Decomposition of Azomethane in Shock Tube as the Example of “Concerted” Decomposition Mechanism

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1 Introduction

High-temperature reactions of methyl radicals are specific and key stages of kinetic mechanisms of pyrolysis and oxidation of hydrocarbons and also play the important role in the kinetic of promoted combustion of different fuels. The vital condition of research of high-temperature processes seems to be a reception of precisely dosed out quantity of methyl radicals so that it was possible to study their interaction with other molecules and atoms (including O, O_2, NO_2 etc.).

The “purest” source of CH_3-radicals (in comparison with decomposition of C_2H_6, CH_3J or metalorganic molecules) is high-temperature decomposition of azomethane (AM). However, until recently some uncertainty in values of AM decomposition rate constants and coefficients of extinction of CH_3 radicals took place. Besides it has not been made appropriate analysis of great discrepancy between low- and high- temperature decomposition of AM.

For example, low-temperature rate constants have extremely high values of the pre-exponential factor, on the order of 10^{16}—10^{17} sec^{-1}, and activation energy value of up to 55.4 kcal/mol. By contrast, the high-temperature rate constants are characterized by low activation energy 26—34 kcal/mol and a low pre-exponential factor 10^{10}—10^{11} sec^{-1} [1].

In this work by direct absorption spectroscopic measurements of AM decomposition and by analysis of low- and high temperature data on this reaction we give answer on some problems of AM decomposition.

2 Experimental

Experiments were carried out in a stainless-steel shock tube of 75 mm inner diameter [2, 3] in incident and reflected shock waves. The absorption of methyl radicals in decompositions of azomethane was recorded in the 216 nm region. The AM absorption was recorded in 198 nm region. Simultaneously two monochromators served as dispersion devices in different spectral regions and two photo-multipliers as receivers. The source of sounding radiation was a capacitor-discharge lamp. This made it possible to record methyl radicals of about 10^{15} cm^{-3} concentration with a signal-to-noise ratio greater than 3 and with time-resolution of electron-optical channels of about 10^{-6} sec. The Ar, He cylinder gases, used in the experiments, were certificated purity of 99.9 percent. The purity of the azomethane in the gas phase was checked spectroscopically. Its extinction factors proved to be in good agreement with the data published in literature.

3 Results and discussion

Azomethane decomposition was studied by recording absorption of azomethane itself and absorption of methyl radicals generated in this reaction in the temperature range of 850 to 1390 K, $M = 3{\cdot}10^{-6}$ — 10^{-4} mol/cm^3 and with an azomethane fraction ranging from 40 to 2000 ppm. The experimentally observed initially rate constants (k_1^{obs}) of azomethane decomposition by reaction:

$$(CH_3)_2N_2\ (+M) \rightarrow 2\dot{C}H_3 + N_2\ (+M)$$

were measured from the initial slope of CH_3 yield curves:

$$k_1^{\text{obs}} = d[\text{CH}_3] \big/ 2dt[\text{AM}_0]$$

and of the azomethane consumption curves:

$$k_1^{\text{obs}} = d\ln[AM_0] \big/ dt$$

Simultaneously decimal coefficients of extinction of methyl radicals (e_{CH3}) were measured at T = 1350—2940 K and p = 0.3—10 bar. After analysis of our and published data on e_{CH3} following approximating semi-empirical expression is received for e_{CH3} (at $\lambda = 216$ nm, $\Delta\lambda = 1$—1.6 nm, T = 500—2940 K) [4]:

$$e_{CH3} = 3.25\ 10^{7}{\cdot}T^{-0.36}{\cdot}\exp(500/T){\cdot}\exp(-T/2500),\ \ \text{cm}^2/\text{mol}$$

This interpolation dependence covers the wide temperature interval and leans on significant number of our and literary experimental data. In our opinion, its use will allow to reduce essentially a significant disorder existing nowadays in values of kinetic data.

Figure 1 demonstrates a typical experimental curve of the decomposition of azomethane. Figure 2 presents temperature dependence of e_{CH3} obtained in this work in comparison with literature data. Figure 3 demonstrates temperature dependence of $[CH3]_{max}/[AM]$. The results of our measurements of k_1^{obs} are compared with the temperature dependence of k_1^{obs} in [1] and in our previous papers [2, 3, 5] in Figure 4. Our measurements of k_1^{obs} correlate well with the data of [1, 2, 3, 5] and are described by the following expression

$$k_1^{obs} = 10^{11.3}{\cdot}\exp(-33.5/RT),\ \text{sec}^{-1}$$

It is established that rate constants of AM decomposition practically do not depend on pressure and on initial concentration of azomethane even if they is varied over a wide ranges These facts, low values of the pre-exponential factor and observed energy of activation (E_1^{obs}) indicate on the “concerted” mechanism of AM decomposition, when the breaks of two chemical bonds is carried out during one kinetically inseparable stage. At the initial phase of azomethane decomposition an extremely instable radical CH_3N_2 is formed, which during the femtoseconds disintegrates in CH_3 and N_2 with energy output approximately 16 kcal/mol. This exothermal process promotes the dissociation, thus the observed energy of activation ($E_1^{obs} \approx 34$ kcal/mol), which is obtained in our measurements, seems to be the difference between the dissociation energy of a single C-N bond (approximately equal to 50 kcal/mol) end energy of 16 kcal/mol, produced in the instant break of CH_3N_2 radical.

In our opinion, the AM decomposition mechanism is “concerted” because of initial stage of reaction (1) not single, but two C-N bonds breaks and AM molecule disintegrates into three parts (instead of two parts in “classical” monomolecular decomposition). Our analysis show that low-temperature decomposition of AM is far from being an exemplary unimolecular reaction, as was claimed. This decomposition was studied using indirect, rather insensitive, time-unresolved and reactant-unselective methods. The low-temperature decomposition of AM turned out to be strongly influenced by chain and heterogeneous processes.

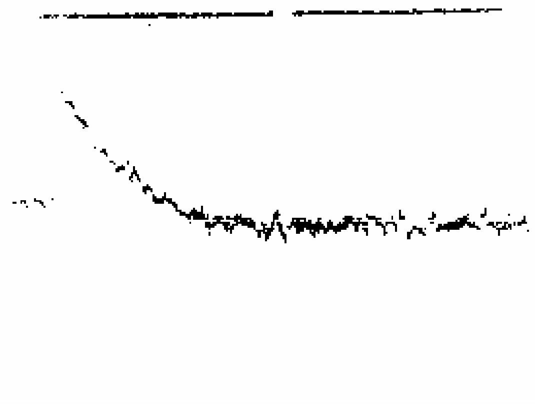

Figure 1. Typical curve of the azomethane decomposition. λ=198 nm, T=1008 K, 10 μsec/point

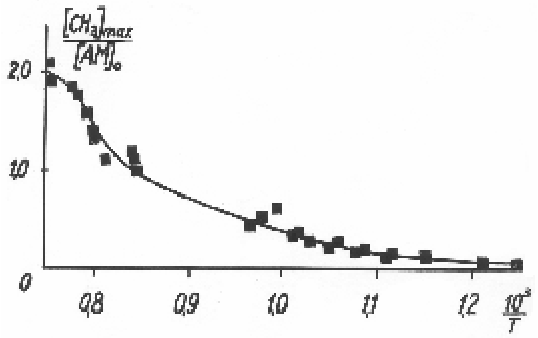

Figure 3. Temperature dependence of $[CH_3]_{max}/[AM]_0$

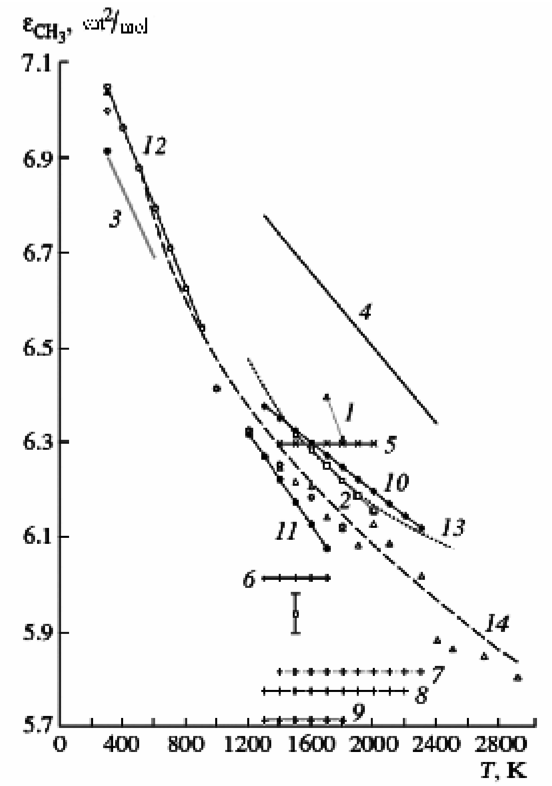

Figure 2. Temperature dependence of e_{CH3}: r — this work (experiment); 14 — this work (calculation and extrapolation to low temperature); other signs and numbers — literature data of other low-, mid- and high- temperature measurements and estimates of e_{CH3} (see details in [4])

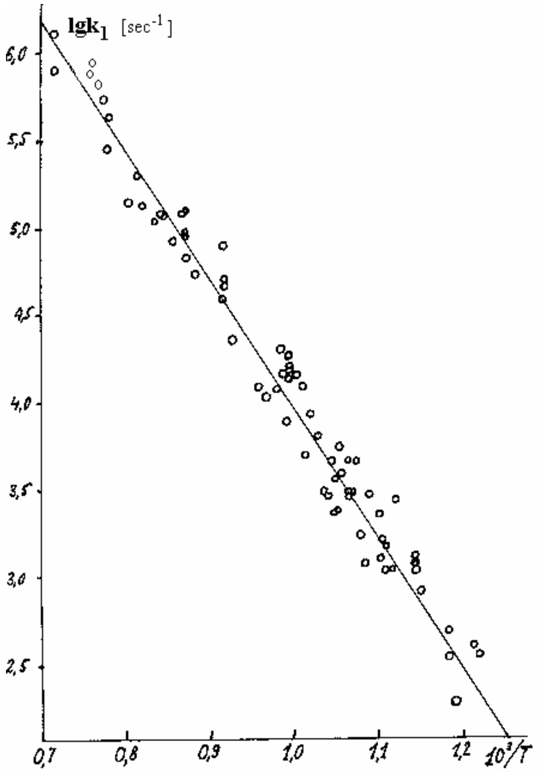

Figure 4. Temperature dependence of the rate constants of AM decomposition: ¡ — this work (experiment), line — k_1^{obs} [1, 2, 3, 5]

4 Conclusions

Our own measurements and published experimental data on azomethane decomposition at 850—1430 K, in conjunction with a theoretical analysis of this reaction, provide convincing evidence for its occurrence via the "concerted" mechanism in this temperature range. Most of the available experimental data cannot be described within the framework of the "classical" theory of unimolecular reactions. The need for direct time-resolved low-temperature data on AM decomposition is emphasized.

The assumption of "concerted" decomposition of azomethane allows to interpret values of k_1^{obs} measured at high temperatures in the newest direct experiments [1, 3, 5, 7, 8 and the present work], as the valid rate constants of decomposition of azomethane. Hence, these kinetic data quite reasonably can be used to describe the decomposition of azomethane as "calibrated" source of CH_3-radicals in a wide range of temperatures and pressures.

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