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MECHANISM OF THERMAL DECOMPOSITION OF N, N-DINITROMETHYLAMINE

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In the work reported in [1], a manometric method was used to study the formal kinetic relationships in the thermal decomposition of N,N-dinitromethylamine (DNMA) in the gas phase. The reaction takes place homogeneously and, with the exception of a small deviation in the initial stages, is described by a first order equation with rate constant

$$k = 10^{14.6 \pm 1.5} \exp\left(-118 \pm 4\right) \text{ kJ/mole/RT·sec}^{-1}$$
(1)

The decomposition rates of ethyl-, propyl-, and butyldinitroamines are similar. Judging from the parameters of the decomposition of DNMA the first step is the splitting off of a nitro group as a result of which the radical CH_3NO_2 is formed. A study of the secondary reactions of DNMA decomposition, associated with the transformation of this radical, would be of interest; there is no information in the literature on the reactions of alkylnitroamine radicals. Meanwhile, these radicals can play a significant role as intermediates in radical processes with the participation of primary or secondary nitroamines, in particular during the decomposition of explosives such as cyclonite. In the present work we have used labeled atoms and GLC to determine the composition of the decomposition products of DNMA and to follow up the route of their formation. From the results obtained a scheme can be put forward for the secondary reactions in DNMA decomposition, including reactions of the methylnitroamine radical in a medium containing oxides of nitrogen.

EXPERIMENTAL

DNMA was prepared by the methods of [2, 3]. A ^{15}N label was introduced into one of the nitro groups to the extent of 86.8% at the stage of the nitration of 1,3,5-trimethyl-1,3,5-triazacyclohexane [3] by means of $H^{15}NO_3$ in acetic anhydride. The isotope composition was determined in terms of the ratio of fragments of mass 46/47 (in the unlabeled compound

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the peak with m/z 47 was absent from the mass spectra). The kinetics of the decomposition were studied manometrically with $m/V = (1.38-13.3) \cdot 10^{-4} g/cm^3$ and $S/V = 0.3-1.6 cm^{-1}$. Analysis of the products was effected by GLC on a Tsvet-1 apparatus and by chromatography-mass spectrometry using MX-1320 and MX-1310 spectrometers. The organic products were chromatographed on a 200 × 0.3 cm column packed with Polysorb-1 (column No. 1) at 100°C in a current of 30 cm³/min helium. Since the starting material decomposes rapidly at 100°C product analysis was carried out only after complete conversion of the DNMA. Volatile gases were analyzed on a 200 \times 0.3 cm column packed with Porapak Q (column No. 2) with a helium flow of 25 cm³/min. Separation of the total diatomic gases, CO_2 and N_2O was achieved at 0°C, and NO and N₂ were run at -78°C (CO was not detected in the products). A column of Polysorb-1 (50 × 0.2 cm) was installed before column No. 2 to trap NO, and heavy products. For chromatography coupled with mass spectrometry, a 500 × 0.2 cm column packed with Polysorb-1 (column No. 3) was used with programmed heating and a helium rate of 1 cm³/min. The products were identified by their retention times and by the mass spectra of standard substances. The appropriate calibrations were carried out for quantitative analysis. Introduction of samples in quantitative analysis was effected through a thermostatted device in which an ampul containing the sample was broken in a current of the carrier gas. The accuracy of the chromatographic analysis was 15%.

The ratio $\alpha = {}^{14}N/{}^{15}N$ was determined for each of the nitrogen-containing products. For this, both molecular (in the case of N₂ or MeNO₂) and fragment (NO⁺ and NO⁺₂ in the case of MeONO and MeONO₂) mass peaks were used. The concentrations of nitrogen atoms for nitro groups (NH) and from the central amine nitrogen (Na) of the DNMA were found from the relationship $\alpha = x + (1 - x)y/(1 - x)(1 - y)$, where x and (1 - x) are respectively the fractions of Na and NH in the product molecule and y is the fraction of ${}^{14}N$ DNMA (y = 0.566).

RESULTS AND DISCUSSION

Measurements of the rate of decomposition of DNMA confirmed the conclusion of [1] that the reaction was homogeneous. As in [1], a deviation from first order kinetics was found (especially at low temperatures); in the region of 15-20% reaction, there is a small minimum in the rate of gas evolution. The first order rate constants, calculated by the method of equal intervals from the reaction of the curves beyond 30% decomposition at 60, 70 and 80° C, were $6 \cdot 10^{-5}$, $2.5 \cdot 10^{-4}$, and $7.8 \cdot 10^{-4}$ sec⁻¹. Calculation from Eq. (1) gave the respective values $1.0 \cdot 10^{-4}$, $3.3 \cdot 10^{-4}$, and $1.0 \cdot 10^{-3}$ sec⁻¹. The ratio P_{∞}/P_{0} , i.e., the molar yield of gaseous products, was 2.65 ± 0.5 and was independent of temperature.

The qualitative and quantitative composition of the products of complete decomposition at 80°C, the ratio α , and the N² content of each of the products together with the molar yield of the products are set out in Table 1. In addition to the products listed in the table, trace amounts of CO, HCN, CH₄, and C₂H₆ were detected by mass spectrometry. Qualitative observations showed that there was much NO₂ and H₂O present in the final products. The quantitative content of these products, as shown in Table 1, was evaluated from the nitrogen and oxygen mass balance. Products determined by GLC gave a 100% balance in carbon. Considering the accuracy of the analytical method, this agreement must be admitted as fortuitous. Some quantitative redistribution of the yields of the different products is possible. After determining the H₂O content from the O balance a satisfactory balance was achieved for H (2.84 moles plus the hydrogen-rich CH₄ and C₂H₆ in small quantities) and for the molar yield of products (2.66 mole per mole DNMA, which is close to the P_∞/P₀ ratio). This is evidence that the quantitative estimates of NO₂ and H₂O were correct.

The analyses showed that NO, NO₂, CH₃ONO, and CH₃ONO₂ contained only N^H. Na entered into the composition of two products: N₂ and MeNO₂, the N₂ being 14% NaNa and 86% N^aN^H. The peak with m/z 30 was absent from the mass spectrum of the nitrogen, which shows that there is no N^HN^H nitrogen molecule and only N^aN^a and N^aN^H are formed. It seems that N^a enters, in equimolar quantity to N^H, into N₂O also but the isotopic composition of this was not experimentally determined. It follows from the results in Table 1 that the N^a content of the N₂ and MeNO₂ amounts to 0.9347 g.atom which exactly corresponds to the yield of N₂O. The formation of N₂O of composition N^aB^HO follows also from the scheme of secondary reactions in the decomposition which will be considered below.

The isotope composition of the N_2 was also determined in the initial stages of the reaction. It was shown that at 1-2% decomposition of the DNMA (60°C, 10 min), over 90% of the N_2 had the composition NaNa.

Using generally accepted concepts for the conversion reactions of free radicals and nitrenes and the experimental results for the composition of the products and the distribu-

TABLE 1

Product	Molar yield, %	$\alpha = {}^{14}N/{}^{15}N$	x - N ^a fraction in product
CO_2	0,2 0,7	4,36 *	0,57
NaNa ** NaNu N2O NO NO2 *** H2O *** CH3NO2	$\begin{array}{c} 0,098\\ 0,602\\ 0,06\\ 0,1\\ 0,58\\ 0,2-0,3\\ 0,2\end{array}$	1,30 1,30 6,3	0,5 0 0 0,684
including: CH ₃ N ^a O ₂ CH ₃ N ^a O ₂ CH ₃ ONO CH ₃ ONO ₂	0,1368 0,0632 0,1 0,5	1,30 1,30	0 0

*Ratio m/z 28/29 = 1.68. **The fraction z of the NaNa molecule in N₂ is connected with x by the equation x = z + 0.5(1 - z). ***Quantitative NO₂ and H₂O content was determined from N and O balance.

tion of Na and N^H therein, one can assemble a fairly complete list of the likely secondary reactions in the decomposition of DNMA and isolate the chief, actually occurring, processes:

$$CH_{3}N(NO_{2})_{2} \rightarrow CH_{3}NNO_{2} + NO_{2}$$
⁽¹⁾

$$CH_3NNO_2 \rightarrow CH_3N:^a + N^{\pi}O_2$$
⁽²⁾

$$CH_{3}\dot{N}NO_{2} + CH_{3}N(NO_{2})_{2} \rightarrow CH_{3}N^{a}(\dot{O})N^{\mu}O_{2} + CH_{3}N^{a}(N^{\mu}O)N^{\mu}O_{2}$$
(4)

$$CH_{3}\dot{N}NO_{2} + NO_{2} \rightarrow CH_{3}N^{a}(\dot{O})N^{H}O_{2} + N^{H}O$$
(5)

$$CH_3NNO_2 + NO \rightarrow CH_3N^a(N^{H}O)N^{H}O_2$$
(6)

$$CH_{3}N(O)NO_{2} \rightarrow CH_{3}N^{a}O + N^{\mu}O_{2}$$
⁽⁷⁾

$$CH_{3}N^{a}(N^{H}O)NO_{2} \rightarrow [CH_{3}N^{a} = N^{H} - O - N^{H}O_{2}] \rightarrow N^{a}N^{H} - CH_{3}ON^{H}O_{2}$$

$$(8)$$

$$CH_3N(NO)NO_2 \rightarrow CH_3 + N^a N^{\mu}O + N^{\mu}O_2$$
(9)

$$CH_{3}N: +CH_{3}N(NO_{2})_{2} \rightarrow (CH_{3})_{2}N^{a} - N^{a}(N^{\mu}O_{2})_{2} \rightarrow 2CH_{3} + N_{2}^{a} + 2N^{\mu}O_{2}$$

$$(10)$$

$$CH_3N: + NO_2 \rightarrow CH_3N^aO + N^{\mu}O$$
(11)

$$CH_3N^{a}O + N^{n}O_2 \rightarrow CH_3N^{a}O_2 + N^{u}O$$
(12)

$$CH_{3}N^{a}O + 2NO^{\pi} \rightarrow CH_{3} + N^{a}N^{\pi} + N^{\mu}O_{3}$$
(13)

$$CH_3NaO \rightarrow CH_2 = NOH \rightarrow HCNa + H_2O$$
 (14)

$$N^{H}O_{3} + N^{H}O \rightarrow 2N^{H}O_{2} \tag{15}$$

$$CH_3 + CH_3N(NO_2)_2 \rightarrow CH_3O + CH_3N^a(N^{\pi}O)N^{\pi}O_2$$
(16)

$$CH_3 + NO \rightarrow CH_3N^{HO}$$
 (17)

$$CH_3 + NO_2 \rightarrow CH_3 N^{_H}O_3 \tag{18}$$

$$CH_3 + NO_2 \rightarrow CH_3O + N^{H}O$$
⁽¹⁹⁾

$$CH_3 + NO_3 \rightarrow CH_3O + N^{H}O_2$$
⁽²⁰⁾

$$CH_{3}O + NO \rightarrow CH_{3}ON^{\pi}O$$
(21)

$$CH_{3}O + NO_{2} \rightarrow CH_{3}ON^{\mu}O_{2}$$
(22)

$$CH_{3}O + NO_{2} \rightarrow CH_{2}O + HN^{\mu}O_{2}$$
⁽²³⁾

$$2HNO_2 \rightarrow H_2O + N^{\mu}O + N^{\mu}O_2$$
(24)

$$CH_2O + NO_2(NO_3) \rightarrow CO_2 + H_2O + NO$$
(25)

Reactions (2) to (6) are possible routes for the transformation of the CH_3NNO_2 radical. Since N₂O is virtually absent from the products, reaction (3) (and also (9)) can be disregarded. The practically thermally neutral process (4) must have an activation energy of ~ 40

kJ/mole and can appear only in the very early stages of the decomposition (up to 0.1%) when no significant amount of NO and NO₂ has accumulated. A similar conclusion can be made in relation to reaction (16) which involves the starting material. In the actual decomposition process the concentration ratio $[NO_2]/[NO] \simeq 6$ and the statistical factors of reactions (5) and (6) differ by a factor of 2. For these reasons alone one would expect a ratio of reaction rates $w_5/w_6 > 10$. Thus, the most likely processes for the transformation of the CH₃NNO₂ radical are reaction (2) in the early stages and reaction (5) in the later stages of the decomposition. Nitrogen N_2^a is formed chiefly via reaction (10) which is effective at the beginning of the decomposition. Reaction (5) must predominate over reaction (2) and reaction (11) over reaction (10) as NO₂ accumulates, i.e., as the participation of the starting material in the secondary reactions decreases and hence the specific rate of decomposition of DNMA is reduced. In an excess of NO₂ the concurrent processes (2) and (11), and (5) and (7) give identical products corresponding to the conversion of DNMA to $CH_3NaO + NHO + NHO_2$. Nitrosomethane decomposes to a small extent at the walls according to (14), and partially undergoes straight oxidation by nitrogen dioxide with the formation of CH_3NO_2 (yield ~14) but in the main it is converted by reaction (13) [4] into $N_2 = N^a N^H$ and the CH₃ radical. In fact, similar reactions involving the CH₃ radical in NO and NO₂ explain the formation of such final products as CH₃N^HO₂, CH₃ON^HO, CH₃ON^HO,* $CH_3ON^HO_2$, CO_2 , and H_2O .

From this scheme, one can effect several quantitative evaluations. The yields of nitrogen and CH₃ radical are connected by the ratios $CH_3/N_2^d = 2$ and $CH_3/N^{a}N^{H} = 1$. The yield of CH_3 radical calculated from these ratios is 0.798 mole. The sum of all the products obtained from CH_3 $(CH_3N^{H}O_2, CH_3ONO, CH_3ONO_2, and CO_2)$ is 0.863 mole which, within the limits of error, corresponds to the calculated yield. The scheme shows that the NO, NO₂, methyl nitrite and methyl nitrate must contain only N^H. This is in agreement with the analytical results. Since the constants k_{21} and k_{22} are approximately equal [5] the ratio of the yields of CH_3ONO_2 and CH_3ONO must be equal to the ratio of the concentrations of NO_2/NO in the products, i.e, ~6, which is also observed in the experiments. There is no N_2^H in the products and hence reaction (17), leading to the formation of $CH_3N^{HO}_2$, does not occur; transformation of the latter by a reaction of the type of (13) would unavoidably lead to the appearance of N_2^H . This is readily explained by the concurrence of reactions (18) and (19) with (17). Taking into account that $k_{18} \ge 3k_{17}$ [6], $k_{19} = 6k_{18}$ [7], and [NO_2] $\simeq 6[NO]$ we obtain ($w_{18} + w_{19}$)/ $w_{17} \ge 100$.

If the CH₃O radical is formed only according to Eq. (19), the ratio $[CH_3ONO_2 + CH_3ONO + CO_2]/[CH_3NHO_2]$ must, according to the scheme, be equal to the ratio of the constants k_{19}/k_{18} , i.e., 6. Experimentally, this ratio is found to be 11.4 and such a difference points to an efficient source of CH₃O radical in addition to (19). It is unlikely that reaction (20) plays a large part because of the destruction of NO₃ in (15). It is possible that the picture presented by reaction (13) is inaccurate. One can postulate that breakdown of the intermediate complex (CH₃N(NO)ONO) leads to the formation of both CH₃ + N₂ + NO₃ and CH₃O + N₂ + NO₂.

CONCLUSIONS

The methylnitroamine radical does not tend to undergo intramolecular oxidation: $Me\dot{N}NO_2 \rightarrow MeO + N_2O$ and breaks down by decomposition into MeN: and NO_2 . In the presence of NO_2 MeNNO₂ and MeN: are efficiently oxidized to MeNO.

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^{*}As in Russian original - Editor.