 1186 (1906).

2. W. Will, *Zs. f. angew. Chem.*, **14**, 774 (1901).

3. J. B. Levy, *J. Am. Chem. Soc.*, **76**, 3790 (1954).

4. J. Schaeffer, J. Treub, *Zs. phys. Chem.*, **81**, 308 (1913).

5. J. Goujon, *Mém. Artill. Franc.*, **8**, 837 (1929).

6. K. K. Andreev, A. P. Glazkova, DAN, **105**, No. 2, 286 (1955).

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