ISSN 0023-1584, Kinetics and Catalysis, 2009, Vol. 50, No. 3, pp. 344–347. © Pleiades Publishing, Ltd., 2009.
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Measuring the Rate Constant of Azomethane Decomposition in Shock Waves

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Received April 25, 2008

Abstract—The rate constant of azomethane decomposition in argon was measured at temperatures of 820 to 1400 K, pressures of 0.25 to 7.5 atm, and initial azomethane concentrations of 40 to 2000 ppm. The amount of azomethane reacted was estimated as UV light absorption at the vacuum UV boundary ($\lambda = 198$ nm), and the concentration of $\dot{C}H_3$ radicals resulting from azomethane decomposition was monitored as absorption at $\lambda =$ 216 nm. The observed temperature dependence of the azomethane decomposition rate constant, $k_1^{app} = 10^{11.3}\exp(-33.5/RT)$ s^{-1}, is in good agreement with the literature. The low values of the activation energy and preexponential factor are unnatural for classical monomolecular decomposition. This confirms the assumption that azomethane decomposition at high temperatures takes place via a concerted mechanism.

DOI: 10.1134/S0023158409030021

It was inferred from rate constant data for azomethane (AM) decomposition in shock waves,

$$(CH_3)_2N_2\ (+M) \longrightarrow 2\dot{C}H_3 + N_2\ (+M), \qquad (I)$$

that this reaction is not purely monomolecular in the classical sense and, at high temperatures, proceeds via a concerted mechanism [1–4]. According to the definition given by Kim et al. [5], a concerted process is a process in which two chemical bonds break within a single, kinetically inseparable reaction step.

There are the following indications that AM decomposition takes place via a concerted mechanism:

(1) The activation energy of the process (E_1^{app}) is low (about 25–35 kcal/mol), and so is the preexponential factor (on the order of 10^{10}–10^{11} s^{-1}).

(2) The rate constant of the reaction (k_1^{app}) remains invariable as the pressure is changed by a factor of 2–6 (although it would be expected that, with an increase in the reaction temperature, the pressure dependence of the rate constant should manifest itself because of the shift of the "normal" monomolecular reaction toward the transitional kinetic region near the lower pressure limit).

(3) E_1^{app} is independent of pressure.

(4) k_1^{app} is independent of the initial content. (Indications 2–4 suggest that the low value of E_1^{app} is not due to the occurrence of AM decomposition complicated by secondary reactions in the transitional pressure region.)

(5) The E_1^{app} values [1–4] are far below the energy necessary for the breaking of the ordinary C–N bond (~50 kcal/mol) with the release of a $\dot{C}H_3$ radical according to the classical monomolecular mechanism.

(6) The methyldiazenyl radical ($\dot{C}H_3N_2$), a very unstable species, forms at the very beginning of the first step of AM decomposition, and this radical decomposes to $\dot{C}H_3$ and N_2 within a few femtoseconds [6].

(7) Two bonds break in the first step of AM decomposition, yielding three fragments of the AM molecule, whereas the classical monomolecular decomposition implies the breakage of one bond and the formation of only two fragments.

In order to substantiate the inference that AM decomposes via the concerted mechanism, it is necessary to measure the rate constant of this reaction in the widest possible ranges of temperatures, pressures, and initial AM concentrations and to prove that this constant refers to an elementary step. The latter seems to be particularly important because even the authors of one of the best studies on AM decomposition [7] suggested discarding their own experimental temperature dependence of the AM decomposition rate constant ($E_1^{app} \approx$ 33 kcal/mol) and accepting a temperature dependence implying an activation energy and a preexponential factor better consistent with the classical monomolecular decomposition mechanism:

$$k_1^{app} = 10^{15.6}\exp(-55/RT)\ \text{s}^{-1}. \qquad (1)$$

These data were apparently taken from old works in which AM decomposition was carried out at low temperatures and was considered to be a model monomolecular reaction [8].

The purpose of this study was to measure the rate constant of high-temperature AM decomposition in the widest possible pressure and temperature ranges. The significance of these data stems primarily from the fact that AM is widely used in producing dosed amounts of the $\dot{C}H_3$ radical. In addition, AM pyrolysis has been used as a model reaction since as early as the 1920s, and studies of this reaction provided a basis for the early variants of monomolecular decomposition theory.

EXPERIMENTAL

Experiments were performed in a shock tube according to an earlier described procedure [2, 9, 10] using a high-intensity UV flash lamp. Light absorption by azomethane at the vacuum UV boundary ($\lambda = 198$–200 nm) and by $\dot{C}H_3$ radicals at $\lambda = 216$ nm was recorded simultaneously. The UV radiation from the flash lamp passed through the observation section of the shock tube and two DMR-4 double prism monochromators and arrived at FEU-39 photomultipliers. The output signal from the photomultipliers was recorded with an S8-13 memory oscilloscope. The time resolution of the electrooptic path was approximately 1 μs. Note that, although a considerable fraction of radiation was lost on the splitting quartz plate, which directed part of the radiation to the side monochromator (tuned to $\lambda = 216$ nm), the signal-to-noise ratio at $\lambda = 200$ nm was approximately 20 : 1, well above the same ratio in our previous studies [9].

Azomethane is practically transparent in the visible and UV spectral regions [11, 12] and absorbs light intensively at the vacuum UV boundary, beginning at $\lambda = 200$ nm. For example, at 273 K, the decimal extinction coefficient of AM (ε_{AM}) is 0.91×10^6 cm^2/mol at $\lambda = 200$ nm and is almost 1.6 times larger (1.43×10^6 cm^2/mol) at $\lambda = 198$ nm [11].

Experiments were performed on mixtures consisting of high-purity argon and 40–2000 ppm azomethane.

Prior to kinetic measurements, the absorption spectra of AM in the UV region and at the vacuum UV boundary were recorded on a Specord spectrograph. The absolute values of the “cold” (room-temperature) coefficient ε_{AM} derived from these spectra ($\lambda = 198$ and 200 nm) were in good agreement with the literature [11, 12].

RESULTS AND DISCUSSION

Figure 1 displays a typical oscillogram of AM decomposition recorded at $\lambda = 198$ nm. Its distinctive feature is the considerable “cold” absorption by AM. This allows ε_{AM} to be determined at room temperature as the difference between the absorption intensity before the arrival of the front of the incident shock wave and the absorption intensity after complete AM decomposition in the wave. The extinction coefficient thus determined coincides closely with the our spectroscopic ε_{AM} value and with the earlier reported value [11].

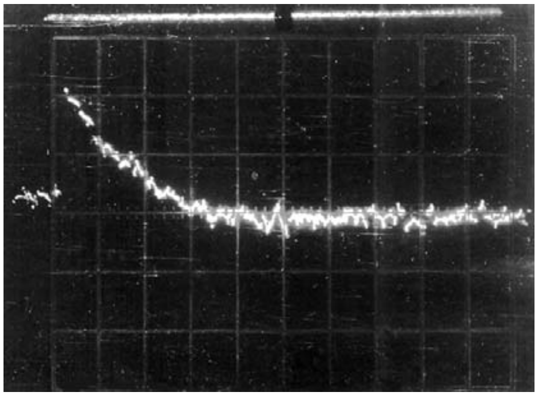

Fig. 1. Typical oscillogram of azomethane decomposition ($\lambda = 198$ nm, $T = 1008$ K); scale interval of 10 μs.

Firstly, the good quantitative agreement between our experimental AM extinction coefficients at room and near-room temperatures and the corresponding data known from the literature [11, 12] allows quantitative measurements of the AM concentration in the shock tube immediately before the arrival of the shock wave. Secondly, this agreement suggests that, in AM decomposition at $\lambda = 198$ nm, absorption by the species other than AM is insignificant.

Along with measuring ε_{AM} at room temperature and various wavelengths, we determined the extinction coefficients of hot AM. To do this, we estimated the initial absorbance behind the shock wave front. As is clear from Fig. 2, ε_{AM} increases with increasing temperature and ε_{AM} at 200 nm is almost twice larger than ε_{AM} at 198 nm.

The apparent rate constant of AM decomposition was derived from the initial portion of the AM disappearance curve:

$$k_1^{\text{app}} = \mathrm{d}\ln(I_0/I)/\mathrm{d}t\,, \qquad (2)$$

where I_0 and I are the intensities of the total and current transmittances of monochromatic light.

The k_1^{app} value was also derived from the initial portion of the $\dot{C}H_3$ yield curve, using the relationship

$$k_1^{\text{app}} = \mathrm{d}[\mathrm{CH_3}]/2\mathrm{d}t[\mathrm{AM}_0]. \qquad (3)$$

Figure 3 shows the Arrhenius plot of k_1^{app} representing the data calculated from the results of over 70 experiments using Eqs. (2) and (3). This plot covers the temperature range from 820 to 1400 K and the pressure range from 0.25 to 7.5 atm. This temperature range is wider than the temperature interval in which the measurements reported in [1, 7] were carried out. The pres-

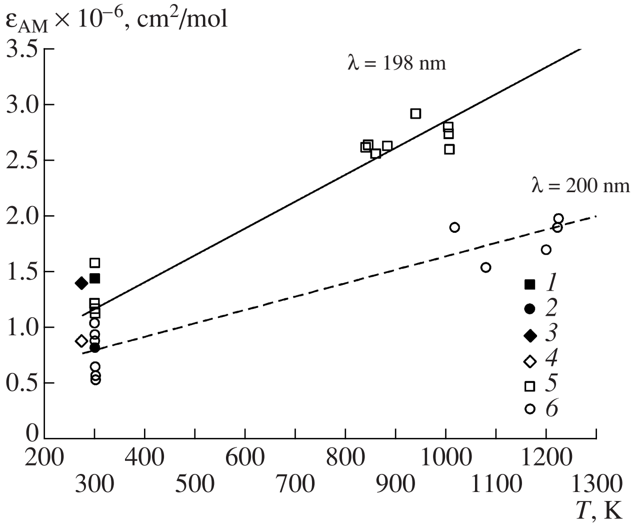

Fig. 2. Temperature dependences of the extinction coefficient of azomethane: (*1*) data from [11] (λ = 198 nm, T = 273 K), (*2*) data from [11] (λ = 200 nm, T = 273 K), (*3*) this study (λ = 198 nm, Specord spectrograph), (*4*) this study (λ = 200 nm, Specord spectrograph), (*5*) this study (λ = 198 nm, shock wave experiment), and (*6*) this study (λ = 200 nm, shock wave experiment).

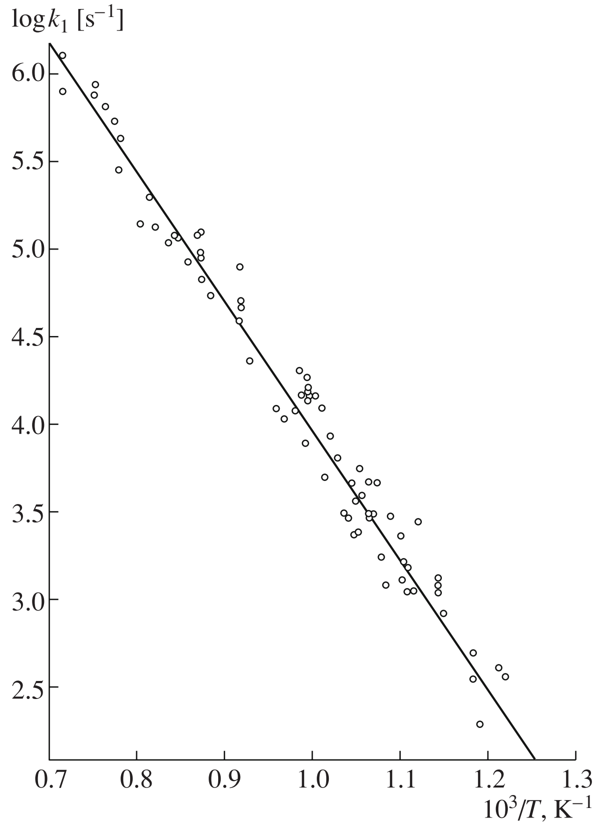

Fig. 3. Temperature dependence of the azomethane decomposition rate constant. The points represent the data obtained in this study, and the line represents the data of other studies [1, 2, 7, 9, 10].

sure range examined in this study is 5 times wider than the pressure range examined in [7]. The AM concentration in argon was varied by a factor of 50. The temperature dependence of the AM decomposition rate constant derived from our experiments,

$$k_1^{\mathrm{app}} = 10^{11.3 \pm 0.3}\exp(-33.5 \pm 1.6/RT) \qquad (4)$$

is in good agreement with earlier data [2, 7, 9, 10]. It leads to small values of the activation energy and preexponential factor characteristic of the concerted decomposition mechanism. Furthermore, we observed other indications of concerted decomposition (see paragraphs (2)–(5) in the introductory section). Thus, the observation of a uniform temperature dependence of the rate constant over the widest possible pressure, temperature, and AM concentration ranges verifies the earlier assumption that AM decomposition at high temperatures proceeds via a concerted mechanism [1, 2, 4, 9, 10].

In the light of the above results and data reported in the literature [1, 2, 4, 9, 10], expression (1) for the AM decomposition rate constant, suggested by Glanzer et al. [7], seems to be unjustified and incorrect for high temperatures. In our opinion, this expression was constructed artificially, looking back at old low-temperature data [13] that had already been revised in [14–16] and other publications. In our review [3], we pointed out that the obviously overestimated values of the AM decomposition activation energy (55 kcal/mol) and preexponential factor (on the order of 10^{16} s^{-1}) are due to the very complex mechanism of low-temperature AM decomposition, which is complicated by heterogeneous and secondary chain reactions. In most cases, these values were obtained by indirect measurements.

Values of E_1^{app} as large as 55 kcal/mol were first obtained in early works in which AM decomposition was studied at low temperatures and the first step of the reaction was considered to be the abstraction of one $\dot{\mathrm{C}}\mathrm{H}_3$ radical, which requires an energy of ~50 kcal/mol. Apparently, Glanzer et al. [7] mechanically transferred these values to their study. The smaller E_1^{app} values of about 34 kcal/mol actually observed in the present study and in other works [1, 2, 4, 7, 9, 10] are characteristic of concerted AM decomposition. In this mechanism, the instantaneous exothermic decomposition of the methyldiazenyl radical $\dot{\mathrm{C}}\mathrm{H}_3\mathrm{N}_2$, estimated at 16 kcal/mol, reduces E_1^{app} by precisely this value, making it equal to 34 kcal/mol. Moreover, our value of the activation energy of high-temperature AM decomposition coincides closely with the enthalpy of reaction (I), which is 34 kcal/mol.

Thus, the rate constants of AM decomposition in shock waves that were determined in this study are confirmed by the results of other studies [1, 2, 4, 7, 9, 10] and by thermochemical and general theoretic data. Apparently, AM decomposition is not an ideal example of a classical monomolecular reaction and its mechanism should be considered to be concerted.

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