ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 1, pp. 87–90. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © R.S. Stepanov, L.A. Kruglyakova, 2013, published in Zhurnal Obshchei Khimii, 2013, Vol. 83, No. 1, pp. 95–98.

Thermal Decomposition of N-Substituted N-Methylnitroamines

R. S. Stepanov and L. A. Kruglyakova

Siberian State Technological University, pr. Mira, 82, Krasnoyarsk, 660049 Russia
e-mail: lakrugl@sibstu.kts.ru

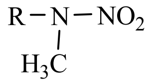
Received December 13, 2011

Abstract—Thermal decomposition of the N-methylnitroamines based on azoles in the liquid phase proceeds as a first-order reaction and is limited by the homolysis of the N–NO_2 bond. The reaction rate is affected by the steric effect of the azole substituent. The activation parameters for the limiting stage of thermal decomposition were determined, and correlations between the logarithm of the rate constant, activation energy, and the steric constant E_s of the substituent were elucidated.

DOI: 10.1134/S1070363213010143

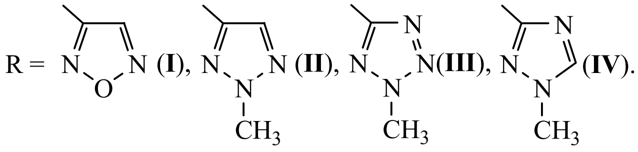
In recent years unabated interest continues in the reactions of thermal decomposition of secondary nitroamines that define the chemical resistance of these energetic compounds and its relationship to the structure.

In this paper we studied the kinetics of thermal decomposition of secondary methylnitroamines **I–IV** to clarify the nature of the substituent effect on the rate and mechanism of the limiting stage.



$$R-N(CH_3)-NO_2$$

I–IV

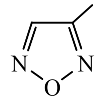
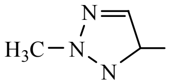
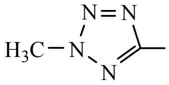
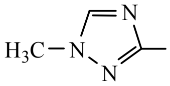
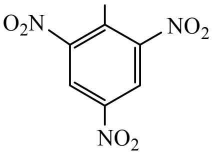


We studied of the kinetics of thermal decomposition of compounds **I–IV** in dilute solutions of these compounds in 1,3-dinitrobenzene and 1,3,5-trinitrobenzene to exclude the decelerating effect of the molecular crystal lattice and the interaction between the intermediate and final reaction products with the precursor and to reveal in pure form the influence of substituents on the specific rate of the process. We found that changes in concentration of the solutions within 2–8 wt % had virtually no effect on the rate constant and that the dielectric constant of the solvents, 1,3-dinitrobenzene (20.6) and 1,3,5-trinitrobenzene (7.1), very weakly affected the rate constant of decay of compounds **I–IV**, increasing the latter by 10–12%, that is, slightly exceeding the errors (7–9 %) of its experimental determination. A similar pattern is usually observed in the case of homolytic reactions [1].

To study the dependence of the rate constant on temperature we used the 2 wt % solutions in which the thermal decomposition of compounds **I–IV** to 40–45% conversion (of the total gas evolution) is described by the equation of the first-order reaction. Reactions of similar order were observed in the study of the thermal decomposition of compounds **I–III** in the melt by measuring evolution of nitrogen dioxide. In the study of the decomposition reaction in the melt the rate constant also was not affected by the weight ratio of substance to the reaction volume in the range $m/V = (1.1–28.2)\times10^{-3}$ g cm^{-3}, and by the ratio of the surface of the reaction vessel to its volume, $S/V = 0.8–4.2$ cm^{-1}, which indicates the homogeneity of the decomposition reaction in the bulk and on the walls of the reaction vessel. In addition, the kinetic curves of compounds **I** and **III** at the decomposition in the melt, according to manometric measurements, were in good agreement with those obtained at measuring the release of nitrogen dioxide to a degree of conversion ~37–40% with respect to the liberation of the nitrogen dioxide.

The qualitative composition of gaseous products of the thermal decomposition of compounds **I**, **III** in the melt was obtained by mass spectrometry at almost the full conversion, and the mass spectrum contained NO, N_2, CO and CO_2, as well as fragment ions with

Activation parameters of thermal decomposition of compounds of general formula $RN(NO_2)CH_3$ and steric constants of substituents R

Comp. no.	R	Decay conditions	ΔT, °C	E_a, kJ mol^{-1}	log A	$k_{250°C}\times10^4$, s^{-1}	$\Delta S^{\neq}_{250°C}$, J mol^{-1} K^{-1}	E_s	References
I		Melt[a] Solution in 1,3-dinitrobenzene	140–165 150–175	151.1 151.8	13.93 13.91	5.07×10^{-5} 3.98×10^{-5}	10.3 9.9	–4.45	This work
II		Solution in 1,3,5-trinitrobenzene	140–170	153.5	13.96	2.81×10^{-5}	10.8	–5.26	″
III		Melt[a] Solution in 1,3,5-trinitrobenzene	150–180 150–180	156.3 155.5	13.98 13.90	1.33×10^{-5} 1.12×10^{-5}	11.2 9.7	–4.25	″
IV		Solution in 1,3-dinitrobenzene	150–180	158.1	13.92	7.09×10^{-5}	10.1	–3.5	″
V	$CH_3N(NO_2)CH_2$	Melt Solution in 1,3-dinitrobenzene	180–230 180–230	169.6 170.6	14.21 14.18	5.61×10^{-7} 4.01×10^{-7}	15.6 15.1	–0.58	[2]
VI	CH_3	Gas	180–260	170.7	14.10	3.15×10^{-7}	13.5	0	[3]
VII	H	Gas	230–260	171.6	13.65	8.96×10^{-8}	4.9	1.24	[4]
VIII		Melt Melt Solution in 1,3-dinitrobenzene	130–155 140–165 150–175	150.6 167.4 150.3	13.80 16.0 13.87	4.32×10^{-5} 6.44×10^{-5} 5.50×10^{-5}	7.8 49.9 9.1	–6.05	[5] [6] [7]

[a] Data obtained by measuring the release of nitrogen dioxide.

m/e = 29, 31 and 15 (traces of CHO^+, CH_3O^+ and CH_3NO_2).

Kinetic and thermodynamic parameters of thermal decomposition of compounds **I–III** are shown in the table, together with the references to the published data on the alkyl- and arylmethylnitroamines.

The analysis of the data in the table shows that a decrease in the size of the α-substituent at the nitroamine group leads to a decrease in the rate constant. Thus, the lowest of the observed rate constants occurs in the case of compound **VII**, and the highest, in compound **VIII**. The decrease in the constant is mainly due to increase in activation energy from 150.3 to 171.6 kJ mol^{-1}. As for the pre-exponential factor, its value remains practically constant, with the mean value log A = 14.05, which, in general, is characteristic of nitroamines. The translational entropy of the transition state is small ($\Delta S^{\neq}_{160°C}$ = 9.7–11.2 kJ mol^{-1} K^{-1}), indicating a very weak solvation of the transition state in solution, regardless of the solvent nature.

While studying the kinetics of the thermal decomposition of compounds **I** and **III** in the melt by measuring the release of nitrogen dioxide at 160°C we found that the concentration of nitrogen dioxide first increases with the degree of conversion, reaches a maximum at 32–35% conversion and then decreases rapidly. It is noteworthy that a similar pattern was observed earlier [6] in the study of decay of 2,4,6-trinitrophenyl-*N*-methylnitroamine.

Activation parameters of the thermal decomposition in the melt for the compounds **I** and **III**, found from the total gas formation and nitrogen dioxide release are in good agreement (see the table). This may indicate a primary homolysis of the N–NO_2 bond, which has been earlier proved fundamentally for compounds **V–VIII**. In the case of compound **III** it is presumable that the limiting stage proceeds as a homolytic opening of

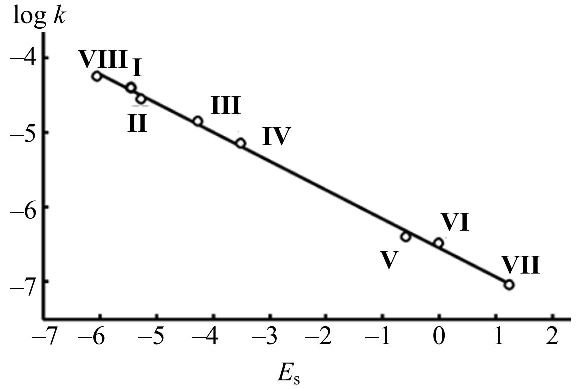


Fig. 1. Dependence log $k = f(E_s)$ for the thermal decomposition of nitroamines $CH_3N(NO_2)R$ in the gas phase and in the 2% solutions in 1,3-dinitrobenzene and 1,3,5-trinitrobenzene.

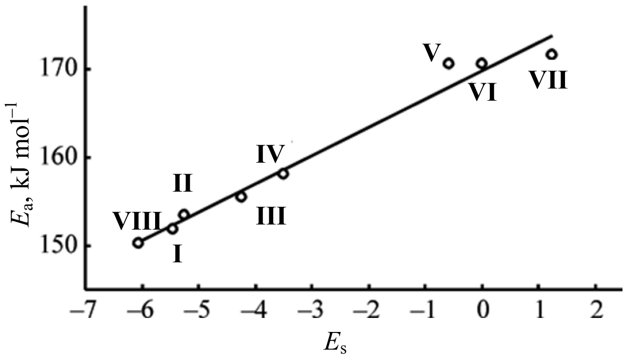
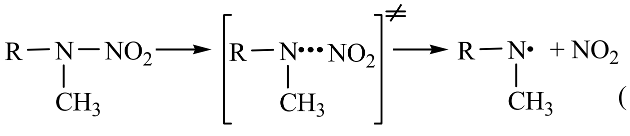


Fig. 2. Dependence of log $E_a = f(E_s)$ for the thermal decomposition of nitroamines $CH_3N(NO_2)R$ in the gas phase and in the 2% solutions in 1,3-dinitrobenzene and 1,3,5-trinitrobenzene.

the tetrazole ring at the N^2–N^3 bond with the formation of azidoazomethane [8] and its subsequent decomposition to simpler products. However, this mechanism is not possible in our case from an energy point of view, since it requires significantly larger activation energy (175–180 kJ mol^{-1}) than we found (see the table). Other heterocycles that we have used to build the nitroamines are more heat resistant than the triazole heterocycle [9]. The problem of the thermal stability of the tetrazole ring arose [10] at the investigation of thermal decomposition of an analog of compound **III**, 1-ethyl-1,2,3,4-tetrazol-1-yl-*N*-ethylnitroamine, and it was concluded that nitrogen dioxide appears in the first stage as a result of the cleavage of the N–NO_2 bond in the nitroamine fragment, which agrees well with our results.

Summing up we can consider that the thermal decomposition of compounds **I–IV** in a solution of 1,3-dinitrobenzene and 1,3,5-trinitrobenzene, as well as in the melt, by analogy with compounds **V–VIII**, is limited by the homolytic cleavage of the N–NO_2 bond in nitroamine group, which in general can be represented by Eq. (1).



$$\underset{\displaystyle CH_3}{R-\overset{}{N}}-NO_2 \longrightarrow \left[\underset{\displaystyle CH_3}{R-N}\cdots NO_2\right]^{\neq} \longrightarrow \underset{\displaystyle CH_3}{R-N^{\bullet}} + NO_2 \qquad (1)$$

From the analysis of structural factors it follows that the logarithms of the decomposition rate constants of compounds **I–VIII** are well correlated with the steric constants of substituents E_s (Fig. 1). The regression equation takes the form (2).

$$\log k_{160°C} = -(0.387\pm0.007)\Sigma E_s - (6.48\pm0.028), \qquad (2)$$
$$r\ 0.998;\ S_y\ 0.140;\ n\ 8.$$

Figure 2 shows the dependence of the activation energy on E_s. The points fit satisfactorily to a straight line that is approximated by Eq. (3).

$$E_a = (3.23\pm0.19)\Sigma E_s + (169.89\pm0.76), \qquad (3)$$
$$r\ 0.988;\ S_y\ 3.72;\ n\ 8.$$

The fact that the sensitivity of the reaction of homolytic decomposition at the N–NO_2 bond to steric effects of substituents R (δ = 0.387±0.007) is approximately a half of the sensitivity of the reaction to the homolysis at the C–NO_2 bond in the substituted geminal dinitromethyl [11] and dihalonitromethyl [12] compounds (δ = 0.752–0.667) attracts attention. We believe that it is due to a different degree of conjugation with the nitro group in different reaction centers, on the one hand, and the degree of conjugation of substituents R with the reaction centers on the other side.

EXPERIMENTAL

Compounds **I–IV** were synthesized and purified by known methods [13–15], and they were chromatographically pure. The kinetics of thermal decomposition was studied manometrically by using a Bourdon type pressure gauge [2] in a vacuum at a residual pressure of air in the reaction chamber of the pressure gauge 10^{-3} to 10^{-2} mm Hg. Along with pressure gauges we used a photocolorimetric method of measuring the release of nitrogen dioxide [7].

Analysis of the gaseous products of thermal decomposition was carried out by mass spectrometry on a MKh-1303 instrument, ionizing voltage 60 V, emission current 2 μA, ion source temperature 190°C, the inlet cylinder temperature 150°C.

The rate constants were calculated along the equation of the first order reaction. The mean square error in determining the activation energy is 4.1 kJ mol^{-1}, of the logarithm of the pre-exponential factor, 0.31 logarithmic units.

REFERENCES

1. Moelwyn-Hughes, E.A., *The Kinetics of Reactions in Solutions*, Moscow: Khimiya, 1975.
2. Kruglyakova, L.A. and Stepanov, R.S., *Izv. Vuzov. Ser. Khim. i Khim. Tekhnol*., 2008, vol. 51, no. 10, p. 31.
3. Korsunskii, B.L. and Dubovitskii, F.I., *Dokl. Akad. Nauk SSSR*, 1964, no. 155, p. 402.
4. Kekin, Yu.V., Shan'ko, V.N., and Stepanov, R.S., *Kinetika i Kataliz*, 1989, vol. 30, no. 4, p. 963.
5. Dubovitskii, F.I., Rubtsov, Yu.I., and Manelis, G.B., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1960, no. 10, p. 1763.
6. Dubovitskii, F.I., Manelis, G.B., and Smirnov, L.P., *Zh. Fiz. Khim.,* 1961, vol. 35, no. 3, p. 521.
7. Stepanov, R.S., Shan'ko, V.N., Medvetskaya, I.P., and Kuznetsov, L.A., *Fizicheskaya khimiya* (Physical Chemistry), Krasnoyarsk: Sibir', 1975, no. 2, p. 3.
8. Prokudin, V.G., Poplavskii, V.S., and Ostrovskii, V.A., *Izv. Akd. Nauk, Ser. Khim*., 1996, no. 9, p. 2209.
9. Stepanov, R.S., Kruglyakova, L.A., and Astakhov, A.M., *Zh. Obshch. Khim*., 2009, vol. 79, no. 5, p. 874.
10. Gao, A., Rheingold, A.L., and Brill, T.B., *Propellants, Explosives, Pyrotechnics*, 1991, vol. 16, no. 3, p. 97.
11. Stepanov, R.S, Kruglyakova, L.A., and Astakhov, A.M., *Zh. Obshch. Khim*., 2007, vol. 77, no. 11, p. 1881.
12. Stepanov, R.S, Kruglyakova, L.A., and Golubtsova, O.A., *Zh. Obshch. Khim*., 2010, vol. 80, no. 6, p. 1202.
13. Pevzner, M.C., *Ros. Khim. Zh*., 1997, vol. 41, no. 2, p. 73.
14. Ostrovskii, V.A. and Koldobskii, G.I., *Ros. Khim. Zh*., 1997, vol. 41, no. 2, p. 84.
15. Tselinskii, I.V., Mel'nikova, S.F., and Vergizov, S.N., *Zh. Org. Khim*., 1981, vol. 17, no. 5, p. 1123.