

Thermal Decomposition Of Nitromethane In A Wide Range Of Pressures And Temperatures

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Introduction

Study of low-temperature ($T \sim 580\text{--}700\text{ K}$) pyrolysis of nitromethane (NM) in static reactors began in the last century [1–6]. Then NM decomposition studied at high temperatures ($\sim 1000\text{--}1400\text{ K}$) in shock tubes [7–16]. As can be seen from Fig.1 and Fig.2, the observed rate constants for the NM decomposition (k_1^{obs}), obtained by different authors, at the same temperatures differs between themselves by almost two orders of magnitude in absolute value and $\sim 20\text{ kcal/mol}$ for the activation energy. In addition, an order of magnitude difference are also observed between the low and high temperature data. In this paper we attempt to quantitatively correct these inconsistencies related to using of different research methodologies for different temperature ranges, and define a common Arrhenius expression for rate constant of NM decomposition, in particular, the values of $k_{1\infty}$ at the high-pressure limit for the low-and high-temperature data on the NM dissociation. We also study the NM decomposition behind shock waves in the atmosphere of various diluent gases to determine their effect on the value of k_{10} at the low-pressure limit. All these tasks are relevant to the practice and theory of unimolecular decomposition.

Experimental, simulations and theory

NM decomposition has been studied experimentally at high temperatures in shock waves and re-interpreted theoretically by primary experimental literature data at low T in static reactors. Numerical simulations of the experimental data has performed. Behind shock waves, in wide ranges of temperature ($\sim 990\text{--}1430\text{ K}$) and pressure ($\sim 0.28\text{--}36\text{ bar}$), the initial concentration of NM in mixtures with Ar from 30 up to 10000 ppm, and the registration of NM absorption at $\lambda = 230\text{ nm}$, the thermal decomposition of NM investigated from the initial to the final stages and deep transformation. By the initial stages of NM consumption determined observed rate constants (k_1^{obs}) of NM decomposition. Experimentally and by numerical simulation using the scheme of 84 reactions [15] is shown that k_1^{obs} are identical to the rate constants k_1 of the primary elementary stage of NM decomposition.



and that all hightemperature k_1 belongs to the falloff region.

Our analysis showed that virtually all of the low-temperature measurements described in the literature, should also be attributed to the falloff region. In connection with the above, in the present work to determine the values of $k_{1\infty}$ и k_{10} for the high- and low-pressure limits in the NM decomposition at high and low temperatures we used a modified Kassel integral method [17].

Results and discussion

Fig.3 shows a typical curve of the NM decomposition behind the shock waves, obtained with automatic system of measurements on the base of high-speed analog-to-digital converter (ADC). Fig.4 demonstrate the most important values of reaction rates that contribute to the change of NM concentration in the calculation with the scheme [15], for the experiment presented in Fig.3. The R_1 , rate of reaction (1), is dominant throughout all decomposition stages. The only noticeable on this background rate of reactions (19) and (20) are very small. At the time of determining the value of k_1^{obs} , they are fractions of a percent on the value of R_1 . Our review and analysis of the NM decomposition schemes and the rate constants of its most important secondary reactions for $T \sim 300\text{--}2000$ K range showed the dominant role of the reactions (19) and (20) in the autoacceleration in the intermediate stages of NM decomposition at $T \sim 1000$ K and a negligible part of the reaction (17) at all stages of high-temperature decomposition of nitromethane (numbering corresponds to the reaction scheme [15], used in this work).

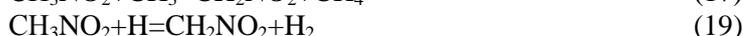
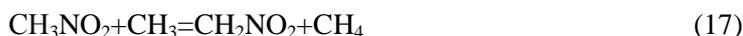


Fig.6 presents the set of temperature dependences of the NM decomposition rate constants k_1 , defined by us in five series of experiments with fixed density of the gas behind the shock waves. With the use of the modified Kassel integral, the values of $k_{1\infty}$ and k_{10} in the high- and low-pressure limits obtained in the decomposition of nitromethane in wide range of $T \sim 990\text{--}1430$ K.

$$k_{1\infty} = (1.8 \pm 0.7) \cdot 10^{16} \exp(-58.5 \pm 2)/RT, \text{ s}^{-1} \quad (\text{I})$$

$$k_{10(\text{Ar})} = (1.2 \pm 0.3) \cdot 10^{17} \exp(-41.8 \pm 0.5)/RT, \text{ cm}^3/\text{mol} \cdot \text{s} \quad (\text{II})$$

It is essential that these experimental-theoretical expressions obtained by shock-wave measurement techniques cover a wide temperature range (about 500 K). Moreover, there is a possibility of further extrapolation of literary and our experimental data, especially with the use of the expression (I). That is why in Fig.1 and Fig.2, in addition to the rate constants from the works on the low-and high-temperature NM decomposition, we present our extrapolation of high-temperature values of $k_{1\infty}$ (I) toward low temperatures.

Conclusions

For $T \sim 580\text{--}700$ K by theoretical interpretations for the first time values of $k_{1\infty}$ have been revealed that corrects previous low-temperature rate constants of the NM decomposition by up to one order of magnitude:

$$k_{1\infty} = 6.92 \cdot 10^{14} \exp(-54.3/RT), \text{ s}^{-1} \text{ for the work [6], } T = 633\text{--}663 \text{ K (see Fig.5);}$$

$$k_{1\infty} = 1.26 \cdot 10^{15} \exp(-55.2/RT), \text{ s}^{-1} \text{ for the work [5], } T = 638\text{--}667 \text{ K;}$$

$$k_{1\infty} = 5.0 \cdot 10^{14} \exp(-53.6/RT), \text{ s}^{-1} \text{ for the work [2], } T = 653\text{--}703 \text{ K;}$$

$$k_{1\infty} = 7.9 \cdot 10^{-5}, \text{ s}^{-1} \text{ for the work [3], } T = 628 \text{ K;}$$

$$k_{1\infty} = 1.7 \cdot 10^{13} \exp(-49.2/RT), \text{ s}^{-1} \text{ for the work [4], } T = 585\text{--}713 \text{ K.}$$

Was first established the expression for the elementary rate constant of NM decomposition in the falloff region with $p/p_0 = 0.03$:

$$k_1 = 6.3 \cdot 10^{13} \exp(-55.2/RT), \text{ s}^{-1} \text{ for the work [5], } T = 578\text{--}713 \text{ K.}$$

Established a good quantitative coincidence between theoretically interpreted low temperature values of $k_{1\infty}$ and the extrapolation toward low temperatures of high-temperature ($T \sim 1000\text{--}1400$) experimental and theoretical values of $k_{1\infty}$ (see Fig.7). Obtained common to two significantly different temperature ranges and very different research techniques Arrhenius expression for the rate of NM decomposition with breaking of the C-N bond in accordance with the reaction (1) at the high-pressure limit at $T \sim 580\text{--}1600$ K and in the range of $k_{1\infty}$ values, overlapping 14 orders of magnitude:

$$k_{1\infty} = (1.8 \pm 0.7) \cdot 10^{16} \exp(-58.5 \pm 2)/RT, \text{ s}^{-1} \quad (\text{I})$$

Direct decomposition of nitromethane observed in thermal conditions at high, medium and low temperatures in shock tubes and static reactors. Any contribution to products or decomposition rate constant from the initial isomerization channels were found.

In the study of NM decomposition behind shock waves in the atmosphere of Ar, He, CO₂, CF₄ found that the decomposition rate constant at low pressures for these diluents are in the ratio: $k_{10(\text{Ar})} : k_{10(\text{He})} : k_{10(\text{CO}_2)} : k_{10(\text{CF}_4)} = 1 : 2 : 3 : 3$. For all the diluent gases (up to five-atom CF₄) the strong collisions limit is not reached, that is $B_c < 1$. This value decreases with increasing temperature; in Argon $B_c = 0.06 \pm 0.01$ at $T = 1000$ K and $B_c = 0.03 \pm 0.01$ at $T = 1400$ K.

Figures

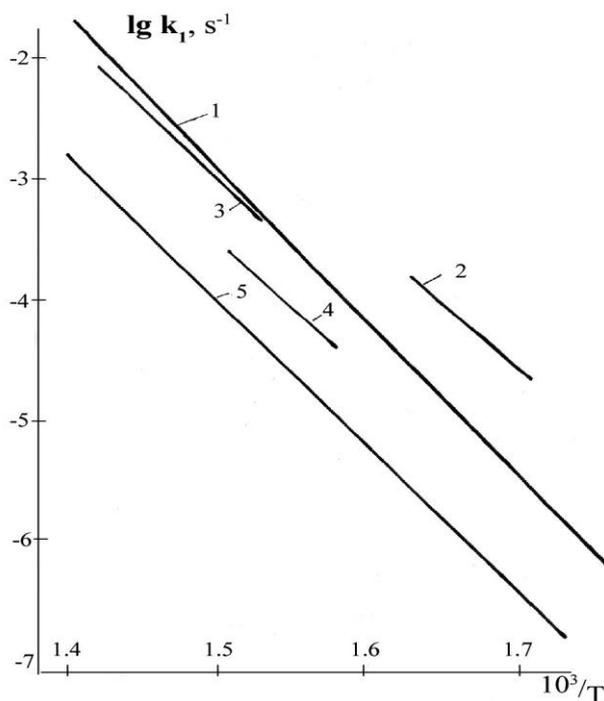
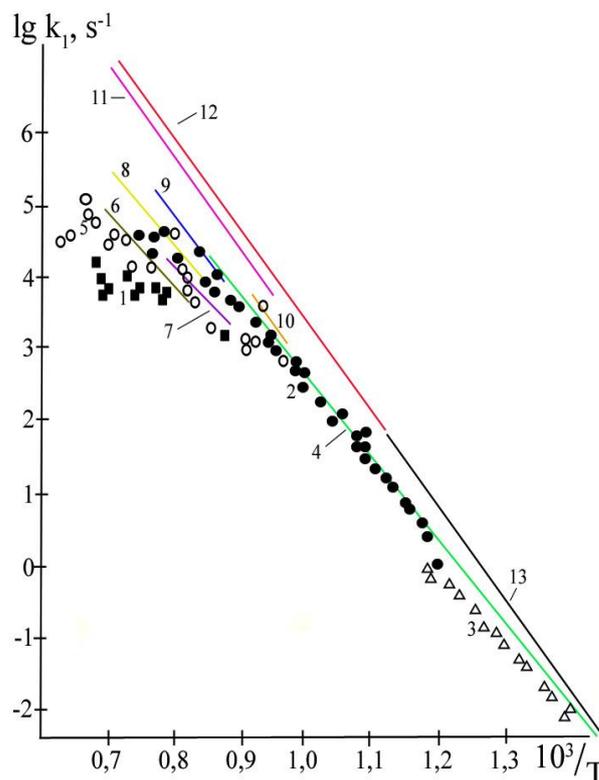


Figure 1. Temperature dependence of k_1 and $k_{1\infty}$ in the low-temperature NM decomposition. 1 – extrapolation to low temperature high-temperature ($T = 1000\text{--}1400$ K) values of $k_{1\infty}$ [10, 16]; 2 – $k_{1\infty}^{\text{obs}}$ from [4]; 3 – $k_{1\infty}^{\text{obs}}$ from [2]; 4 – $k_{1\infty}^{\text{obs}}$ from [6]; 5 – k_1^{obs} from [5].

Figure 2. Temperature dependence of k_1 and $k_{1\infty}$ in the high-temperature NM decomposition. 1 – k_1^{obs} from [7]; 2 – $k_{1\infty}^{\text{obs}}$ from [8] (shock tube); 3 – $k_{1\infty}^{\text{obs}}$ from [8] (adiabatic compression device); 4 – $k_{1\infty}^{\text{obs}}$ из [8] (final expression); 5 – k_1^{obs} from [9]; 6–10 – k_1^{obs} from [10] with relative densities in the experiments 0.112, 0.224, 1.12, 2.24, 6.73; 11 – $k_{1\infty}$ from [10, 16]; 12 – $k_{1\infty}$ from [14]; 13 – extrapolation of $k_{1\infty}$ by [10, 16].



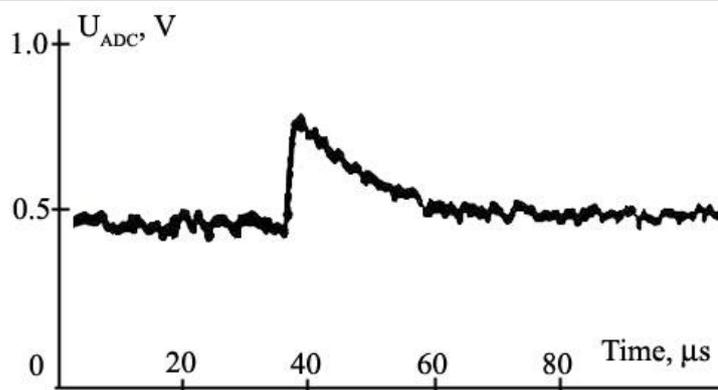


Figure 3. NM decomposition in the incident shock wave. $\lambda = 230$ nm, $T = 1363$ K, $p \sim 0.28$ bar, 5000 ppm of NM in Argon, output signal of high-speed analog-to-digital converter (ADC) F4226.

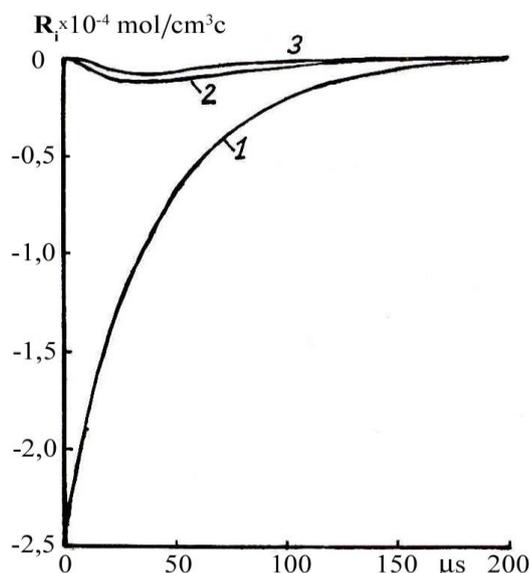


Figure 4. Reaction rates that have the greatest impact on the change in the concentration of NM in the process of its thermal decomposition. The calculation of the scheme [15] for the experiment shown in Fig.3 at $T = 1363$ K. 1, 2, 3 — rates of the reactions (1), (19), (20).

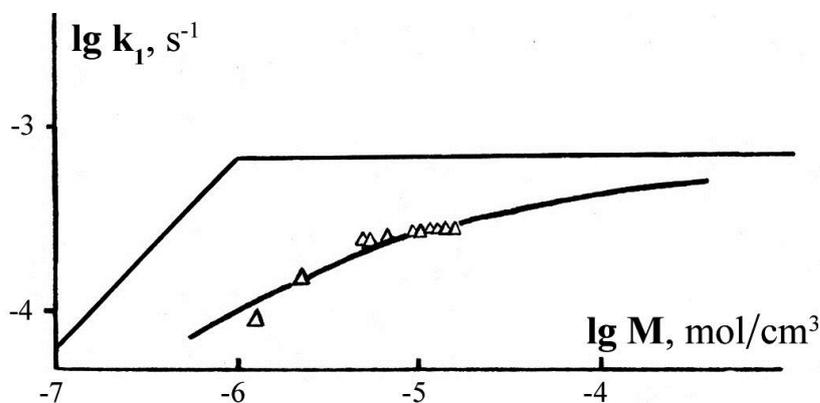


Figure 5. Falloff curve for the rate constant of NM pyrolysis at $T = 663$ K. Points on the curve — the primary experimental data of [6], the curve and the limit values of $k_{1\infty}$ and k_{10} obtained by approximating with the modified Kassel integral.

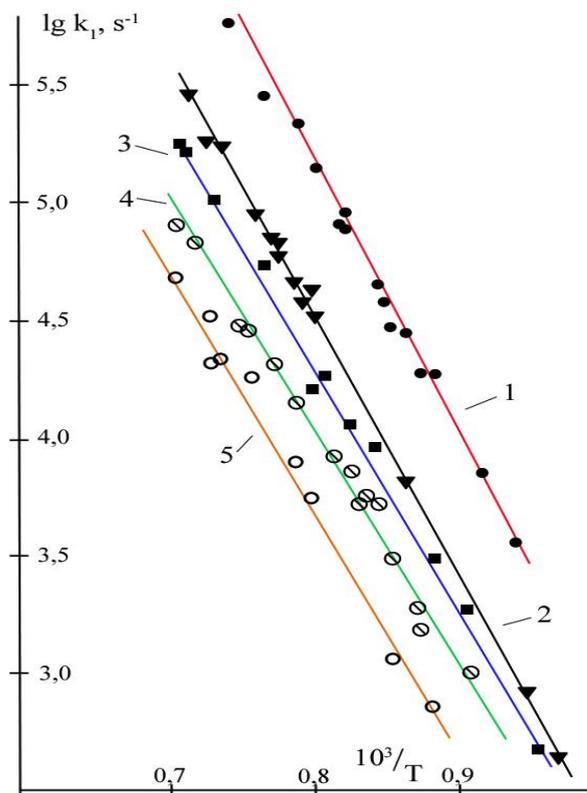
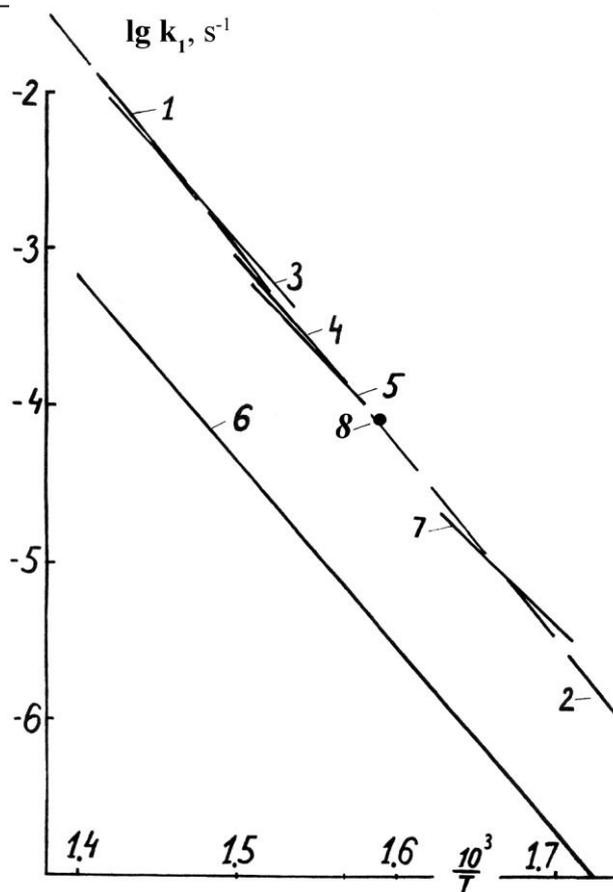


Figure 6. Temperature dependences of elementary rate constants k_1 of the NM decomposition in the falloff region in range from 36 to 0.28 bar. 1–5 — corresponding series of experiments, provided by authors of this work

Figure 7. Temperature dependences of the theoretically interpreted in this work values of k_1 and $k_{1\infty}$ in the low-temperature decomposition of NM. 1, 2 — extrapolation to low T high-temperature ($T = 1000\text{--}1400\text{ K}$) values of $k_{1\infty}$ [10, 16] (experimental data); 3–5 — $k_{1\infty}^{\text{obs}}$ from [2, 5, 6], obtained by extrapolation to the high-pressure limit; 6 — k_1 values for low pressures from [5]; 7 — corrected values of $k_{1\infty}$ from [4]; 8 — $k_{1\infty}$ value from [3]



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