

High-Temperature Decomposition of Nitromethane in the Shock Waves at Pressures 0.15–36 atm and Hypothesis of the Isomerisation in Its Decomposition Mechanism

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Nitromethane (NM) is the simplest aliphatic nitrocompound, and its decomposition represents a great interest for studying of combustion and oxidation chemistry, and also from the point of view of the theory of elementary high-temperature act of dissociation. Nevertheless, some uncertainty remain in interpretation of a initial stage of the NM decomposition. It traditionally is represented as $\text{CH}_3\text{NO}_2 \rightarrow \text{CH}_3 + \text{NO}_2$ (1). However, until now in the literature there are not direct and time-resolved experimental data on initial stages of NM decomposition in a fairly wide temperature range. In some works [2,3] a primary stage of NM decomposition has represented not as the direct channel of C-N bond breaking, but as channel of NM isomerization in the methyl nitrite with subsequent its disintegration into CH_3O and NO .

The purposes of present work were: direct time-resolved measurements of NM consumption and NO_2 radicals yield in NM decomposition behind shock waves in as much as possible wide ranges on pressure and temperature; computer simulation of experimental results; theoretical analysis of the hypothesis about NM isomerization in the process of its thermal decomposition.

Our experiments were carried out in strongly diluted mixes of NM with Ar at $T=990\text{--}1600\text{ K}$ and $p=0.15\text{--}36\text{ atm}$ in incident and reflected shock waves. We used the direct absorption spectroscopic technique, described in [4], with monitoring of NM consumption at $\lambda = 230\text{ nm}$ and yield of NO_2 at $\lambda = 405\text{ nm}$. We made six sets of experiments with fixed densities of the investigated gas, corresponding pressures of 0.15; 0.28; 0.5; 1.5; 4 and 36 atm.

The observed rate constants of the primary stage of NM decomposition were determined immediately behind the shock wave front from the initial portion of the NM consumption curve, and observed constants of rate of the yield of NO_2 radicals were determined by the initial slopes of the NO_2 radicals yield curves: $k_1^{\text{obs}} = d\ln(I_0/I)/dt$, and $k_{1\text{NO}_2}^{\text{obs}} = d\lg(I_0/I)/dt \cdot L \cdot [\text{HM}]_0 \cdot e_{\text{NO}_2}$. Here, I_0 and I are the intensities of incident and passed light, L – optical path length equal to the shock tube diameter (75 mm), e_{NO_2} – decimal absorption coefficient of NO_2 radicals at $\lambda = 405\text{ nm}$.

A computer modelling of NM decomposition kinetics was performed by means of CHEMKIN program with kinetic scheme [5]. Theoretical analysis of NM pyrolysis was spent by means of quantum-mechanical calculations.

It was established, that the process of NM decomposition can be described by exponential dependence only at its initial stages and at high temperatures. It was shown that with reduction of temperature a concave curves of NM decomposition vary on convex that specifies in autoacceleration of the decomposition process. Computer simulation gives a good agreement of experimental and calculated concentrations of NM. Arrhenius expressions k_1 for six series of experiments with fixed density demonstrate a strong dependence of k_1 on the pressure. At 0.15; 0.28; 0.5; 1.5; 4 and 36 atm elementary k_1 were defined as, respectively: $k_1 = 10^{11.09} \exp(-44.8/RT)$; $10^{11.82} \exp(-46.2/RT)$; $10^{11.94} \exp(-45.1/RT)$; $10^{12.58} \exp(-47.5/RT)$; $10^{13.4} \exp(-50.9/RT)$; $10^{14.41} \exp(-52.8/RT)$. That values are consistent with the data of [1], and significantly expands their range. So it is the “classical” monomolecular decomposition.

As it is shown on Fig.1, temperature dependences of rate constants of NM decomposition measured at initial stage of NM consumption (k_1) and at initial stage of NO_2 yield ($k_{1\text{NO}_2}$), practically coincide with each other in wide range of $T = 1190\text{--}1490\text{ K}$ and $p=1.5\text{ atm}$. That measurements, in our opinion, exclude (anyway, at high temperatures) a hypothesis about NM isomerization in the methyl nitrite at initial stage of the thermal NM decomposition.

A quantum-mechanical analysis made in the present work suggests that in thermal conditions in shock waves at low or average pressure a molecule of NM breaks up on the direct channel with C-N bond breaking (with $E_{\text{act}} \sim 54\text{ kcal/mol}$) earlier, than activation barrier ($59 \pm 1\text{ kcal/mol}$ [6]) for reaction of the isomerisation could be reached.

Thus, our experimental and theoretical data and analyzed literary data, concerning the hypothesis of the isomerisation, allow us to state that isomerisation in high-temperature thermal NM decomposition at low and average pressure is not realized or is negligible, and products of NM decomposition are $\text{CH}_3 + \text{NO}_2$.

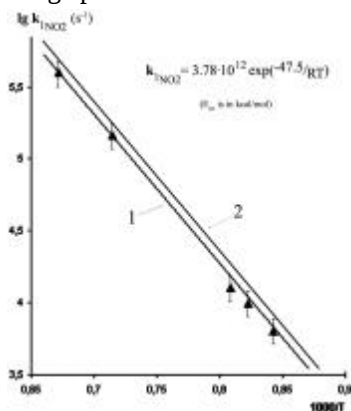


Fig 1. Temperature dependences of rate constants of NM decomposition at $p \sim 1.5\text{ atm}$: $\blacktriangle$ – this work (experiment), 1 – extrapolation of $k_{1\text{NO}_2}$; 2 – extrapolation of k_1

References

- [1]. Glanzer K., Troe J. (1972). Thermische Zerfallsreaktionen von Nitroverbindungen I: Dissoziation von Nitromethan. *Helv. Chim. Acta.* 55:2884.
- [2]. Dewar M.J.S., Ritchie J.P., Alster J. (1985). Thermolysis of Molecules Containing NO_2 Groups *J.Org.Chem.* 50: 1031.
- [3]. Wodtke A.M., Hints A.E., Lee Y.T. (1986). The observation of CH_3O in The Collision Free Multifoton Dissociation. *J. Chem. Phys.* 84. № 2:1044.
- [4]. Petrov Yu.P., Turetskii S.V., Bulgakov A.V. (2007). High-Temperature Decomposition of Azomethane in Shock Waves: 1. Initial Stage of Decomposition. *Rus. J. Khim. Fiz.* 26: 26.
- [5]. Seljeskog M. (2002). Shock Tube Experiments on Nitromethane and Promotion of Chemical Reactions by Non-Thermal Plasma. *Doct.thesis. Norweg. Univers. Science and Technology.*
- [6]. Zhu R.S., Lin M.C. (2009). CH_3NO_2 Decomposition / Isomerization Mechanism and Product Branching Ratios: An Ab Initio Chemical Kinetic Study. *Chem. Phys. Letters.* 478: 11.