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Application of the Monte Carlo Method to Modeling Kinetic Processes of Polyatomic Molecules and Clusters: II. Kinetics of Unimolecular Reactions of Polyatomic Molecules

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Abstract—The method for statistical modeling of the kinetics of unimolecular decomposition of polyatomic molecules based on the construction of nonequilibrium functions of the distribution over the energies of the vibrational excitation of molecules is developed. The rate constants for the two-channel decomposition of a model molecule depending on temperature and pressure are reported. The relaxation characteristics for the dissociation of the model molecule are determined.

INTRODUCTION

The methods of statistical modeling, also called Monte Carlo (MC) methods, are an efficient tool for solving problems of molecular kinetics [1]. Thus, the MC method was used to model the processes occurring during heating the molecular gas with a constant laser beam and exponentially damping laser pulses [2–4]. To describe energy exchange during collisions, the exponential model was used. Other examples of the MC simulations of chemical reactions is described in [5, 6], where on the basis of the method proposed by Berd [7], simple bimolecular ($A + B \longrightarrow C + D$) [5] and reversible unimolecular ($AB + M \rightleftarrows A + B + M$) [6] reactions were modeled. It was assumed that energy required for overcoming the potential barrier is supplied by collisions, and the internal energy was neglected.

Vlasov *et al.* [8, 9] proposed the method for describing emission properties of metallic clusters (emission of atoms, electrons, and light) formed during condensation of supersaturated metal vapors behind the shock waves. When modeling the kinetics of emission properties, the ideas of the statistical theory of unimolecular reactions were used. Using the MC method, the functions of cluster distribution over internal energy were calculated for the processes of energy exchange during cluster collisions with the atoms of diluent gas and due to energy loss in emission processes. The processes of energy exchange between clusters with medium species were described using the step-ladder model.

MC simulations of energy exchange processes during collisions in the framework of the statistical theory of unimolecular reactions were further developed in [10]. In that paper, we developed the mathematical model describing the process of energy exchange in collisions within the framework of the model of activation via the formation of the statistical collisional complex. According to this model, the overall energy of the complex is statistically distributed during collision and redistributed during complex decomposition between the internal energy of the molecule and the kinetic energy of species. The function of cluster distribution over internal energy was calculated using the MC method that imitated random changes in the energies of molecules during collisions with medium species. We also simulated the kinetics of the relaxation of the function of distribution over energy during jumpwise changes in the temperature of a diluent gas and determined the characteristics of energy exchange during collisions (the average energy and the average square of energy transferred during collisions) depending on the complete energy of the molecule.

In this work, we attempt to develop the method proposed in [10] to describe the transformations of the function of distribution over energy during unimolecular decomposition of polyatomic molecules.

Problem Statement

According to the statistical theory of unimolecular reactions, the apparent rate constant of the unimolecular decomposition of a polyatomic molecule is determined by the expression

$$k_d(T) = \sum_i k_i x_i,$$

where x_i is the population of the ith quantum state above the dissociation threshold E_d normalized to unity; k_i is the rate constant of the spontaneous decomposition of the molecule at an ith state [11]. When the excitation energy is close to E_d, the distances between the levels

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† Deceased.

are small and the summation can be replaced by an integral

$$k_{\mathrm{d}}(T) = \int_{E_{\mathrm{d}}}^{\infty} k(E)F(E)dE, \qquad (1)$$

where $k(E)$ is the specific rate constant of the decomposition of molecules at the state with energy E, where $F(E) = x(E)\rho(E)$ is the function of distribution over energy for reacting molecules and $\rho(E)$ is the density of energy states of a molecule. We believe that all energy states of the molecule are equivalent. In this work, we assume for simplicity that only vibrational degrees of freedom participate in the decomposition reaction, whereas rotational degrees of freedom should be taken into account only when calculating energy exchange with medium species.

Thus, to calculate the rate constants of unimolecular reactions, it is necessary to have the functions $\rho(E)$ and $k(E)$ and find the method for estimating the populations of the energy states $x(E)$ or the function of distribution over energy for the reacting molecule. Let us consider a chloroform molecule as a model to illustrate the method for obtaining the above functions for the decomposition reaction.

The dissociation of chloroform may occur via two channels [12–15]:

$$\mathrm{CHCl_3} \longrightarrow \mathrm{CCl_2} + \mathrm{HCl}, \qquad \mathrm{(I)}$$

$$\mathrm{CHCl_3} \longrightarrow \mathrm{CHCl_2^{\bullet}} + \mathrm{Cl}. \qquad \mathrm{(II)}$$

This fact allows us to demonstrate the capabilities of the MC method in studying the two-channel process of dissociation, which is difficult to describe using other methods. To solve the problem, it is necessary to determine the density of energy states $\rho(E)$ for the model molecule and the rate constants $k_1(E)$ and $k_2(E)$ of spontaneous decomposition via the channels of the reaction.

CALCULATION PROCEDURE

Calculation of Vibrational States of Polyatomic Molecules

The expression for the number of vibrational states of the molecule $W(E)$ in the interval of energies $[0, E]$ takes simplest form in the classical approximation:

$$W(E) = \frac{E^n}{n!\prod_{i=1}^{n}\hbar\omega_i},$$

where n is the number of the vibrational modes of the molecule and ω_i is the frequency of vibrations. It is harder to derive formulas that are convenient for calculations (specifically, integration) and that take into account the quantum nature of the distribution of the vibrational energetic states of molecules. The Witten–Rabinovitch interpolation formula [16] is used most widely and approximates the step function

$$W(E) = \frac{1}{n!}\left(\frac{E + \alpha(E/E_z)E_z}{\hbar\omega}\right)^n,$$

where E_z is the sum of zero-point vibration energy of molecules, $\alpha(E/E_z)$ is the combination of molecular parameters and the universal empirical function dependent on energy. However, without additional simplifying assumptions (e.g., $\alpha(E/E_z) = \mathrm{const}$), this expression is inconvenient for integration.

In this work, we had the goal of determining the number and density of the vibrational states of molecules by the numerical integration of the step function $W(E)$ for a specific molecule and further approximating it with a simple function.

The $\mathrm{CHCl_3}$ molecule has the following set of frequencies 3033, 1205 (2), 760 (2), 667, 364, 260 (2) $\mathrm{cm^{-1}}$ [17]. In calculation, we divided the energy interval to the maximum possible N equal portions. In our example, $E_{\max} = 500$ kJ/mol, $N = 5000$. The number of states in the energy interval from 0 to E_i ($i = 1, \ldots, N$) for one random vibrational mode of the molecule is

$$W_1(E_i) = 1 + \mathrm{trunc}(E_i/\varepsilon_1), \quad E_i = i\delta, \quad i = 1\ldots N,$$

where $\delta = E_{\max}/N = 0.1$ kJ/mol; ε_1 is the energy of the vibrational quantum of the chosen vibrational mode; the value of the trunc(x) function is the integer part of the real number x. The addition of states related to other vibrational modes was carried out using the recurrent relation

$$W_L(E_i) = \sum_{j=0}^{I} W_{L-1}(E_J), \qquad (2)$$

where $W_L(E_i)$ is the number of states for L vibrational modes in the interval of energies from 0 to E_i, $I = \mathrm{trunc}(i\delta/\varepsilon_L)$, $J = \mathrm{trunc}(i - j\varepsilon_L/\delta)$; and ε_L is the energy of the vibrational quantum of the Lth vibrational mode.

For the convenience of further use, the step function was approximated by a smooth function of the form

$$W(E) = \left(1 + \frac{E}{E_z}\right)^s, \qquad (3)$$

where E_z and s are the parameters of approximation. However, s can be considered as an effective statistical weight of the vibrational states of a given molecule. For the given molecule, we obtained $E_z = 25.9$ kJ/mol and $s = 8.157$. For the sake of comparison, we note that the number of vibrational modes of the $\mathrm{CHCl_3}$ molecule is equal to 9, and the sum of zero-point vibrations is $\frac{1}{2}\sum\hbar\omega_i = 48.4$ kJ/mol. The table shows the calculated number of states using Eqs. (2) and (3), the number of states calculated using the grouped frequencies method [17], and those calculated using the Witten–Rabinovitch formula. The results of grouped-frequencies calculations coincide with those obtained using Eq. (2). The Witten–Rabinovitch formula gives close results for the number of states. The approximation using Eq. (3) only slightly alter the results.

The expression for the density of states $\rho(E)$ can easily be obtained by differentiating Eq. (3):

$$\rho(E) = \frac{s}{E_z}\left(1 + \frac{E}{E_z}\right)^{s-1}. \qquad (4)$$

Rate Constants of Spontaneous Decomposition

In the framework of the statistical theory of unimolecular reactions, the rate constant of the spontaneous decomposition of the molecule is defined by the ratio [11]

$$k(E) = \frac{1}{h}\frac{W^+(E - E_d)}{\rho(E)},$$

where $W^+(E - E_d)$ is the number of vibrational states of the activated molecule in the interval from 0 to $E - E_d$. When calculating $W^+(E - E_d)$, we neglected the states associated with the motion along the reaction coordinate. The question of the structure of the activated molecule was outside the scope of this work. We restricted ourselves two considering two limiting cases that correspond to the model of so-called rigid and loosened activated complexes [11].

The model of a rigid complex. If the transition to the activated state occurs with a slight change of bond lengths, than the activated and active molecules [11] have similar vibrational spectra of frequencies. For example, this is possible when there is a pronounced potential maximum on some reaction coordinate. The energy of molecule rotation as whole is ineffective and can be neglected. To a first approximation, for the number of states of the activated molecule, we write

$$W^+(E - E_d) \sim \left(1 + \frac{E - E_d}{E_z}\right)^{s-1}.$$

Then, for the rate constant of spontaneous decomposition we obtain

$$k(E) = n_s\nu\left(1 - \frac{E_d}{E + E_z}\right)^{s-1}, \qquad (5)$$

where n_s is the number of equivalent reaction channels and ν is the vibration frequency of the activated molecule.

In further developments below, we assume that reaction (I) occurs via the formation of a rigid activated state. The rate constant of this reaction was measured by several authors [12–14]. According to [14], at high pressures, the dependence of the rate constant of this reaction on temperature takes the following form:

$$k_{d,1}(T) = 1.82 \times 10^{14} \exp(-228/RT)$$

with the activation energy in kJ/mol. If the expression for $k_{d,1}(T)$, obtained using the integration according to formula (1) at the equilibrium distribution function and the rate constant of spontaneous dissociation having the form (5), is compared with the experimental dependence, we find that in this case $n_s\nu = 1.82 \times 10^{14}$ s^{-1}. The barrier to reaction (I) is $E_{d,1} = 228$ kJ/mol.

The model of loosened complex. If the activated molecule is close in its structure to the reaction products, than the model of loosened complex can be used. The frequencies of vibrations and the number of vibrational degrees of freedom of the complex are assumed to be the same as for nonreacting molecules (products). In the simple case when one atom is abstracted from a

Numbers of the vibrational states of the $CHCl_3$ molecule

E, kJ/mol	$W(E)$			
	calculation using formula (2)	calculation using formula (3)	calculation with frequency grouping [17]	calculation using the Witten–Rabinovitch formula
4.2	3	3.4	4	2.40
8.4	10	9.9	10	9.67
12.6	34	26	32	28.9
16.8	70	59	67	71
25.1	320	258	331	316
33.5	1054	895	1086	1072
41.9	2998	2632	3151	3045
83.8	1.33×10^5	1.35×10^5	1.34×10^5	1.35×10^5
125.7	1.77×10^6	1.90×10^6	1.77×10^6	1.79×10^6
167.6	1.29×10^7	1.40×10^7	1.30×10^7	1.31×10^7
251.4	2.55×10^8	2.65×10^8	2.56×10^8	2.58×10^8

polyatomic molecules, the expression for the rate constant of the spontaneous decomposition takes the form

$$k(E) = n_s \nu \frac{\left(1 + \dfrac{E - E_d}{E_z^+}\right)^{s^+}}{\left(1 + \dfrac{E}{E_z}\right)^{s-1}}, \qquad (6)$$

where the plus symbol marks the parameters that refer to a molecule or a radical that is the product of decomposition.

Let us assume that reaction (II) occurs via the formation of loosened activated state. There are no experimental data on the rate constant of reaction (II). Only the fact that this reaction can occur as a step of multiple-step process is known [15]. To calculate the formula for the rate constant of spontaneous decomposition, it is necessary to determine the values of $E_{d,2}$, n_s, ν, E_z^+ and s^+. The activation barrier of the reaction was set equal to the energy of the C–Cl bond, which is 239 kJ/mol. For the chloroform molecule, there are three equivalent ways to abstract the chlorine atom; therefore, $n_s = 3$. For the frequency, we adopted the value $\nu = 1 \times 10^{13}$ s^{-1}. To determine the values of E_z^+ and s^+, we calculated the vibrational states of the $CHCl_2$ radical using formulas (2) and (3): $E_z^+ = 17.3$ kJ/mol and $s^+ = 5.45$.

Procedure for Calculating Nonequilibrium Functions of Distribution over Energies

A detailed description of the method for constructing the equilibrium functions of distribution over energies was given in [10]. The method is based on the play-off of a random change in the internal energy of a molecule during its collisions. The essence of the method is as follows. The molecule is considered with a complete internal energy E_0 consisting of vibrational and rotational components: $E_0 = E_{v,0} + E_{r,0}$. It is assumed that the medium consists of atomic gas and that the energy of translational motion is thermolyzed (i.e., corresponds to the equilibrium value).

The energy of collision E_t was found by the play-off of a random number and finding the corresponding value of energy. Then, we determined the distribution of full energy of the collisional complex $E_0 + E_t$ over the kinetic energy of colliding partners moving away and the internal energy of molecules after collision. The latter consists of the vibrational and rotational components. It was assumed that the probability of each possible energy distribution is proportional to the density of energy states corresponding to this distribution. The distribution of energies between the vibrational degrees of freedom and other kinds of motion was also determined by the play-off of a random number. Finally, one more play-off of a random number was used to determine the distribution of energy between vibrational and translational degrees of freedom. As a result we determined new values of the vibrational energy $E_{v,1}$, rotational energy $E_{r,1}$, and full internal energy $E_{0,1}$ acquired by a molecule in collision. The function of molecule distribution over full, vibrational, and rotational energies was obtained as a result of multiple repetitions of this procedure and fixing each successively determined energy state of the molecule.

The above procedure allowed us to obtain the equilibrium distribution of a molecule over the energies of vibrational and rotational states of a molecule. Chemical reactions disturb the equilibrium distribution. Let us discuss how the MC procedure makes it possible to obtain nonequilibrium distribution functions and determine the reaction rate constants.

At the first stage, the $N \sim 10^6$ molecules were distributed according to an arbitrary initial distribution function over energies. The molecules were placed in the cells having sizes of $RT/10$ in the range of full energies of molecules $(4–5)sRT$. This range is sufficient for describing the dissociation kinetics of a given molecule. In the calculation, we showed that all molecules collide at the same time after equal intervals between collisions. This simplification somewhat distorts the distribution function over energies, but this distortion can be taken into account as described below.

Let us refer to the collision of a molecule with a species of surrounding gas or the decomposition of a molecule via one of the channels as an *event*, and let us define a *cycle* as a procedure consisting of a play-off of events for each of N molecules. As a result of calculations for one cycle, a new distribution function over energies appears for unreacted molecules, and this new function is used as a further approximation to the final quasistationary distribution function over energies.

A play-off for each molecule was carried out as follows. We determined the vibrational and rotational components of the full energy by solving the equation

$$\xi = \frac{\displaystyle\int_0^{E_v} \left(1 + \frac{\varepsilon}{E_z}\right)^{s-1} \sqrt{E_0 - \varepsilon}\, d\varepsilon}{\displaystyle\int_0^{E_0} \left(1 + \frac{\varepsilon}{E_z}\right)^{s-1} \sqrt{E_0 - \varepsilon}\, d\varepsilon}, \qquad (7)$$

where E_0 and E_v are the full and vibrational energies of a molecule and ξ is a random number. When the vibrational energy of a molecule was below the barrier of a reaction, we assumed that the state of molecules did not change between collisions, carried out a new play-off and determined a new energy state of a molecule. If the value E_v was higher than the reaction barrier, we determined which of the attempts occurred between collisions. For that, we calculated the rate constants of spontaneous decomposition $k_1(E_v)$ according to formula (5) and $k_2(E_v)$ according to formula (6) and the frequency of collisions

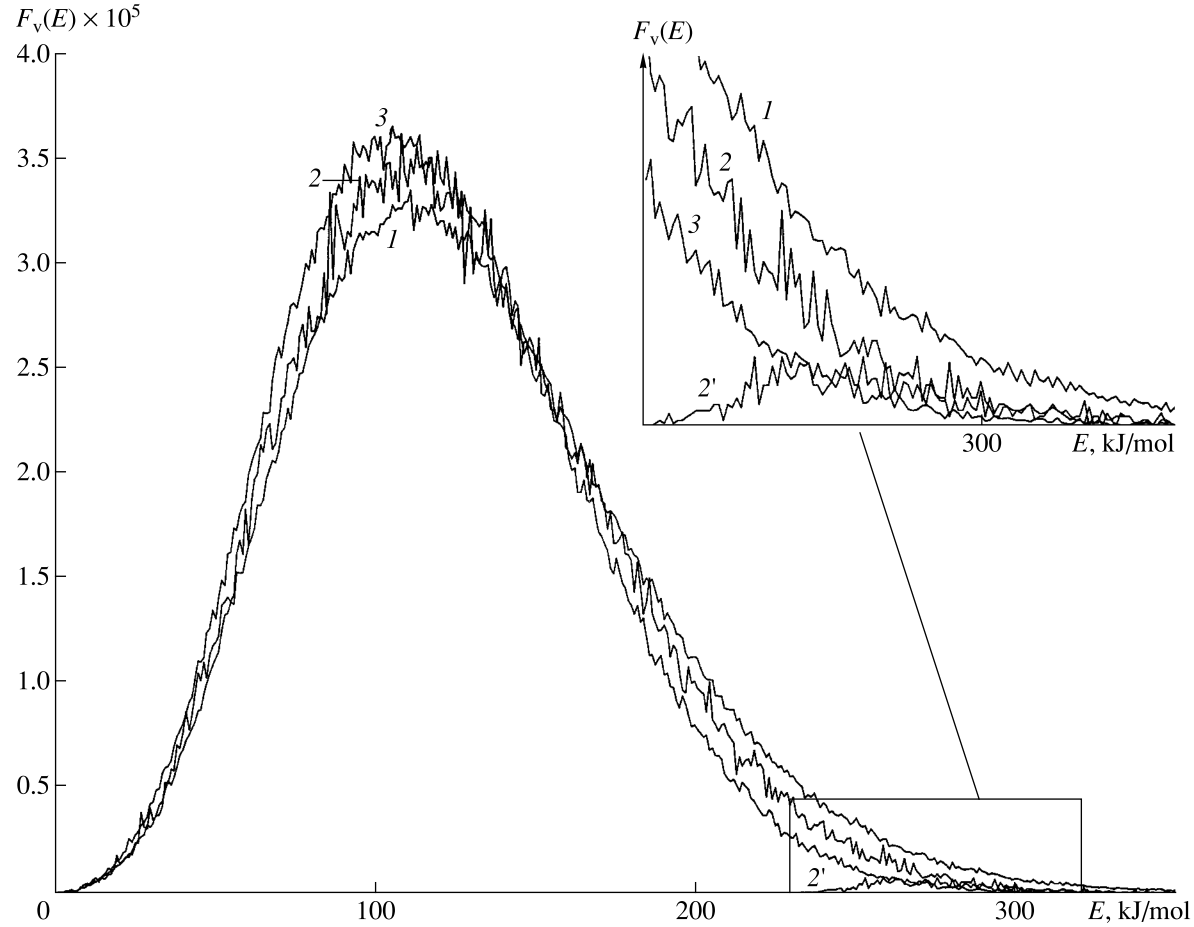

Fig. 1. Functions of distribution over vibrational energy at 2250 K and pressures of (*1*) 10^3; (*2*) 1, and (*3*) 10^{-3} atm. Curve *2*' corresponds to the distribution of reacted molecules at 1 atm. The insert on the top shows the increased fragment of the spectrum at E ~300 kJ/mol.

according to the formula $Z = 2.7 \times 10^{11} PT^{-1/2}$ s^{-1} (P is the gas pressure). Then, the random number ξ_1 was played off. If $\xi_1 < X_1 = k_1(E_v)/[k_1(E_v) + k_2(E_v) + Z]$, then we considered that the reaction occurs through channel (I). In this case, the counter for the number of acts through channel (I) incremented the previous value ΔN_1. If $X_1 < \xi_1 < X_2 = [k_1(E_v) + k_2(E_v)]/[k_1(E_v) + k_2(E_v) + Z]$, then we considered that reaction occurs through channel (II) and counter (II) incremented the value ΔN_2. At $\xi_1 > X_2$, collision was played off and a new energy state of the molecule was established.

After each cycle, the function of distribution over energies was normalized so as to compensate for a decrease in the number of molecules due to the reaction. The general number of molecules in each next cycle was always equal to N. The apparent rate constants of reactions were determined by the formula $k_{d,i}(T) = Z\Delta N_i/N$ ($i = 1, 2$). The quasistationary function of distribution over energies was formed by multiple repetitions (25–50 times) of the cycle. A criterion for the achievement of the stationary state was the achievement of constant values with the accuracy of the $k_{d,i}(T)$ values.

Note that the described procedure for constructing nonequilibrium functions of distribution over energies and determining the rate constants of the two-channel unimolecular reaction can also be applied to a simpler case of the one-channel decomposition of polyatomic molecules.

RESULTS OF CALCULATION

Figure 1 shows the functions of distribution over vibrational energy at 2250 K and different frequencies of molecule collisions with the species of medium obtained by the method described above. The functions shown in this figure are normalized to unity. Curve *1* corresponds to the case when the frequency of decomposition acts is negligible compared to the frequency of collisions (the high-pressure limit). In this case, the distribution function coincides with the equilibrium function. Curve *2* is the distribution function at a pressure of

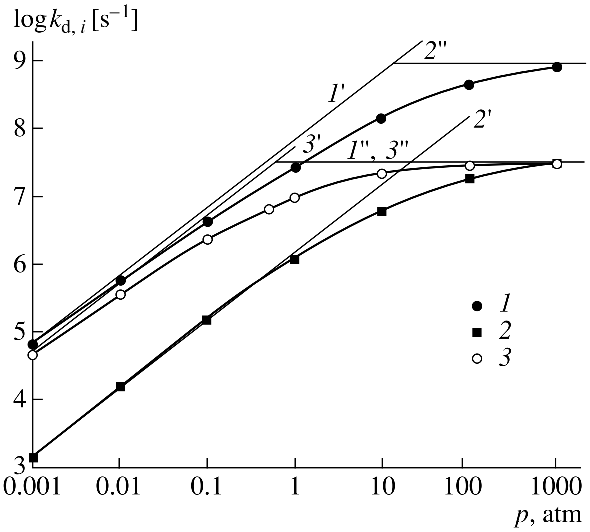

Fig. 2. Pressure dependences of calculated rate constants ($k_{d,\,i}$) of reactions (I) (curve *1*) and (II) (curve *2*), reaction (II) assuming that reaction (I) does not occur (curve *3*). Lines *1'*, *2'*, *3'* and *1''*, *2''*, *3''* correspond to the dependences of $k^0_{d,\,i}$ [M] and $k^\infty_{d,\,i}$, where $k^0_{d,\,i}$ and $k^\infty_{d,\,i}$ are the rate constants in the low- and high-pressure limits, respectively.

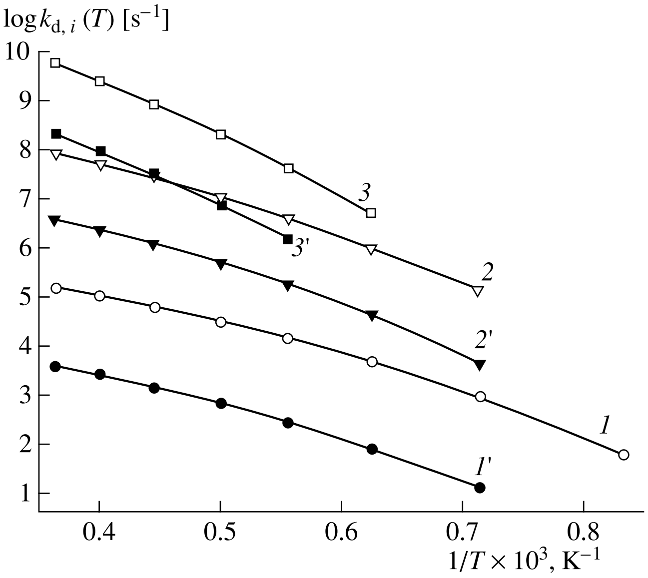

Fig. 3. Temperature dependences of calculated rate constants ($k_{d,\,i}$) of (*1*, *2*, *3*) reaction (I) and (*1'*, *2'*, *3'*) reaction (II) at (*1*,*1'*) 10^{-3}; (*2*, *2'*) 1, and (*3*, *3'*) 10^3 atm.

1 atm. In this case, only some portion of molecules that overcome the barrier react (this is a transition region of pressures). Curve *2'* shows the distribution of reacted molecules. Curve *3* corresponds to the case when each molecule that overcame the barrier dissociates via one of the reaction channels (the low-pressure limit).

Note that due to the simplifying assumption mentioned above (all molecules collide at the same time at equal intervals), the functions of distribution over energies shown in Fig. 1 differ from actual function in that they describe the molecules immediately after collision. The actual function of distribution over energies at any moment of time accounts for molecules that existed at this energy state for different periods, and some of them dissociated after overcoming the reaction barrier. This is reflected in the depletion of the actual function of distribution over energies. Therefore, formula (1) is inapplicable to calculating the apparent rate constants of using the calculated function of distribution over energies shown in Fig. 1, and correction is necessary. It is easy to show that in this case one should use

$$k_{d,\,i}(T) = Z\int_{E_{d,\,i}}^{\infty} F_v(\varepsilon)\frac{k_i(\varepsilon)}{k_1(\varepsilon)+k_2(\varepsilon)+Z}d\varepsilon \quad (i = 1, 2). \tag{8}$$

instead of Eq. (1). This formula coincides with Eq. (1) at the high-pressure limit.

Note the shift in the function of distribution over energies toward lower energies with a decrease in the frequency of collisions, which can be interpreted as a decrease in the apparent temperature of reacting molecules with a decrease in the intensity of their energy exchange with thermolyzed species of the medium. Note that the energetically nonequilibrium condition that appears in the course of chemical reactions is often taken into account in practice by using the approximation that makes use of apparent temperature idea. The results obtained illustrate well that such an approximation is justified.

Figure 2 shows the plots of calculated apparent rate constants vs. pressure for channels (I) (curve *1*) and (II) (curve *2*) at 2250 K. Slanting lines *1'* and *2'* describe the respective dependences of $k^0_{d,\,i}$ [M], where $k^0_{d,\,i}$ are the rate constants in the low-pressure limit with the dimensionality of second-order rate constantans and [M] is the diluent concentration. The horizontal lines describe the values of the rate constants of channels (I) and (II) in the high-pressure limit $k^\infty_{d,\,i}$.

Let us estimate the mutual effect of channels on each other. Because reaction (II) is much slower than reaction (I), its effect on reaction (I) is weak. The effect of reaction (I) on the rate of reaction (II) is rather strong. Curve *3* in Fig. 2 shows the dependence of the rate constant of reaction (II) on pressure calculated assuming that reaction (I) does not occur. It can be seen that the effect of reaction (I) on channel (II) becomes stronger as the pressure decreases. In the high-pressure limit, the mutual effect of reactions is absent because chemical reactions do not affect the equilibrium function of distribution over energies in this case.

Figure 3 shows the temperature dependences of the calculated apparent rate constants at different pressures. Note that the dependences at 0.001 atm virtually coincide with the dependences for $k^{0}_{\mathrm{d},\,i}(T)$[M], and those at 1000 atm coincide with the dependences for $k^{\infty}_{\mathrm{d},\,i}(T)$.

Let us consider the characteristic time for the relaxation of the function of distribution over energies (and the respective reaction rates) at drastic changed in the conditions. This is called the incubation period. This situation is characteristic of shock tubes when, after passing the front of a shock wave, the temperature and pressure of gas increase in a jumpwise fashion. When modeling the relaxation kinetics of the distribution function over energies to new thermodynamic conditions, the zero approximation was the distribution function at an initial gas temperature equal to 300 K. Then, using the method described above, we calculated the transformations of the distribution function in a series of cycles assuming that the temperature of the diluent gas is equal to the final preset temperature. After each cycle the new state of the distribution function was determined and the apparent rate constants for both channels of the model reaction were determined. Figure 4 shows changes in the apparent rate constants $k_{\mathrm{d},\,1}$ and $k_{\mathrm{d},\,2}$ divided by their final quasistationary values at 2250 K and 1 atm depending on the number of played-off collisions. It is seen that both constants change according to the same law and the quasistationary state is achieved for 20–30 cycles.

The characteristic relaxation time τ can be determined as time required for achieving the quasistationary values of apparent rate constants as shown in Fig. 4. Figures 5 and 6 show changes in the characteristic relaxation time expressed in the number of collisions as functions of pressure at 2000 K and temperature at 10^{-3} atm. Note that changes in the number of collisions necessary for achieving the quasistationary value of the rate constant are small. Thus, when the temperature increases from 1400 to 2750 K, the number of collisions decreases ~1.5 times. When the pressure increases by a factor of 10^{6}, the number of collisions increases by 15–20%. It can be assumed that the relaxation of the distribution function requires approximately 20–25 collisions. Nevertheless, more collisions are required for the relaxation when the conditions are closer to the high-pressure limit. This can be explained by the fact that, in the high-pressure limit, the distribution function should be restored up to the very high values of energy excitation in the course of relaxation. In the low-pressure limit, the reaction does not exist behind the barrier and relaxation requires fewer collisions.

As can be seen, the Monte Carlo method makes it possible o obtain the complete spectrum of necessary data on the rate constants over a wide range of temperatures and pressures without using substantial simplifying assumptions. Specifically, the method helps to

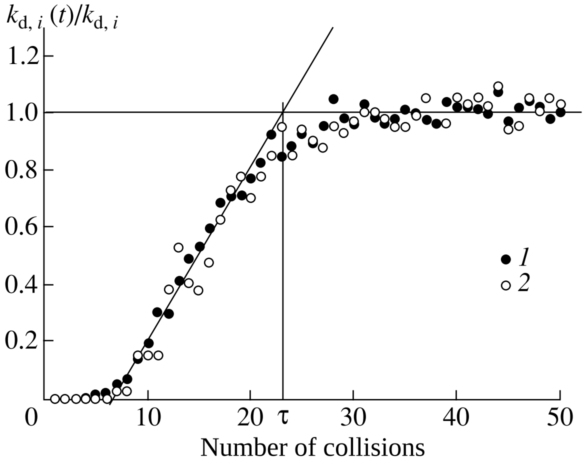

Fig. 4. Relaxation to the quasistationary values of the rate constants of the decomposition via (*1*) channel (I) and (*2*) channel (II). τ is the relaxation time.

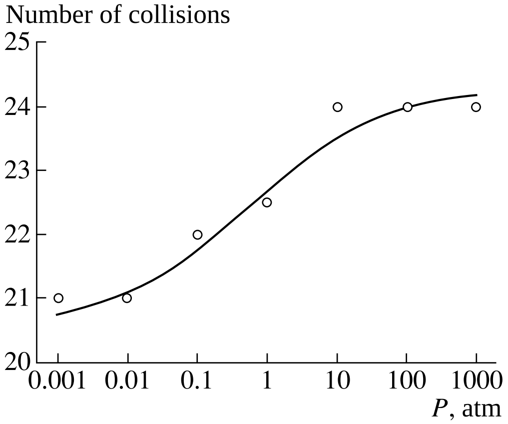

Fig. 5. Dependence of the characteristic time of relaxation (in numbers of collisions) of the function of distribution over energies on pressure at 2000 K.

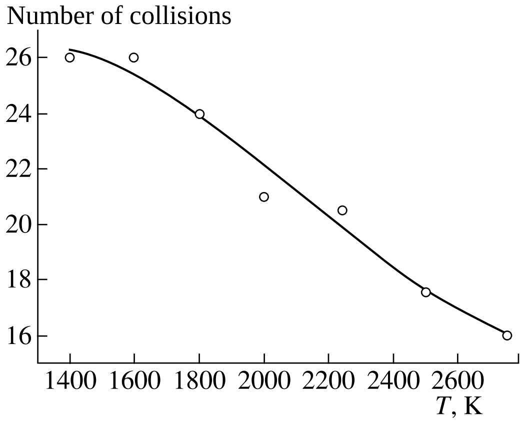

Fig. 6. Dependence of the characteristic time of relaxation (in numbers of collisions) of the function of distribution over energies on temperature at 10^{-3} atm.

solve the problem on the nonstationary behavior of the distribution function at a jumpwise change in the conditions of the reaction. This problem is hard to solve using other methods. The method proposed in this work is a useful supplement to the set of tools for describing the kinetics of unimolecular reactions. We plan to develop it further for the description of other kinetic processes, specifically reversible isomerization and dissociation reactions, as well as reactions influenced by external sources of energy, and others.

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