HIGH-TEMPERATURE DECOMPOSITION OF NITROMETHANE IN SHOCK WAVES

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The decomposition of nitromethane (NM), the simplest aliphatic nitrocompound, represents a great interest for studying of the combustion [1,2]. Until now the question has been discussing about the possibility of NM isomerization in methyl nitrite on the initial stage of NM decomposition [3-5]. In the present work, the decomposition of NM was investigated at temperatures 990–1600 K, initial concentration of NM in mix with Ar in range of 30–10000 ppm, and maximum variation of pressure behind the shock waves by factor of 240. The consumption of NM was observed at $\lambda = 230$ nm and yield of NO_2-radicals – at $\lambda = 405$ nm [5]. The elementary rate constants (k_1) of NM decomposition were measured: $CH_3NO_2\ (+M) = CH_3 + NO_2\ (+M)$.

Even in diluted mixes with Ar the process of NM decomposition can be described by exponential dependence only at its initial stages and at high temperatures. With reduction of temperature concave curves of NM decomposition vary on convex. This points that the decomposition process goes with autoacceleration. Computer simulation with the reaction mechanism [7] gives a good agreement of experimental and calculated concentrations of NM. Arrhenius expressions k_1 for the six series of experiments with fixed densities, that corresponds to pressures of 0.15, 0.28, 0.5, 1.5, 4 and 36 atm., demonstrate a strong dependence of k_1 on the pressure [8]. Using so-called “transition curves” of pressure and theoretical expressions for modified Kassel integral, rate constants of NM decomposition in low (k_{1_0}) and high (k_{1_∞}) pressures limit were obtained: $k_{1_0} \approx 10^{17.3} \cdot \exp(-42/RT)$, $cm^3/mol \cdot s$, and $k_{1_\infty} \approx 10^{16.2} \cdot \exp(-59.7/RT)$, s^{-1}.

Experimentally obtained yield curves of NO_2 initially are convex, indicating that NO_2 here is the primary product. Rate constants determined to spend of NM and yield of NO_2, coincide with each other. This measurements exclude (anyway at high temperatures) a hypothesis about NM isomerization into methyl nitrite on the initial stage of NM decomposition. An theoretical analysis of this hypothesis was provided for both photolysis and thermal decomposition of NM. The vibrational energy of activation, necessary for decomposition of NM molecule on the direct channel with C-N bond breaking, can be theoretically estimate as about 54 kcal/mol. This value is less than an activation barrier energy for the isomerisation reaction which was estimated in [4] as 55.5 kcal/mol and then was corrected in [5] up to 61 kcal/mol.

Considering our experimental and theoretical data and our analysis of literary data, concerning the hypothesis of the isomerization, it seems reasonable to say that isomerization in high-temperature thermal NM decomposition at low and average pressure is not realized or is negligible, and products of NM decomposition are $CH_3 + NO_2$.

References

[1] Zaslonko, I.S., Kogarko, S.M., Petrov, Yu.P, “Thermal Decomposition of Nitromethane in Shock Waves”, *Sov. J. Kinet. and Catal*. 13: 1113 (1972)

[2] Glanzer, K., Troe, J., “Thermische Zerfallsreaktionen von Nitroverbindungen I: Dissoziation von Nitromethan”, *Helv. Chim. Acta*. 55: 2884 (1972)

[3] Dewar, M.J.S., Ritchie, J.P., Alster, J., “Thermolysis of Molecules Containing NO_2 Groups”, *J. Org. Chem*. 50: 1031 (1985)

[4] Wodtke, A.M., Hintsa, E.J., Lee, Y.T., “The observation of CH_3O in The Collision Free Multifoton Dissociation”, *J. Chem. Phys*. 84: No2. 1044 (1986)

[5] Zhu, R.S., Lin, M.C., “Decomposition / Isomerization Mechanism and Product Branching Ratios: An Ab Initio Chemical Kinetic Study”, *Chem. Phys. Letters* 478: 11 (2009)

[6] Petrov, Yu.P., Karasevitch, Yu.K., Turetskii, S.V., “Decomposition of Azomethane in Shock Tube as the Example of “Concerted” Decomposition Mechanism”, *Proc. 22nd ICDERS,* Minsk, Belarus #0133 (2009)

[7] Seljeskog, M., “Shock Tube Experiments on Nitrometane and Promotion of Chemical Reactions by Non-Thermal Plasma”, Doctoral thesis, Norweg. University of Science and Technol. Trondheim, (2002)

[8] Petrov, Yu.P., Turetskii, S.V., Bulgakov, A.V., “High-Temperature Decompositions of Nitromethane and Azomethane in the Shock Waves”, *Proc.33rd Symp.(Int.) on Comb.* W1P005 (2010)