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Kinetics of $\dot{N}O_2$ Formation upon the Decomposition of Nitromethane behind Shock Waves and the Possibility of Nitromethane Isomerization in the Course of the Reaction

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Abstract—The decomposition of nitromethane behind shock waves was studied at $T = 1190–1490$ K and $P \approx 1.5$ atm; the reaction was monitored based on the formation and consumption of $\dot{N}O_2$, radicals, which were detected by their absorption in the region of $\lambda = 405$ nm. It was found that the curves of the yield of $\dot{N}O_2$ have a convex shape, which is characteristic of the formation of primary decomposition products. Based on an analysis of the initial sections of the experimental curves of the yield of $\dot{N}O_2$, the temperature dependence of the rate constants of formation of these radicals upon the decomposition of nitromethane was found for the first time: $k_1(\dot{N}O_2) = (6.3 \pm 2) \times 10^{12} \exp(-48.9 \pm 2/RT)$ s^{-1} (the dimensionality of E_a is kcal/mol). It was found that the rate constants of nitromethane decomposition measured from the consumption of the parent substance and the yield of $\dot{N}O_2$ radicals almost coincide with each other. A kinetic simulation of the formation and consumption of $\dot{N}O_2$ upon the decomposition of nitromethane was performed. A good agreement between experimental and calculated data was achieved. A brief theoretical analysis of competition between the channels of direct disintegration and isomerization under conditions of the thermal decomposition of nitromethane was performed. The advantage of the direct disintegration channel with the rupture of the C–N bond was shown. Both experimental and published data on the isomerization of nitromethane into methyl nitrite upon its thermal decomposition and photolysis were analyzed.

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INTRODUCTION

Nitromethane (CH_3NO_2) is the simplest aliphatic nitro compound; the study of the thermal decomposition of the nitro derivatives of methane and aliphatic nitro compounds in general originated with this compound even in the past century [1–16]. The decomposition of nitromethane has been examined in studies of combustion and explosion processes; it is important for the theory of an elementary act of dissociation, including the participation of different isomerization steps in the decomposition of nitromethane, and also for the more precise determination of the dependence of the rate constant of unimolecular disintegration on pressure and temperature [5–17].

The discussion of the possibility of an initial intramolecular rearrangement of a molecule into another in the process of its high-temperature disintegration has gone on throughout the past decades. In this case, the discussion deals with the isomerization of nitromethane into methyl nitrite (CH_3ONO) in the course of the primary stage of the thermal or photolytic disintegration of nitromethane. It is assumed that $\dot{C}H_3O$ and $\dot{N}O$ radicals are formed as the decay products of nitromethane rearranged into methyl nitrite if isomerization occurs.

According to Cottrel et al. [2], the primary step of the thermal decomposition of nitromethane is traditionally represented as the reaction

$$CH_3NO_2 \rightarrow \dot{C}H_3 + \dot{N}O_2 \qquad \text{(I)}$$

with the rate constant k_1. This mainly follows from the chemical analysis of the composition of decay products and energy considerations. Unfortunately, there are no direct quantitative data on the initial stages of the formation of these products over a wide temperature range. However, scarce early experimental evidence for the occurrence of isomerization [3, 7] has not been analyzed until now and specific conclusions have not been drawn from it. At the same time, new theoretical [18] and then experimental studies [19, 20] on this basis appeared, whose authors insist on the initial isomerization of nitromethane into methyl nitrite upon its pyrolysis and photolysis and assert that the $\dot{C}H_3O$ and $\dot{N}O$ radicals are the decay products of nitromethane.

Therefore, we carried out experiments in shock waves with the direct spectroscopic detection of the

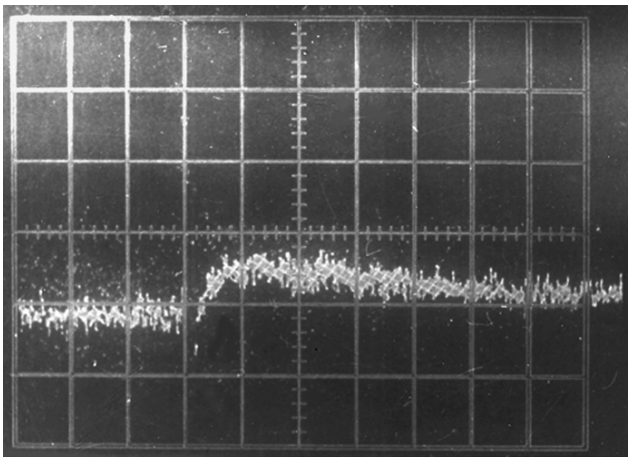

Fig. 1. Oscillogram of the yield and consumption of $\dot{N}O_2$ under conditions of the decomposition of 1% nitromethane in Ar at a temperature of 1187 K and a pressure of ~1.3 atm. $\lambda = 405$ nm; scanning rate, 20 μs/scale division.

initial stages of the formation of nitromethane decay products over a sufficiently wide temperature range and also performed theoretical calculations and a numerical simulation of our experimental data. We assume that the results of this work will make it possible to give answers to some of the above questions.

EXPERIMENTAL

The experiments were carried out in a shock tube of stainless steel with an inside diameter of 75 mm in incident and reflected shock waves in accordance with an absorption procedure [16]. The emission of a DKSSh-1000M high-pressure krypton–xenon lamp with a continuous spectrum in the region of $\lambda = 405$ nm, which operated in a steady state, was used to control the formation and consumption of $\dot{N}O_2$ in the mixtures of nitromethane with Ar. The kinetics of $\dot{N}O_2$ conversion was measured at $T = 1190–1490$ K and $P \approx 1.5$ atm simultaneously on several time scans of S8-13 storage oscillographs and also in the electronic form on a computer. The time resolution of electron-optical paths was about 1 μs.

The observed rate constants of $\dot{N}O_2$ radical formation ($k_1^{obs}(NO_2)$) were determined from the slopes of the initial portions of the experimental yield curves, which showed the absolute concentrations of $\dot{N}O_2$: radicals:

$$k_1^{obs}(\dot{N}O_2) = \frac{d\log(I_0/I)}{dtL[NM]_0\varepsilon_{NO_2}}, \quad (1)$$

where I_0 and I are the intensities of the full and current transmission of monochromatic radiation at the wavelength $\lambda = 405$ nm, respectively; L is the optical path length, which is equal to the diameter of a shock tube; NM = nitromethane; and ε_{NO_2} is the decimal extinction coefficient of $\dot{N}O_2$ in the region of $\lambda = 405$ nm [21].

RESULTS

Figure 1 shows a typical oscillogram, which reflects the formation and consumption of $\dot{N}O_2$ radicals in the thermal decomposition of a 1% nitromethane mixture with Ar behind a reflected shock wave at a pressure of about 1.5 atm and a temperature of 1187 K. The detection was performed at $\lambda = 405$ nm with a scanning time of 200 μs (20 μs per scale division). Note that even traces of nitromethane and $\dot{N}O_2$ absorption were absent from an incident shock wave. The absorption of nitromethane was also absent behind a reflected shock wave. This fact suggests that nitromethane does not absorb in the region of $\lambda = 405$ nm even at elevated temperatures, and the decomposition of nitromethane in the incident wave is not detected under the conditions of a shock tube.

The extinction coefficient of $\dot{N}O_2$ at $\lambda = 405$ nm has a maximum value [21]; therefore, the $\dot{N}O_2$ radicals were detected at this wavelength. The yield curve of $\dot{N}O_2$ radicals in Fig. 1 has a clearly convex shape from the very beginning of nitromethane decomposition; this is consistent with the formation of a primary reaction product. Then, the concentration of $\dot{N}O_2$ reaches a quasi-steady-state level at a sufficiently late step and this radical is further consumed in secondary reactions to a zero level, as is evident from 500-μs survey scans. At higher temperatures, $\dot{N}O_2$ is consumed more rapidly and also to the zero concentration level.

The previously determined rate constants of nitromethane decomposition k_1 [16] and the rate constants of formation $k_1(\dot{N}O)_2$ measured in this work almost coincide with each other in terms of absolute values and observed activation energies. Figure 2 shows the temperature dependence $k_1^{obs}(\dot{N}O_2)$, which was determined in this work for the first time over a sufficiently wide range. As follows from the experimental results supported by a computer kinetic simulation, these values are described by the expression

$$k_1(\dot{N}O_2) = (6.3 \pm 2) \times 10^{12}\exp(-48.9 \pm 2/RT)\ s^{-1}. \quad (2)$$

Equation (2) coincides (with consideration for experimental error in the determination of Arrhenius parameters) with the temperature dependence of the rate constants of nitromethane decomposition k_1, which was found previously from nitromethane consumption at pressures of about 1.5 atm [15]:

$$k_1 = (3.2 \pm 2) \times 10^{12}\exp(-46.8 \pm 2/RT)\ s^{-1}. \quad (3)$$

In our opinion, the above data are direct experimental evidence for the fact that the thermal decomposition of nitromethane in a high-temperature region occurs through the cleavage of the C–N bond and $\dot{N}O_2$ is the primary product of nitromethane decomposition.

Up to now, direct evidence for the formation of $\dot{N}O_2$ radicals upon nitromethane decomposition has not been given in the literature. Only Glanzer and Troe [11] published hand-drawn points that related to only a single experiment performed at $T = 1080$ K and $P \approx 6$ atm. We processed published data [11] and found that, as in our experiments, the rate constants of nitromethane decomposition and the formation of $\dot{N}O_2$ radicals coincide with each other (neither Glanzer and Troe [11] nor anybody noted this circumstance). Figure 2 shows the result of our calculation of the constant $k_1(\dot{N}O_2)$ according to published data [11]. The difference between this constant and the measured constants in absolute values (at the same temperature) is caused by the fact that they relate to a transition region, and they were obtained at different pressures. In our opinion, a significant correspondence of the results of our measurements and data published by Glanzer and Troe [11] confirms the correctness and reliability of our experiments, in which we directly detected for the first time the formation of $\dot{N}O_2$ radicals upon nitromethane decay.

We believe that the above consistence of experimental and calculated results makes it possible to exclude the hypothesis of the isomerization of nitromethane into methyl nitrite at the initial stage of the thermal decomposition of nitromethane with the formation of $\dot{C}H_3O$ and $\dot{N}O$ as primary decomposition products (in any case, in the range of high temperatures).

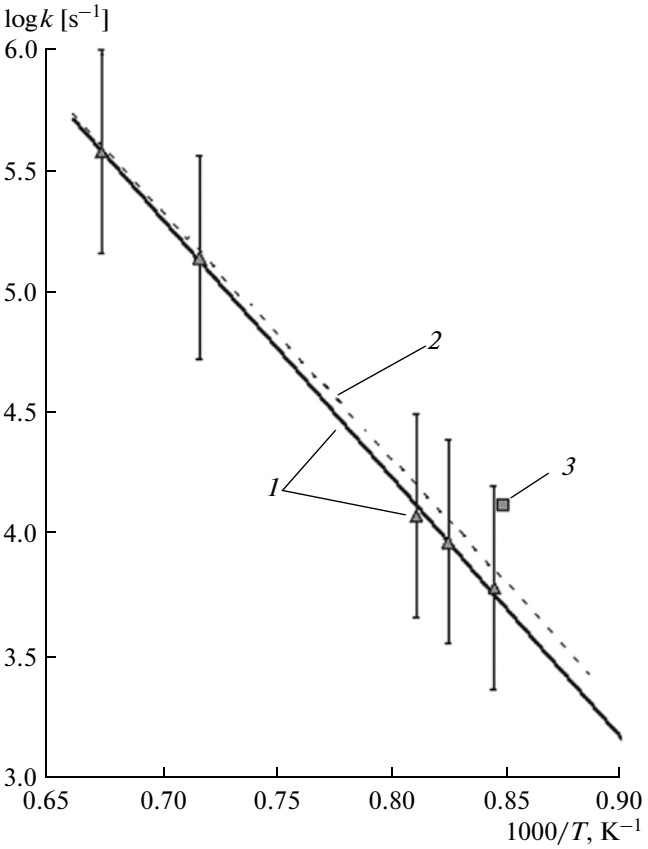

Fig. 2. The temperature dependence of constants $k_1(\dot{N}O_2)$ and k_1 in experiments on nitromethane decomposition at pressures of about (*1*, *2*) 1.5 and (*3*) 6 atm: (*1*) values of $k_1(\dot{N}O_2)$ measured in this work; (*2*) values of k_1 measured by Petrov et al. [15] from the consumption of nitromethane; and (*3*) value of $k_1(\dot{N}O_2)$ calculated based on published data [11].

NUMERICAL SIMULATION OF THE THERMAL DECOMPOSITION OF NITROMETHANE

We accomplished a kinetic simulation of the curves of formation and further consumption of $\dot{N}O_2$ upon the thermal decomposition of nitromethane. For the numerical simulation, were used published kinetic schemes of the decay of nitromethane [11, 22, 23]. In the examination of a scheme [23], it was necessary to correct the rate constant of a reaction, namely, the important reaction of the interaction of $\dot{C}H_3$ and $\dot{N}O_2$ radicals

$$\dot{C}H_3 + \dot{N}O_2 \rightarrow \dot{C}H_3O + \dot{N}O, \qquad \text{(II)}$$

because Srinivasan et al. [24] recently proposed a controversial expression for the numerical value of this constant, especially, in the region of high temperatures.

Figure 3 shows three calculated curves for the yield of $\dot{N}O_2$ and the absolute values of $\dot{N}O_2$ concentrations measured in this work under the conditions of the decay of 0.35% nitromethane in Ar at $T = 1235$ K and $P \approx 1.0$ atm. Curve *1* corresponds to the kinetic scheme [23], and the constant $k_1(\dot{N}O_2)$ experimentally measured in this work was used conducting the calculation; this constant coincides with the rate constant k_1 of nitromethane decay (as noted above). The reaction scheme [23] includes reaction (II), whose rate constant is 1.3×10^{13} cm^3 mol^{-1} s^{-1} according to published data [11, 12]. Curve *1* almost completely corresponds to our experimental data and very accurately reproduces the observed initial section of the dependence of the yield of O_2 radicals on reaction time with a maximum near 16 μs and the subsequent decrease in the concentration of $\dot{N}O_2$ in the section to 50 μs.

Curve *2* was obtained by calculation in accordance with the kinetic scheme [23] with the use of the experimentally measured constant $k_1^{obs}(NO_2)$ and the rate constant of reaction (II) reduced in accordance with the recommendations of Srinivasan et al. [24]. Based on an analysis of published data, we proposed the following expression for calculating the constant k_2 (especially at $T > 1000$ K):

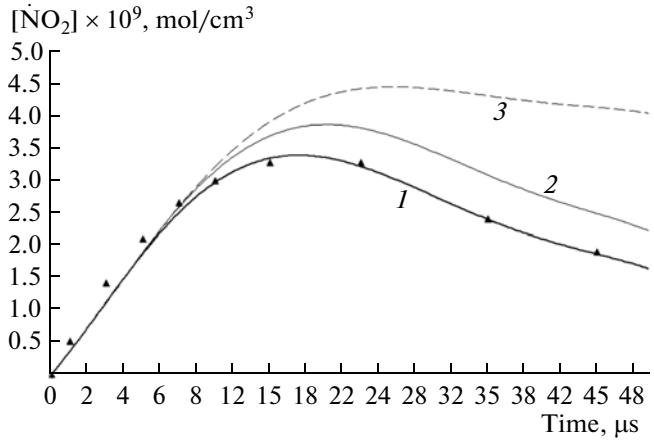

Fig. 3. Dependence of the concentration of $\dot{N}O_2$ on the time of the decomposition of 0.35% nitromethane in Ar at $T = 1235$ K and $P \times 1.0$ atm (points) and calculated data (curves): (*1*) calculation according to a published scheme [23], (*2*) calculation according to the scheme [23] with a decreased constant k_2, and (*3*) calculation according to a published scheme [11].

$$k_2 = 4 \times 10^{13} T^{-0.2} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}. \quad (4)$$

Calculated curve *2* at the very initial step (to ~6 μs) coincides with curve *1*, but then a more extended maximum in terms of time and higher concentrations of $\dot{N}O_2$ are observed; this is inconsistent with experimental data. It is obvious that the reason for this is an underestimated value of the rate constant k_2, which is insufficient for matching with the experimentally observed consumption of $\dot{N}O_2$.

Curve *3*, which corresponds to the kinetic scheme [11], which includes only two reactions, with the same values of the rate constant of nitromethane decomposition $k_1^{obs}(\dot{N}O_2)$ coincides with curve *2* up to a time of ~6 μs, but then is sharply climbs to reach a maximum near 30 μs (i.e., considerably later than in the experiment) and demonstrates a very weak decrease in the concentration of $\dot{N}O_2$, which also contradicts experimental data. At the point in time at 50 μs, the concentrations of $\dot{N}O_2$ in curve *3* and in the experiment differ by a factor of >2.

The results of the numerical simulation show that, first, all of the three kinetic schemes adequately describe the yield of $\dot{N}O_2$ radicals at the initial stage up to ~6 μs. This is reasonable because the experimentally found rate constant $k_1^{obs}(\dot{N}O_2)$ of the formation of $\dot{N}O_2$ upon the thermal decomposition of nitromethane, which almost coincides with the constant k_1, was used in the calculations performed according to all of the kinetic schemes. Second, a scheme of two reactions does not make it possible to describe the experiment even qualitatively because the steps of $\dot{N}O_2$ consumption are absent from this scheme (if we do not consider reaction (II)). Third, the kinetic scheme [23] with a reduced constant k_2 is also inconsistent with experimental data. Only the detailed scheme [23] with the rate constant k_2 reported by Glanzer and Troe [11, 12] very accurately reproduces the experimental dependence of the concentration of $\dot{N}O_2$ on the time of nitromethane decay.

DISCUSSION

Hypothesis on the Isomerization of Nitromethane under Conditions of Its Thermal Decomposition and Photolysis

Based on the experimental evidence for the primary yield of $\dot{N}O_2$ upon the decomposition of nitromethane (which is indicative of the absence of initial nitromethane isomerization in the process of its thermal decomposition behind shock waves) obtained in this work over a sufficiently wide temperature range, we attempt to analyze information on the isomerization of nitromethane under various conditions.

The hypothesis on the intramolecular rearrangement of nitromethane into methyl nitrite or another isomer in the process of the thermal decomposition of nitromethane was discussed in a number of publications [3, 5, 7, 18]. The results of studies on the isomerization of nitromethane upon its photolysis are contradictory. In our view, they are unreasonably extended to the thermal decomposition of nitromethane, although pyrolysis and photolysis occur at substantially different temperatures and pressures and (that is very important) they are different in the method of reaction initiation and the nature of the excitation of different degrees of freedom of the molecule.

Therefore, it is reasonable to divide the brief consideration of the problem of nitromethane isomerization into two parts: the possibility of isomerization under the conditions of the high-temperature thermal decomposition of nitromethane at low and medium pressures (which was studied in detail in the shock-wave experiments) and the possibility of isomerization under the conditions of the relatively low-temperature process of photolysis in the absence of collisions between the molecules (collision activation). The hypothesis of isomerization was proposed for the first time precisely in photodissociation studies. Thus, Napier and Norrish [25] found spectroscopically that methyl nitrite is an important intermediate in the low-temperature photolysis of nitromethane. Napier and Norrish [25] explained this fact by the formation of methyl nitrite according to the reaction

$$\dot{C}H_3 + \dot{N}O_2 \rightarrow CH_3ONO. \quad (III)$$

However, there is another hypothesis published by Bradley [5], according to which the composition of nitromethane photolysis products, which was observed in earlier publications [26–28], is due to the initial rearrangement of nitromethane into methyl nitrite at the very beginning of photodissociation.

Isomerization upon the Thermal Decomposition of Nitromethane

The hypothesis of isomerization was discussed in some works dedicated to the thermal decomposition of nitromethane. Thus, Hillenbrand and Kilpatrick [3], who studied the disintegration of nitromethane at medium temperatures of 693–753 K, mentioned the possibility of using this hypothesis for explaining experimental data. Bradley [5] also used the hypothesis of isomerization to explain the rate constants of nitromethane decomposition (which were underestimated in terms of absolute values and activation energy) found by him at 1145–1460 K in a shock tube equipped with a time-of-flight mass spectrometer. However, it is well known that the results of measurements executed with the aid of a time-of-flight mass spectrometer in a molecular beam, which escapes through a narrow nozzle at the end of a shock tube (and, generally, in any molecular beams) are characterized by systematic errors. This is caused by the complexity of this procedure and by the fact that, under the action of ionizing and magnetic fields, considerable disturbances are introduced into the flow of test molecules and their products. Publications [5, 29], where the disintegration of nitromethane and azomethane $(CH_3)_2N_2$ in shock tubes was studied with the aid of time-of-flight mass spectrometers, are the examples of the application of not completely correct procedures. It is likely that Bradley [5], restricted himself to only general words concerning isomerization because the mass spectrograms obtained by him (which were indicative of a monotonic decrease in the concentrations of initial molecules and in the yields of decay products ($\dot{C}H_3$, $\dot{N}O_2$, $\dot{N}O$, CO, H_2O, and CH_4)) did not exhibit the signs of nitromethane isomerization into methyl nitrite, in particular, any traces of the $\dot{C}H_3O$ radical or its fragments.

Borisov et al. [7], who referred to publications [5, 6], noted that the rate constants of nitromethane disintegration measured at $T \geq 1200$ K are too small in terms of absolute values and activation energy in comparison with the values obtained by the extrapolation of low-temperature data. Borisov and coauthors [6, 7] assumed that the passage of the unimolecular reaction of nitromethane disintegration from the region of high pressures, which is characterized by the rate constant of disintegration $k_{1\infty}$, to the region of intermediate pressures occurs at temperatures much higher than 1200–1300 K. Therefore, Borisov et al. [7] related the underestimated values of the rate constants of nitromethane disintegration at $T \geq 1200$ K and also the low observed activation energy of only 23 ± 4 kcal/mol to the process of intramolecular nitromethane rearrangement before disintegration.

Borisov et al. [7] stated that nitromethane initially isomerized into methyl nitrite under the conditions of the disintegration of a mixture of 2.5% nitromethane with Ar behind shock waves at 1260 K and products other than those of reaction (I) were formed upon the decomposition of the rearranged molecule. The oscillogram obtained upon the measurement of nitromethane disintegration at the wavelength $\lambda = 239$ nm was considered as the experimental evidence for this rearrangement. The oscillogram, which was characterized by low time resolution, a quasi-steady-state absorbance of nitromethane behind the shock wave was observed for about 30 μs. According to Borisov et al. [7], this seemed to indicate an intramolecular rearrangement of nitromethane into methyl nitrite. However, this oscillogram was unique. In all of the subsequent experiments of the same authors and in our numerous experiments [10, 13–16] performed at similar temperatures and with similar and even more concentrated ("dense") mixtures of nitromethane, this effect was never observed. It was also not noted in the publications of foreign authors. In our opinion, possible reasons for an artifact of this kind in a thick and dense mixture can be instrumental errors or limitations, for example, a limited vertical linearity range of rays on the screen of a five-beam S1-33 oscillograph, which was used by Borisov et al. [7]. Therefore, we assume that the test oscillogram cannot serve as evidence for the isomerization of nitromethane into methyl nitrite upon the thermal decomposition of nitromethane.

Borisov et al. [7] also considered the S-shaped curve of the yield of $\dot{N}O_2$ radicals as evidence for the initial isomerization of nitromethane into methyl nitrite upon its thermal decomposition. According to Borisov et al. [7], this indicates that $\dot{N}O_2$ it the secondary rather than primary decay product; that is, the isomerization of nitromethane occurs. However, in our opinion, the S-shaped curve is explained by only an insufficiently high time resolution (caused by the technical capabilities of measuring instrumentation of that time) in the detection of $\dot{N}O_2$.

Zaslonko et al. [10], who performed their study in the same shock tube as that used by Borisov et al. [7] but with an improved time resolution, spectroscopically detected the consumption of nitromethane and also the formation and consumption of $\dot{N}O_2$ radicals at temperatures from 1030 to 1580 K, pressures from 1 to 2.8 atm, and parent substance concentrations of 1–3.7%. Direct experimental evidence for the occurrence of nitromethane disintegration according to reaction (I) with the formation of the $\dot{N}O_2$ radical as the primary product was obtained for the first time. However, the curves of the yield of $\dot{N}O_2$ were not processed quantitatively.

The experimental data obtained in this work in a sufficiently wide temperature range allow us to conclude the absence of nitromethane isomerization into methyl nitrite upon the high-temperature thermal decomposition of nitromethane and its conversion into $\dot{C}H_3O$ and $\dot{N}O$, rather than into $\dot{C}H_3$ and $\dot{N}O_2$.

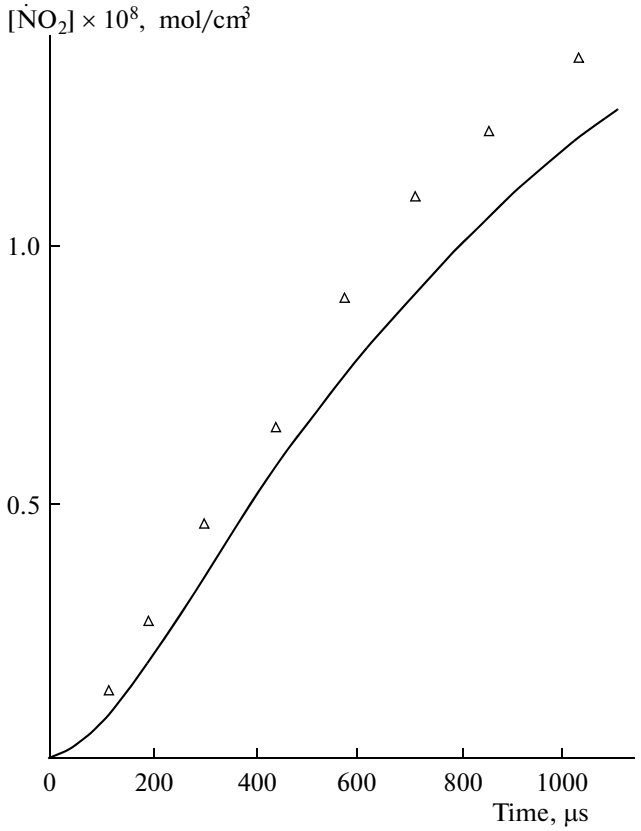

Fig. 4. Dependence of the concentration of ṄO radicals on the time of the decomposition of 0.25% nitromethane in Ar at $T = 1051$ K and $P = 0.83$ atm: the points and the curve refer to experimental results and calculated values based on published data [30], respectively.

This conclusion is based on the following results: (1) the primary formation of $\dot{N}O_2$ radicals as the decay products of nitromethane; (2) the coincidence of the rate constants of nitromethane disintegration and $\dot{N}O_2$ formation; (3) the evident secondary appearance of ṄO radicals (as evidenced by a noticeable induction period and the S-shaped curve of their yield, which was noted in all of the our calculations and observed studies [22, 30, 31] (Fig. 4); and (4) a good description of the curves of formation and consumption of $\dot{N}O_2$ with the aid of the same kinetic scheme that was used earlier for the interpretation of data on the disintegration of nitromethane [16]. As can be seen in Fig. 4, the experimental curve of the yield of ṄO radicals is S-shaped in the section to 400 μs. Curves of the same shape were measured in entire test temperature range up to 1400 K.

The question put by Borisov et al. [7]—what is responsible for underestimated rate constants of the thermal decomposition of nitromethane at high temperatures (in comparison with the results of the extrapolation of low-temperature data)—is answered both experimentally and theoretically to date. Glanzer and Troe [11] and, earlier, Zaslonko et al. [10] demonstrated that the answer is that the rate constant of the unimolecular disintegration of nitromethane depends on pressure, as was theoretically confirmed in a number of studies [32–36].

However, theoretical [18] and experimental [19, 20] reasons in favor of the hypothesis of the initial isomerization of nitromethane into methyl nitrite upon pyrolysis and photolysis appeared once again 13–14 years after the publication by Glanzer and Troe [11], when, in our opinion, the question on the isomerization of nitromethane under the conditions of the high-temperature thermal decomposition of nitromethane was finally solved. Dewar et al. [18] considered them in detail; we assume that they only repeat the consideration of Borisov et al. [7] in a worsened form. Dewar et al. [18] noted that the dissociation energy of the C–N bond in nitromethane is 59.5–60 kcal/mol, whereas the experimental values of the activation energy of the disintegration of nitromethane (taken from early publications concerning studies performed in the 1950–1960s [6, 37, 38], including those performed at high temperatures) seem to be much lower, up to 42.8 kcal/mol. However, an obvious error is here: the publications [37, 38] did not mention the decomposition of nitromethane; they were dedicated to the study of the disintegration of other molecules, namely, 1,2-nitropropanes ($C_3H_7NO_2$), and they were not related to the decomposition of nitromethane.

Dewar et al. [18] ignored the newest cited publication [6] (by the way, the only publication concerning the disintegration of nitromethane). In this publication, it was established that the activation energy of nitromethane disintegration is 57 kcal/mol, which removes all questions concerning the low activation energy of this process. However, based on values not related to the disintegration of nitromethane, Dewar et al. [18] believed that the first stage of disintegration cannot be the simple act of nitromethane dissociation into two radicals and the only acceptable hypothesis is the intramolecular rearrangement of nitromethane into methyl nitrite. In this case, the most important cycle of earlier classical publications [11, 12, 17, 32–36] was ignored. In these publications, a decrease in the rate constants of the unimolecular decomposition of moderately complex molecules (including nitromethane) is explained by their passage from $k_{1\infty}$ to the values characteristic of an intermediate-pressure region.

Isomerization upon the Photolysis of Nitromethane

Wodtke et al. [19, 20] studied the photolysis of nitromethane by infrared multiphoton dissociation in a molecular beam. The molecular beam of nitromethane was generated by passing a flow of helium under a pressure of 145 Torr through a vessel with nitromethane at room temperature. This mixture arrived at a nozzle with a diameter of 125 μm heated to

580 K. Heating made it possible to prevent the formation of clusters and increased the level of multiphoton absorption. Nitromethane underwent dissociation under the action of a pulse infrared CO_2 laser, which operated at the R(20) line of an IR band with $\lambda = 9.6$ μm. After the action of that ionizing and magnetic fields on this beam when it travelled a distance of 37 cm, the composition of the products of the photodissociation decomposition of nitromethane was studied using a time-of-flight mass spectrometer. The mass spectrum exhibited the signals of NO_2^+ ($m/z = 46$), NO^+ ($m/z = 30$), and CH_3^+ ($m/z = 15$) ions and a photolysis product with a mass of 29, which was hypothetically identified as the HCO^+ ion. Wodtke et al. [19, 20] explained the presence of NO_2^+, NO^+, and CH_3^+ by nitromethane decomposition via the direct reaction path

$$CH_3NO_2 \rightarrow [CH_3NO_2]^+ \rightarrow \dot{C}H_3 + NO_2, \qquad \text{(IV)}$$

however, they believed that the formation of the product with a mass of 29 cannot be related to the occurrence of this reaction. It should be noted that Wodtke et al. [19, 20] did not experimentally observe an ion with $m/z = 31$, that is, the desired radical $\dot{C}H_3O$, which would serve as direct evidence for the isomerization of nitromethane. However, they assumed that, after the electron ionization of the $\dot{C}H_3O$ radical, it was impossible to expect the appearance of a product with a mass of 31 because the methoxyl cation CH_3O^+ decomposes into H_2 and HCO^+ due to the fact that the reaction of the elimination of molecular hydrogen is highly exothermic. At the same time, the $\dot{C}H_3O$ radical very rapidly decomposes under normal conditions in the completely different reaction

$$\dot{C}H_3O + M \rightarrow CH_2O + \dot{H} + M. \qquad \text{(V)}$$

Nevertheless, Wodtke et al [19, 20] believed that they observed the appearance of $\dot{C}H_3O$ radicals, which was predicted by Dewar et al. [18], in the course of nitromethane photodissociation and postulated (as noted by Kilic et al. [39]) that this is connected with the isomerization of nitromethane according to the reaction

$$CH_3NO_2 \rightarrow [CH_3NO_2]^+ \rightarrow [CH_3ONO]^+ \rightarrow \dot{C}H_3O + \dot{N}O. \qquad \text{(VI)}$$

Here, Wodtke et al. [19, 20] made a not entirely correct substitution. In this case, the discussion deals with the mechanism of nitromethane photolysis, whereas Dewar et al. [18] studied its pyrolysis; furthermore, as shown above, the latter publication contains clearly pronounced inaccuracies. According to Wodtke et al. [19], the height of the activation barrier of the isomerization reaction of nitromethane under conditions of its IR-photodissociative decomposition was estimated at 55.5 kcal/mol, which is 4–4.5 kcal/mol smaller that the energy of the direct dissociation of the C–N bond upon the decay of nitromethane. Wodtke et al. [19, 20] also estimated the fraction of reaction (VI) with respect to reaction (IV) at about 60%. Their conclusion on nitromethane isomerization upon photolysis was based on the assumed detection of the $\dot{C}H_3O$ radical. However, for example, the publication by Napier and Norrish [25], who experimentally observed the strong absorption of $\dot{C}H_3$ radicals immediately after the flash photolysis of nitromethane for several microseconds, was not mentioned in this case. The publication by Bielski and Timmons [40], who detected the EPR signal from $\dot{C}H_3$ and $\dot{N}O_2$ radicals upon the low-temperature photolysis of nitromethane, was also not mentioned. Published data [41, 42] on the measurement of the dynamics of nitromethane photodissociation in the picosecond regime with its excitation in the region of $\lambda \approx 270$ nm were not taken into account. In both of these studies, a high quantum yield of $\dot{N}O_2$ in the ground state was observed for 5–6 ps after the absorption of a single photon by nitromethane.

Experimental and theoretical studies in which data on the disintegration of nitromethane were interpreted and, in particular, the energy of an intramolecular rearrangement of nitromethane was considered for analyzing the possibility of the isomerization of these molecules under both thermal decomposition and photodissociation, appeared after publications [18–20]. MacKee [43] performed the ab initio calculation of the unimolecular isomerization of nitromethane into methyl nitrite with the use of a model that assumed the existence of a so-called free transition state of the nitromethane molecule with the C–N and C–O bond lengths of 3.617 and 3.7 Å, respectively (Fig. 5a). As a result, the energy barrier of the isomerization reaction was estimated at a value about 10 kcal/mol higher than the energy of the direct cleavage of the C–N bond upon nitromethane decay with the formation of $\dot{C}H_3$ and $\dot{N}O_2$. This estimation contradicts both theoretical and experimental published data [18–20]. The results obtained by MacKee [44] contradict theoretical considerations [18]. MacKee [43] used the concept of another so-called compressed transition state of the nitromethane molecule (Fig. 5b), in which the C–H and C–O bond lengths are shorter by a factor of almost 2 (1.93 and 2.0 Å, respectively). Unfortunately, the experimental results of Wodtke et al. [19, 20] were not discussed and experimentally checked by other researchers.

Saxon and Yoshimine [45] attempted to determine the transition state parameters of the nitromethane molecule upon its disintegration and the height of the energy barrier of the isomerization reaction of nitromethane into methyl nitrite. According to Saxon and Yoshimine [45], the transition state of nitromethane can be approximately represented in the form of the almost completely separated $\dot{C}H_3$ and

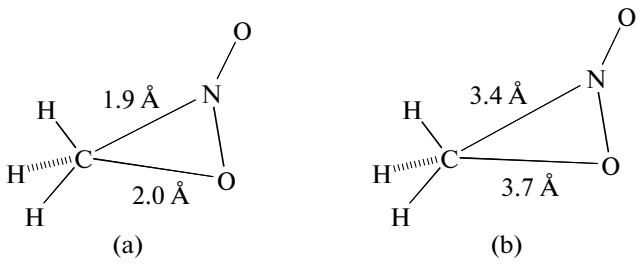

Fig. 5. Theoretical diagrams of the transition states formed in nitromethane decomposition: (a) compressed and (b) free structures [48].

$\dot{N}O_2$ radicals with extremely long C–N and C–O bonds (to 3.396 and 3.654 Å, respectively, which are close to published values [43]). It was calculated that the barrier of nitromethane isomerization is ~56.7 kcal/mol and the C–N bond dissociation energy is about 57.1 kcal/mol; that is, taking into account approximations made in the calculation, these values are almost coincident.

Hu et al. [46] included 10 nitromethane isomers, 46 transition states, and 16 decay products into the multifactor theoretical calculation of the complex potential energy surface in the process of unimolecular dissociation and possible isomerization of nitromethane. Geometric parameters and corresponding energy values were determined at different stationary points; they were found consistent with available experimental data. It was found that the reaction path that leads to the formation of $\dot{C}H_3$ and $\dot{N}O_2$ at the primary step is the most energetically accessible and most probable channel of nitromethane decomposition. This occurs as a result the direct rupture of the C–N bond in nitromethane. Other theoretically possible reaction paths of disintegration, which lead to the appearance of the products $\dot{C}H_3O$ and $\dot{N}O$, $H_2C{=}O$ and HNO; or HCNO and H_2O, can occur only on condition of the initial isomerization of nitromethane. The dissociation energy of the C–N bond in nitromethane was theoretically estimated at 61.9 kcal/mol [46], which it is somewhat greater than the previously recommended value of 59–60 kcal/mol. However, even this C–N bond dissociation energy is lower than the barriers of nitromethane isomerization into methyl nitrite or the aciform of nitromethane ($CH_2N(O)OH$) at least by 2.7 and 2.1 kcal/mol, respectively. Thus, the results of this works also contradict the above data on the pyrolysis [18] and photolysis [19, 20] of nitromethane.

Guo et al. [47] described the newest experiment on the study of the dynamics of nitromethane photodissociation by laser excitation at $\lambda = 226$ and 271 nm with the use of time-of-flight mass spectrometry and also laser-induced fluorescence spectroscopy in the nano- and femtosecond ranges of measurements. The above two laser wavelengths correspond to the excited of states nitromethane $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$. They also performed a detailed analysis of all of the previously known data on the photolysis of nitromethane, which were compared with the newly obtained results. To study the dynamics of nitromethane photodissociation and to analyze its numerous and contradictory mechanisms proposed by different authors, they performed experiments under collision (inside a quartz capillary) and collisionless conditions in the zone of ionization and molecular excitation with the use of a resonance multiphoton ionization technique and time-of-flight mass spectrometry. Furthermore, the $\dot{O}H$ and $\dot{C}H_3O$ radicals as dissociation products were detected by laser-induced fluorescence.

It is significant that the $\dot{C}H_3O$ radicals were observed only under collision conditions; Guo et al. [47] explained this fact by interaction between $\dot{C}H_3$ and $\dot{N}O_2$. In the femtosecond experiments with laser excitation at the wavelength $\lambda = 226$ nm, $\dot{C}H_3$, $\dot{N}O_2$, and $\dot{N}O$ were observed as the products. These results demonstrate that the cleavage of the C–N bond is the main process upon the photolysis of nitromethane after its $\pi^* \leftarrow \pi$ excitation at the wavelength $\lambda = 226$ nm and that the formation of $\dot{N}O_2$ upon nitromethane decay precedes the appearance of the $\dot{N}O$ radical. According to Guo et al. [47], the formation of the $\dot{C}H_3O$ radical after the recombination of the of $\dot{C}H_3$ and $\dot{N}O_2$ radicals under the collision conditions makes it possible to reject the mechanism of intramolecular nitromethane isomerization into methyl nitrite with the generation of the $\dot{C}H_3O$ and $\dot{N}O$ radicals from the excited states of nitromethane.

In the nanosecond experiments on the photolysis of nitromethane excited at the wavelength $\lambda = 271$ nm ($\pi^* \leftarrow n$), Guo et al. [47] attempted to detect dissociation products such as CH_3, NO_2, CH_3O, and OH. However, these attempts were unsuccessful. In the femtosecond experiments performed under the same conditions, a high-intensity signal from the initial nitromethane molecule was observed together with the weak signals from the decay products CH_3, NO_2, and NO. Analyzing these data, Guo et al. [47] concluded that the dissociation of nitromethane from the electronically excited state n does not occur at all under collisionless conditions in a supersonic molecular beam. Thus, it was found that the isomerization of nitromethane into methyl nitrite upon its photodissociation in electronically excited states (at least $\pi \rightarrow \pi^*$) does not occur.

Nguyen et al. [48] theoretically checked the mechanism of the unimolecular rearrangement of nitromethane into methyl nitrite. The calculations were performed as applied to the potential energy surface constructed with the use of quantum chemistry

methods, including the construction of several isomeric low-energy transition states. Special attention was given to the following two questions posed in the previous experimental and theoretical studies: (1) how the conversion of nitromethane into methyl nitrite (i.e., the rapid migration of methyl radicals from the N atom to the O atom) occurs, through a free or compressed transition structure and (2) does the energy barrier of nitromethane rearrangement into methyl nitrite exceed the C–N bond dissociation energy? The calculations showed that the methyl radicals migrate through a compressed transition state with the C–N and C–O bond lengths of 1.897 and 1.971 Å, respectively, and the energy required for the isomerization of nitromethane is higher than the energy of the direct dissociation of the C–N bond with the formation of $\dot{C}H_3$ and $\dot{N}O_2$ by no less than 6 kcal/mol. Thus, the results of this work do not confirm theoretical conclusions [18] and experimental data [19, 20].

More recently, Zhu and Lin [49], who theoretically studied the decomposition and isomerization of nitromethane, performed somewhat different calculations and made other conclusions. The new calculations performed with the use of a very free transition-state structure (whose parameters were not specified) showed that $\dot{C}H_3O$ and $\dot{N}O$ radicals seem the predominant products of nitromethane decay at the energy of 59 ± 1 kcal/mol. However, it is well known that, actually, the rupture of the C–N bond occurs at the same energy (59–60 kcal/mol) and $\dot{C}H_3$ and $\dot{N}O_2$ are the products of nitromethane decay. Although Zhu and Lin [49] refused the height of an isomerization barrier (which is 6 kcal/mol higher than the C–N bond dissociation energy), which was reported previously by Nguyen et al. [48], they considerably increased the height of the energy barrier of isomerization (from 55.5 to 59 ± 1 kcal/mol) upon the analysis of experimental data [19, 20]. Moreover, they came to the conclusion that the multiphoton excitation energy of the nitromethane molecule should be about 61 kcal/mol for the adequate description of these data. However, this value is completely sufficient for the cleavage of the C–N bond and the disintegration of nitromethane into $\dot{C}H_3$ and $\dot{N}O_2$ according to the usual reaction path.

Correlating data on the kinetics and the composition of products of the thermal decomposition nitromethane and methyl nitrite, Zhang and Bauer [50] drew the conclusion that the possible contribution of nitromethane isomerization to its thermal decomposition was negligible at high temperatures (~1090 K). They also noted that theoretical studies concerning the decomposition and possible isomerization of nitromethane contradict each other, for example, with respect to the structure of the transition state of the decomposed molecule. Therefore, more detailed theoretical studies of the mechanism of the thermal and photolytic disintegration of nitromethane and the possible contribution of the stage of isomerization of the initial molecule to these processes should be performed.

Brief Theoretical Analysis of Competition between Direct Decomposition and Isomerization Reaction Paths upon the Thermal Decomposition of Nitromethane

Evaluating competition between the reaction paths of the direct decomposition of nitromethane and its isomerization, we should consider the specific character of conditions under which the corresponding experimental data were obtained [51]. The direct decomposition of nitromethane was observed under thermal conditions at low or medium pressures in shock waves. In this case, a noticeable contribution of the second channel (isomerization) to the formation of reaction products was not detected. This means that the first channel is opened earlier than the second one in the process of the multistage collision activation of the nitromethane molecule and nitromethane decomposes with the cleavage of the C–N bond before the generation of necessary conditions for isomerization. Consequently, the population density of the energetically active states for the isomerization under these conditions is almost zero. It is possible to assume that the yield of the reaction products via the second channel can increase as the pressure is increased to a level close to the limit of high pressures, that is, to the value of $k_{1\infty}$ and the products can be detected experimentally.

It is likely that the kinetics of nitromethane decomposition with preliminary isomerization can be observed under other rarely encountering conditions on the photoactivation of nitromethane with infrared photons [19, 20]. A considerable difference of collision activation from photolytic activation is that, in the former case, both vibrational and rotational degrees of freedom of the molecule are excited, whereas the rotational degrees of freedom are almost not excited in the latter case because the photon momentum (and the moment of momentum) is very small. Therefore, the moment of momentum, which can be imparted to the nitromethane molecule upon its collision with an IR photon is also very small.

The moment of momentum, which could be transferred to the nitromethane molecule upon collision with a photon, is of the following order of magnitude:

$$(\hbar w/c) r_{\text{nitromethane}}, \quad (4)$$

where $\hbar w$ is the photon energy, c is the velocity of light in a vacuum, and $r_{\text{nitromethane}}$ is the linear size of the nitromethane molecule. In the IR region of the spectrum, for example, at $\hbar w = 0.1$ eV (i.e., 1.6×10^{-13} erg) and $r_{\text{nitromethane}} = 10^{-8}$ cm,

$$(\hbar w/c)\, r_{\text{nitromethane}} = 1.6\times10^{-13}\,\frac{10^{-8}}{3\times10^{10}} = 5.3\times10^{-32}\text{g cm}^2\ \text{s}^{-1}. \quad (5)$$

This value is lower than Planck's constant $\hbar$, which is equal to a minimum quantum of angular momentum, by five orders of magnitude. Therefore, the rotational molecular excitation of nitromethane by photons in the IR range does not occur. Comparing the active states of the molecule excited in collisions with IR photons and atomic particles, one should take into account that, in the latter case, the number of degrees of freedom that contribute to the reaction coordinate of the simple cleavage of the C–N bond is greater than that in the former case according to the Rice–Ramsperger–Kassel–Marcus (RRKM) theory.

The average energy per rotational degree of freedom of the active molecule is lower than the average energy of each oscillator by a factor of 2. There are 15 vibrational degrees of freedom in the initial nitromethane molecule. It is likely that the nitro group NO_2 in the active nitromethane molecule rotates about the C–N bond. In this case, the number of vibrational degrees of freedom of nitromethane is 14.

There are also three rotational degrees of freedom of the nitromethane molecule as a whole and (in the case of the free rotation of the nitro group) one additional rotational degree of freedom. The average rotational energy (E_r) of all of the four rotations in the active molecule is

$$E_r = 2E/16 = E/8, \quad (6)$$

where E is the activation energy of reaction (I) with the cleavage of the C–N bond. According to published data [18], $E = 60$ kcal/mol; in this case, $E_r = 7.5$ kcal/mol.

Consequently, for nitromethane decomposition by the direct channel, the following vibrational energy (E_v) is sufficient:

$$E_v = E - E_r^1, \quad (7)$$

where E_r^1 is the portion of rotational energy that can be transferred to the reaction coordinate. This value is somewhat smaller than E_r because the angular momentum (M_r) of the molecule about two axes perpendicular to the reaction coordinate is retained upon the spontaneous disintegration of the active molecule. With the retention of the angular momentum M_r, the rotational energy decreases proportionally to the squared distance r between the centers of gravity of two parts of the nitromethane molecule—the nitro group NO_2 and the methyl radical CH_3. Assuming that this distance in the activated molecule (expanded along the C–N bond) is greater than that in the nonactivated molecule by a factor of about 1.5, we obtain the following value:

$$E_r^1 = \tfrac{1}{2}E_r + \tfrac{1}{4}E_r = \tfrac{3}{4}E_r. \quad (8)$$

In this case, according to Eq. (7), $E_v = 54.4$ kcal/mol. This energy is lower than the height of an activation barrier for the isomerization reaction, which was estimated at 55.5 kcal/mol according to published data [19, 20], whereas Zhu and Lin [49] increased this value to 59 ± 1 or even to 61 kcal/mol. Hence it follows that the nitromethane molecule decomposes by a direct reaction path with the cleavage of the C–N bond under thermal conditions in shock waves at low or medium pressures before the activation barrier of the isomerization reaction is reached.

In general, our experimental and theoretically calculated results and all of the analyzed published data confirm the conclusion made in this work that isomerization does not occur or is negligible under the conditions of the high-temperature thermal decomposition of nitromethane at low and medium pressures and $\dot{C}H_3$ and $\dot{N}O_2$ are the products of nitromethane decomposition. Different conclusions reported in a theoretical publication [18] may be explained by the inaccuracy of used data and by ignoring classical results [11, 32–36] on the dependence of the rate constants of the thermal decomposition of nitromethane on pressure and temperature.

Both our results and published data suggest that nitromethane isomerization does not occur upon high-temperature thermal decomposition. Therefore, a so-called concerted mechanism of decomposition, when two kinetically indivisible processes (as, for example, in the thermal decomposition of azomethane [52–55]) occur at a single step of the reaction, does not occur in the dissociation of nitromethane. The high-temperature disintegration of the nitromethane molecule consists in the elimination of $\dot{N}O_2$ radicals from it as a result of the C–N bond rupture, and this process is a classical unimolecular reaction, which took place in our experiments in a transition region in terms of pressure with the clearly pronounced dependence of the rate constants of disintegration on pressure. The pressure dependence of this kind was not observed at all in the decomposition of azomethane by a concerted mechanism. This is explained by specific intramolecular processes of azomethane decomposition.

It is likely that published data [47, 49] make it possible to expand the range of experimental conditions under which the isomerization of nitromethane is absent or plays a very insignificant role in the photolysis of nitromethane. Isomerization is not observed in the photodissociation of nitromethane in electronically excited states and, apparently, it is not very significant in the infrared multiphoton dissociation of nitromethane. Indeed, even according to published data [19], the ratio of the rate of reaction (VI) to the sum of the rates of reactions (IV) and (VI), that is, to the overall rate of nitromethane consumption, determined as $[\dot{N}O]/([\dot{N}O] + [\dot{N}O_2])$, is only 37%. Without considering the details of this sophisticated experiment, note that it is reasonable to take into account conclusions made in a number of publications [40–50] on the isomerization of nitromethane during its

decomposition under various conditions in the interpretation of experimental data.

Thus, we studied for the first time the disintegration of nitromethane behind shock waves at temperatures of 1190–1490 K and a pressure of ~1.5 atm in terms of the yields and consumption of $\dot{N}O_2$ radicals, which were detected by their absorption at the wavelength $\lambda = 405$ nm. The curves of the yield of $\dot{N}O_2$ have a convex shape in the initial section, which is characteristic of the formation of primary decomposition products. The temperature dependence of the rate constants of formation of the $\dot{N}O_2$ radicals at the very initial stage of nitromethane decomposition was found for the first time.

It was established that the rate constants of nitromethane decomposition measured based on the consumption of the parent substance and the yield of $\dot{N}O_2$ radicals quantitatively coincide with each other. A kinetic simulation of the formation and consumption of $\dot{N}O_2$ radicals was performed and a good agreement between experimental and calculation data was achieved. A brief theoretical analysis of competition between the reaction paths of direct disintegration and isomerization under conditions of the thermal decomposition of nitromethane was performed and the advantage of the direct channel with the cleavage of the C–N bond was demonstrated. The experimental results and published data on the possibility of nitromethane isomerization into methyl nitrite upon thermal decomposition and photolysis were analyzed. Some inaccuracies in a number of publications on the thermal decomposition of nitromethane, where a conclusion on the possibility of its isomerization into methyl nitrite was drawn, were noted. Based on our and published experimental and theoretically calculated data, the secondary formation of the NO radicals was shown; the curves of the yield of these radicals upon the thermal decomposition of nitromethane are characteristically S-shaped. Because of the absence of nitromethane isomerization into methyl nitrite at the initial step of its high-temperature thermal decomposition, a conclusion was made that the concerted mechanism is inapplicable to the disintegration of nitromethane; it is likely that the contribution of nitromethane isomerization under conditions of IR photodissociation is low.

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