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Role of the Supramolecular Structure of the Reactants in the Kinetics of the Liquid-Phase Synthesis and Decomposition of Explosives

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Abstract—Formulas relating the observed rate constant of the initial reaction step (k_{ef}) to the rate constants of the elementary steps (k_i), to the monomer–association species equilibrium constants (K_i), and to the concentrations of the reactants (A_i) and solvent have been obtained for a number of simple kinetic models of liquid-phase explosive material synthesis and decomposition reactions involving associating reactants. The $k_{ef} = F(k_i, K_i,$ and $A_i)$ relationship is independent of the rate law of the reaction and is governed by the association species type (autoassociation or heteroassociation species) and by the number of association species kinds. In the case of parallel reactions involving association species, as distinct from the same reactions involving unassociated reactants, concentration variations have an effect on the ratio of the rates of the parallel steps and on the product yield ratio. By varying the reaction temperature, it is possible to make the rates of the parallel steps to vary in opposite ways. When monomers, dimers, and tetramers are present in the reaction mixture, the temperature dependence of $\ln k_{ef}$ may have an extremum. These deduced regularities are in qualitative agreement with experimental data.

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Recent studies of liquid-phase reactions (particularly polymer syntheses) have revealed facts that cannot be explained within the framework of the classical chemical kinetics of homogeneous reactions [1]. In particular, it was found that the effective rate constant k_{ef} depends on the reactant concentrations, the temperature dependence of $\ln k_{ef}$ passes through an extremum, and acoustic treatment exerts an effect on the reaction rates [2–5]. Among the possible explanations of these facts, the idea that the medium undergoes structural organization due to intermolecular interactions turned out to be the most fruitful. It is assumed in this approach that ordered structures, such as association species, clusters, aggregates, and complexes, appear in the liquid at the supramolecular level owing to noncovalent forces [2–4, 6–12]. As distinct from the chaotic fluctuations of liquid density, these structures are very stable owing to cooperative bonding and are characterized by size discreteness, which is limited by the possibility of energy compensation for the loss of entropy.

However, there is no consensus as to the role of supramolecular structures in the kinetics of liquid-phase reactions. Even for the most extensively studied and comparatively simple processes, such as polymer synthesis, the existence of association species is considered to be hypothetical [13]. As a consequence, the roles of the supramolecular structure of the reaction medium in the kinetics of liquid-phase reactions is still ignored and no mathematical model of this phenomenon has been analyzed even for simple kinetic schemes. At the same time, it is noted that studies of the structural order of the liquid medium and the energetic and spectroscopic characteristics of clusters could show a new approach to a wide variety of applied problems and could add to the understanding of the evolution of chemical and biological systems [14–16]. It is, therefore, pertinent to carry out a mathematical modeling of the kinetics of liquid-phase reactions in order to verify the significant role of the structural ordering of the reaction medium. It is natural to begin such investigation with an analysis of the kinetic effect of association species, which are the simplest elements of the supramolecular structure, on the decomposition and synthesis of explosive materials (EMs), because it is likely that these systems have no supramolecular structure elements more complex than association species. Obviously, because EM synthesis and particularly EM decomposition are multistep processes, this analysis should first be made for simple (conceptual) kinetic models of reactions involving associating reactants. Naturally, as the number of details taken into account by a model is increased, the model becomes more predictive; however, even simple models taking into consideration only the basic features of the reacting medium are capable of revealing the similarities and distinctions between the evolutions of different types of nonlinear dynamic systems.

Although the kinetics and mechanisms of EM decomposition reactions have been investigated for several decades [17], many problems in this field still remain unsolved [18]. For example, the supramolecu-

lar structure of the reaction medium in the liquid-phase EM synthesis and decomposition, the changes in this structure during the reaction, and the kinetic effect of this structure are unknown. This circumstance makes it impossible to determine the true rate constants of the elementary steps of EM synthesis and decomposition, which are necessary for establishing fundamental relationships between the reactivity and the molecular structure.

Here, we analyze the kinetics of the liquid-phase reactions involved in EM synthesis and decomposition by means of mathematical modeling for a number of simple kinetic schemes, taking into account the association of reactant molecules and its effect on reactivity. By this analysis, we will find those characteristics of the structured reaction medium which must be known for determining the true rate constants of the elementary steps, for establishing the true correlation between the EM reactivity and structure, and for optimizing the synthesis and processing conditions.

ASSOCIATION AND REACTIVITY OF EM MOLECULES IN THE LIQUID PHASE

Experimental data and quantum chemical calculations demonstrate that EMs and the chemicals used in their synthesis can form hydrogen, dipole–dipole, and other noncovalent bonds [8–11, 19–22]. The energy of these bonds ranges between 10 and 60 kJ/mol; for example, the mean hydrogen bond energy for the most stable dimer of 4-amino-1,2,4-triazole-5-one is twice higher than the same energy for the water dimer [8].

The association of reactant molecules exerts an effect both on the kinetics and on the mechanism of EM synthesis [23, 24] and decomposition [9, 12, 22]. It was demonstrated that the effective rate constant of EM decomposition depends on the nature of the solvent [25, 26]. As in the case of polymer synthesis, this suggests the formation of association species differing in reactivity from the unassociated molecules.

The effect of the association of EM molecules on their reactivity can be due to a number of factors, namely, changes in the structure of the outer electron shells favoring (or hampering) the chemical reaction, a decrease in the concentration of reactant molecules or reactive functional groups (if the latter are involved in association), and a decrease in molecular mobility. According to Manelis et al. [17], the association of EM molecules does not affect their decomposition, because, at the EM thermal decomposition temperature, association possibly does not take place. However, this assumption, based on indirect evidence (observance of Trouton's rule), does not simplify the situation, since kinetic data obtained at elevated temperatures are generally inappropriate for predicting the thermal stability of EMs at the lower temperatures used in EM production and storage without applying a correction for molecular association.

Kinetic studies of liquid-phase EM synthesis do not usually elucidate the role of the supramolecular structure of the reaction medium. For example, in the kinetic and mechanistic studies of the nitration of organic compounds with nitric acid, it is ignored that nitric acid dissolved in water forms monohydrates and trihydrates [20]. The state of the art in EM synthesis kinetics is adequately illustrated by a study by Ostrovskii et al. [27], who carried out an analysis of the synthesis of 5-vinyl-1-methyltetrazole and 5-vinyl-2-methyltetrazole. However, even that comprehensive study does not consider the possibility of the formation of isomers of the resulting EM due to the association of the initial reactant.

Note that the association of EM molecules markedly affects not only the kinetics of chemical reactions, but also the kinetics of the solid-to-liquid phase transition in the EM [28].

In earlier works, the problem of the effect of molecular association on the kinetics of bimolecular reactions was most rigorously solved analytically under the assumption that the reactants form a prereaction complex [3]. At present, the structure and reactivity of association species are determined by computer modeling [19–22].

Kinetic Models of Structured Reaction Media

Although the significant effect of association on the reactivity of reactants is indicated by experimental data (indirectly) and theoretical calculations (directly), the difference between the reactivities of unassociated molecules and association species is usually ignored in experimental data processing and in the determination of reaction rate constants. Accordingly, so-called effective (apparent) rate constants (k_{ef}) are obtained, which differ from the true rate constants of the elementary steps. Experimental data are often represented only as the dependence of k_{ef} on the concentration of one of the reactants (or as so-called kinetic curves).

Here, we simulate reactions simultaneously involving both unassociated and associated molecules of the reactants. This is done under the assumption that the concentrations of the unassociated and associated molecules are interrelated by the thermodynamic equilibrium condition. This assumption is substantiated by the existence of molecular motion in the liquid phase, which changes the spatial arrangement of the particles, their structure, and the structure of their surroundings.

Because of the diversity of association species and the complexity of the mechanisms of real reactions, it is impossible to analytically solve the problem of the effect of reactant association on k_{ef}. In this work, the mathematical modeling of the effect of reactant association on k_{ef} is carried out for a number of comparatively simple kinetic schemes with molecular dimer and tetramer formation taken into account.

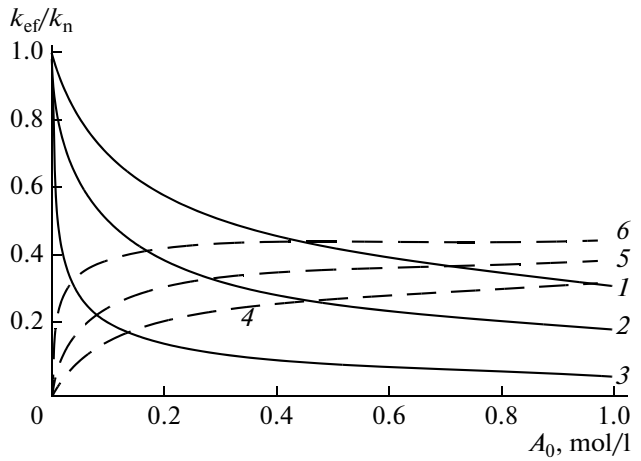

Fig. 1. k_{ef}/k_n versus the initial reactant concentration A_0 at $\alpha = 0$: (*1–3*) $k_n = k_1$, $k_2 = 0$; (*4–6*) $k_n = k_2$, $k_1 = 0$. K_1 = (*1*, *4*) 3, (*2*, *5*) 10, and (*3*, *6*) 100 l/mol. Calculated via Eq. (4).

First-order reactions. A first-order reaction is often the initial elementary step of a complicated chemical reaction, and this is typical of the thermal decomposition of EMs [17, 18]. Experimental data demonstrate that the thermal decomposition of many EMs at its initial stage proceeds via several parallel channels [18].

First, we will consider the case in which the association of the reactant A into a dimer does not change the mechanism of the reaction, but only leads to a difference between the rate constants of the reactions involving the monomer A_1 and those of the reactions involving the dimer A_2. The rate of the first-order reaction in which the initial reactant A turns into the product B is expressed as $w = k_{ef}A$, where A is the total concentration of the reactant.

In this case, the kinetic scheme taking into account the association of the reactant A appears as

$$A_1 \longrightarrow B, \quad \text{(I)}$$

$$A_2 \longrightarrow B + A_1, \quad \text{(II)}$$

$$2A_1 \longleftrightarrow A_2. \quad \text{(III)}$$

Let the rate constant of elementary reactions (I) and (II) be k_1 and k_2, the monomer concentration be A_1, and the dimer concentration be A_2. It follows from equilibrium (III) that $A_2 = K_1A_1^2$. The reaction rate w can be expressed as the sum of the rates of the parallel steps (I) and (II):

$$w = k_{ef}A = k_1A_1 + k_2A_2 = k_1A_1 + k_2K_1A_1^2. \quad (1)$$

According to the material balance constraint, $A = A_1 + 2A_2 = A_1 + 2K_1A_1^2$; hence, the current monomer and reactant concentrations are interrelated by the expression

$$A_1 = (0.0625K_1^{-2} + 0.5K_1^{-1}A)^{0.5} - 0.25K_1^{-1}. \quad (2)$$

Equations (1) and (2) make it possible to determine k_{ef} as a function of the concentration of the reactant A, equilibrium constant K_1, and elementary step rate constants:

$$k_{ef} = k_1A^{-1}[(0.0625K_1^{-2} + 0.5K_1^{-1}A)^{0.5} - 0.25K_1^{-1}] + K_1k_2A^{-1}[(0.0625K_1^{-2} + 0.5K_1^{-1}A)^{0.5} - 0.25K_1^{-1}]^2. \quad (3)$$

After the introduction of the reactant conversion $\alpha = (A_0 - A)/A_0$, where A_0 is the initial concentration of the reactant, Eq. (3) can be rewritten as

$$k_{ef} = k_1A_0^{-1}\{[0.0625K_1^{-2} + 0.5K_1^{-1}A_0(1-\alpha)]^{0.5} - 0.25K_1^{-1}\}(1-\alpha)^{-1} + K_1k_2A_0^{-1}\{[0.0625K_1^{-2} + 0.5K_1^{-1}A_0(1-\alpha)]^{0.5} - 0.25K_1^{-1}\}^2(1-\alpha)^{-1}. \quad (4)$$

Therefore, the rate constant k_{ef} depends on the conversion as well.

Using Eq. (4), we calculated the ratio k_{ef}/k_n, where k_n is the largest of the rate constants (i.e., always $k_{ef}/k_n < 1$), as a function of A_0. It is demonstrated in Fig. 1 (curves *1–3*) that, when the unassociated molecules are more reactive (the limiting case of $k_1 = k_n$ and $k_2 = 0$ is considered here), the k_{ef}/k_n ratio decreases with increasing A_0 (particularly sharply at small A_0 values), and the larger the K_1 value the larger the decrease in k_{ef}/k_n. This decline in k_{ef}/k_n is due both to the difference between the rate constants of the elementary steps and to the decrease in the reactant concentration because of association.

In the opposite case, in which the association species are more reactive, k_{ef}/k_n is again below unity, but it increases with increasing A_0 (particularly sharply at small A_0 values), and the larger the K_1 value the larger the increase in k_{ef}/k_n. However, k_{ef}/k_n grows only to a certain limit because the reactant concentration decreases due to association (Fig. 1, curves *4–6*). Note that the run of these curves is in qualitative agreement with the decomposition kinetics of 1,3,3-trinitroazetidine in *meta*-dinitrobenzene [26] under the assumption that the EM forms association species that are more reactive than the unassociated molecules. It was indeed established that, as the EM concentration is raised from 5 to 80 wt %, the initial decomposition rate increases by a factor of 2–3 [26].

At $k_1 > k_2$, k_{ef}/k_n grows with increasing α; in the opposite case ($k_2 > k_1$), it decreases with increasing conversion (Fig. 2).

Equations (1)–(4) make it possible to obtain an analytical expression for α as a function of the reaction time t. By introducing the dimensionless variables and

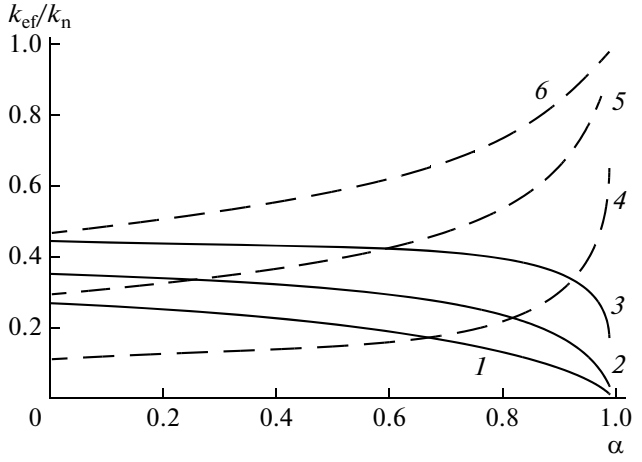

Fig. 2. k_{ef}/k_n versus conversion α at $A_0 = 0.4$ mol/l: (*1–3*) $k_n = k_1$, $k_2 = 0$; (*4–6*) $k_n = k_2$, $k_1 = 0$. $K_1 =$ (*1*, *6*) 3, (*2*, *5*) 10, and (*3*, *4*) 100 l/mol. Calculated via Eq. (4).

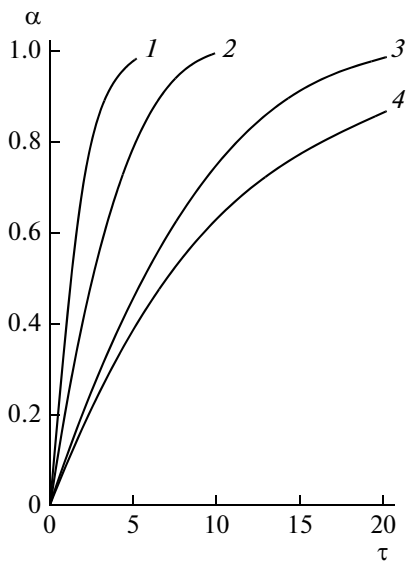

Fig. 3. α(*t*) curves calculated (*1–3*) using Eq. (5) for β = (*1*) 1, (*2*) 10, and (*3*) 100 and (*4*) using the formula $\alpha = 1 - \exp(-0.1t)$.

parameters $\tau = k_1 t$, $\beta = K_1 A_0$, and $\kappa = k_1/k_2$, we will transform Eq. (1) into

$$\begin{aligned}\tau = (1-4\kappa)\ln\{[\kappa + (0.0625 + 0.5\beta(1-\alpha))^{0.5} \\ - 0.25]/[\kappa + (0.0625 + 0.5\beta)^{0.5} - 0.25]\} \\ - \ln\{[0.0625 + 0.5\beta(1-\alpha)]^{0.5} \\ - 0.25]/[(0.0625 + 0.5\beta)^{0.5} - 0.25]\}.\end{aligned} \quad (5)$$

Calculations using Eq. (5) demonstrated that, when reactant association takes place, the α(*t*) curves are almost identical in shape to the curve defined by the canonical first-order rate equation, $\alpha(t) = 1 - \exp(-kt)$ (Fig. 3).

The temperature dependence of the effective rate constant k_{ef} for the monomer–dimer reaction system is given by Eq. (3) under the assumption that the temperature effects on the rate constants of the elementary steps and on the equilibrium constant are described by the Arrhenius and van't Hoff equations:

$$k_i = k_{0i}\exp(-E_i/RT), \quad K_1 = p_{01}\exp(\Delta H_1/RT),$$

where k_{0i} and E_i are, respectively, the preexponential factor and activation energy of the *i*th step, and p_{01} and ΔH_1 are, respectively, the preexponential factor and enthalpy change for dimer formation.

Figure 4 shows the temperature dependence of $\ln k_{ef}$. We assumed in the calculations that $E_1 = 168$ kJ/mol, $E_2 = 113$ kJ/mol, $k_{01} = 10^{14}$ s^{-1}, $k_{02} = 10^{12}$ s^{-1}, $\Delta H_1 = 25$ kJ/mol, and $p_{01} = 10^{-4}$ l/mol. This dependence in the Arrhenius coordinates is represented by two rectilinear segments, the slope of either one being determined by the most rapid step, and by a curvilinear portion corresponding to the transition region in which the rates of the steps are similar. Thus, the association of the reactants exerts no effect on the shape of the $\ln k_{ef}$ versus temperature curve, and the difference between the curve referring to two parallel reactions accompanied by reactant association and the curve for the same reactions without reactant association is only quantitative.

If the process includes two parallel reactions yielding different products B and C (the monomer and dimer react via different mechanisms), step (II) will appear as

$$A_2 \longrightarrow C. \quad \text{(IIa)}$$

In this case, in the above formulas, including Eqs. (3) and (4), the rate constant k_2 should be replaced with $2k_2$ because two molecules of A disappear in step (IIa), as distinct from one A molecule disappearing in step (II). A similar molecular association effect on the liquid-phase decomposition mechanism supposedly takes place for trinitrotoluene [9], as well as for trini-

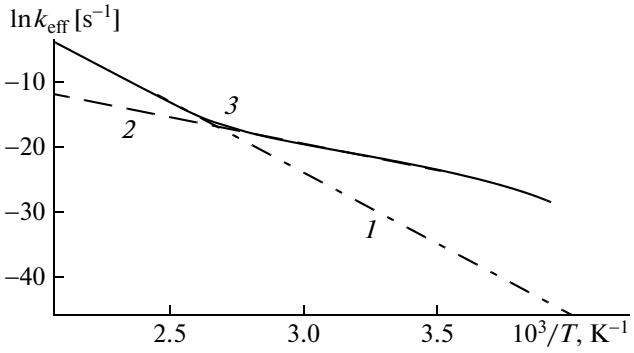

Fig. 4. $\ln k_{ef}$ versus the inverse reaction temperature (T^{-1}), calculated using Eq. (4) for $\alpha = 0$ and $A_0 = 0.4$ mol/l: (*1*) $k_1 \neq 0$, $k_2 = 0$; (*2*) $k_1 = 0$, $k_2 \neq 0$; (*3*) $k_1 \neq 0$, $k_2 \neq 0$.

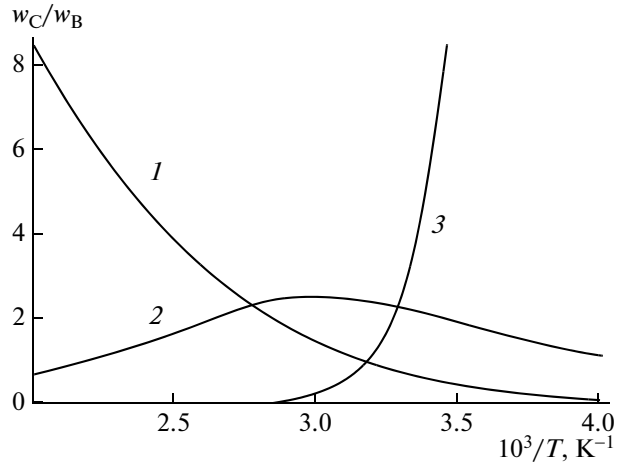

Fig. 5. Ratio of the formation rates of the products C and B (w_C/w_B) as a function of the inverse temperature: (*1*) $k_1 = 10^{12}\exp(-113000/RT)$ s^{-1}, $k_2 = 10^{14} \times \exp(-168000/RT)$ s^{-1}, $K_1 = 10^{-4}\exp(25000/RT)$ l/mol; (*2*) $k_1 = 10^{12}\exp(-113000/RT)$ s^{-1}, $k_2 = 10^{14} \times \exp(-168000/RT)$ s^{-1}, $K_1 = 10^{-8}\exp(50000/RT)$ l/mol; (*3*) $k_1 = 10^{14}\exp(-168000/RT)$ s^{-1}, $k_2 = 10^{12} \times \exp(-113000/RT)$ s^{-1}, $K_1 = 10^{-8}\exp(50000/RT)$ l/mol. Calculated using Eq. (6) for $A_0 = 1.0$ mol/l and $\alpha = 0$.

trophenylnitramine, which decomposes to yield trinitroanisole, picric acid, and *N*-methyltrinitroaniline [29].

The ratio of the B and C formation rates (w_B/w_C) is given by the formula

$$\begin{aligned} w_C/w_B &= 2k_2K_1A_1/k_1 \\ &= 2k_2\left[\left(0.0625 + 0.5K_1A\right)^{0.5} - 0.25\right]/k_1 \\ &= 2k_2\left\{\left[0.0625 + 0.5K_1A_0\left(1-\alpha\right)\right]^{0.5} - 0.25\right\}/k_1. \end{aligned} \quad (6)$$

It follows from Eq. (6) that, as distinct from what is observed for two parallel reaction occurring without reactant association, the w_B/w_C ratio depends not only on the rate constant ratio k_1/k_2, but also on the equilibrium constant K_1, initial concentration A_0, and conversion α. Therefore, by varying these parameters, it is possible to control the yield of the desired product. It can be demonstrated that, by varying the reaction temperature, it is possible to change the rates of elementary steps (I) and (IIa) in opposite ways (Fig. 5). Taking into consideration the temperature dependences of k_1 and k_2 (which are described by the Arrhenius and van't Hoff equations), taking into account the equilibrium constants, and equating the derivative of w_C/w_B with respect to temperature, we obtain a formula for the temperature at which the rates of the above elementary steps begin to change in opposite ways (T_{ch}):

$$\begin{aligned} T_{ch} = \Delta H\{ R\ln[0.5\gamma(\gamma+1)/A_0(1-\alpha) \\ \times p_0(2\gamma-1)^2]\}^{-1}, \end{aligned} \quad (7)$$

where $\gamma = (E_2 - E_1)/\Delta H$, (dimensionless parameter); E_1 and E_2 are the activation energies of steps (I) and (IIa), respectively; A_0 isd the initial concentration of the reactant; α is the reactant conversion; p_0 is the pre-exponential factor in the van't Hoff equation, and ΔH is the enthalpy of association.

If the first-order reaction occurs in solution and the formation of reactant–solvent association species S is possible, the kinetic scheme for the process will appear as

$$A_1 \longrightarrow B, \quad \text{(Ib)}$$

$$A_1S \longrightarrow B + S, \quad \text{(IIb)}$$

$$A_1 + S \longleftrightarrow A_1S. \quad \text{(IIIb)}$$

In this case, the effective rate constant k_{ef} is related to the rate constants of elementary steps (Ib) and (IIb)—k_1 and k_2—through the equilibrium constant K_1 of step (IIIb):

$$\begin{aligned} k_f &= (k_1 + k_2K_1S)(1+K_1)^{-1} \\ &= k_1(1+\chi K_1S)(1+K_1)^{-1}, \end{aligned} \quad (8)$$

where $\chi = k_2/k_1$ and S is the solvent concentration.

Equation (8) demonstrates that, when the reactant and solvent molecules form association species, k_{ef} is independent of conversion, but it depends on the parameters K_1 and χ and on the solvent concentration (therefore, indirectly on the reactant concentration) and may differ significantly from the rate constants of the elementary steps.

In the more complicated case of a tetramer forming in the reaction system along with the dimer, the first-order kinetic scheme (I)–(III) should be supplemented with dimer association into the tetramer (step (III), equilibrium constant K_2) and with tetramer conversion (step (II'), rate constant k_3):

$$A_4 \longrightarrow B + 3A_1, \quad \text{(II')}$$

$$2A_2 \longrightarrow A_4. \quad \text{(III')}$$

The observed rate of the process is the sum of the rates of elementary steps (I), (II), and (II'):

$$w = k_{ef}A = k_1A_1 + k_2A_2 + k_3A_4.$$

The concentrations of the dimer (A_2) and tetramer (A_4) can be derived from the equilibrium condition for steps (III) and (III'):

$$\begin{aligned} A_2 &= K_1A_1^2, \\ A_4 &= K_1K_2A_1^4. \end{aligned} \quad (9)$$

The effective rate constant is given by the equation

$$k_{ef} = (k_1A_1 + k_2K_1A_1^2 + k_3K_1K_2A_1^4)/A, \quad (10)$$

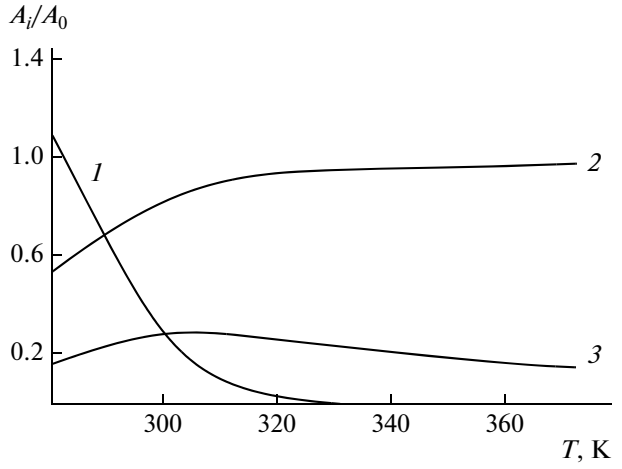

Fig. 6. Relative concentrations A_i/A_0 versus temperature: (*1*) $10A_4/A_0$, (*2*) A_1/A_0, and (*3*) $10A_2/A_0$. Calculated using Eqs. (9)–(11) for $A_0 = 1.0$ mol/l and $\alpha = 0$.

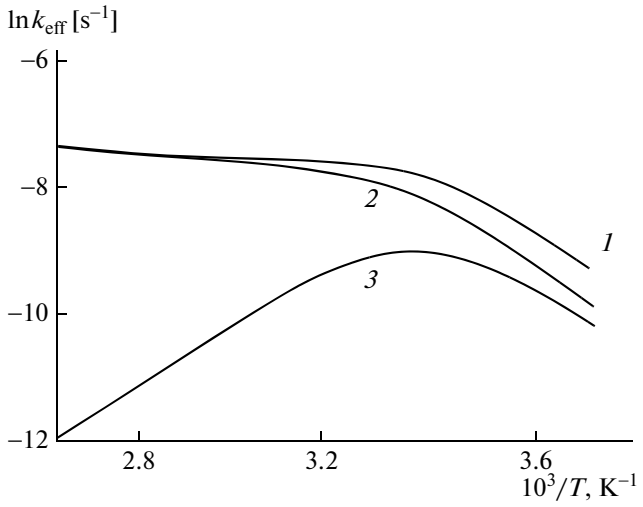

Fig. 7. Temperature dependence of ln k_{ef} calculated via Eqs. (9)–(11) for $A_0 = 0.1$ mol/l and $\alpha = 0$: (*1*) $k_1 = 0, k_2 \neq 0, k_3 \neq 0$; (*2*) $k_1 = 0, k_2 \neq 0, k_3 = 0$; (*3*) $k_1 = 0, k_2 = 0, k_3 \neq 0$.

where, according to the material balance constraint, the total reactant concentration A is defined by the following fourth-degree equation:

$$A = A_1 + 2K_1A_1^2 + 4K_1K_2A_1^4. \quad (11)$$

Figure 6 shows how the concentrations A_1, A_2, and A_4 in the initial reaction system ($\alpha = 0$) vary with temperature, as calculated via Eqs. (9)–(11). The effects of temperature on the rate constants of elementary steps and on the equilibrium constants were described in terms of the following equations:

$$k_i = k_{0i}\exp(-E_i/RT) \text{ and } K_j = p_{0j}\exp(\Delta H_j/RT).$$

Here, the preexponential factor and the enthalpy of formation of the dimer ($j = 1$) and tetramer ($j = 2$) are designated p_{0j} and ΔH_j, respectively. The values of the parameters used in the calculations were close to the corresponding experimental values [2]: $E_2 = 170$ kJ/mol, $E_3 = 62.8$ kJ/mol, $k_1 = 0$, $k_{02} = 10\ s^{-1}$, $k_{03} = 10^{8.5}\ s^{-1}$, $\Delta H_1 = 12.8$ kJ/mol, $\Delta H_2 = 96.6$ kJ/mol, $p_{01} = 10^{-2.6}$ l/mol, and $p_{02} = 10^{-14.6}$ l^2/mol^2.

As the temperature is raised, the monomer concentration increases, the dimer concentration passes through a maximum, and the tetramer concentration decreases (Fig. 6). Accordingly, as the temperature increases, $\ln k_{ef}$ first grows and then stops changing both at $k_1 = 0$, $k_2 \neq 0$, and $k_3 \neq 0$ and at $k_1 = 0$, $k_2 = 0$, and $k_3 \neq 0$ (Fig. 7). At $k_1 = 0$, $k_2 \neq 0$, and $k_3 = 0$, $\ln k_{ef}$ passes through a maximum. Calculations demonstrated that, as the initial concentration A_0 is increased, the maximum in the $\ln k_{ef}$ versus temperature curve shifts to higher temperatures.

The results of the calculations are in qualitative agreement with experimental data of Bondarenko et al. [2], who reported that the temperature dependence of ln k_{ef} has an extremum. Unfortunately, that study is seemingly the only one in which the association of the reactants and the kinetics of the reactions involving the association species were investigated simultaneously in a wide temperature range.

Second-order reactions (A + D ⟶ C) take place in EM synthesis and decomposition processes important in practice and under the action of various reagents (water, acids, etc.) on EMS [30, 31]. Although EM synthesis reactions typically involve molecules bound together by strong intermolecular interaction (association species) [16, 23, 32], this circumstance is sometimes ignored (see, e.g., [30, 31, 33]). It was noted [23, 24] that, when cellulose is treated with a nitric acid solution, the direction of the process depends on the HNO_3 concentration. At concentrations below 60%, nitric acid is in the form of a trihydrate, which mainly executes an oxidizing and destructing action, while cellulose nitration needs the presence of the pseudoacid form (HO–NO_2), which exists only at concentrations above 70%.

If only molecules of the reactant A undergo association, the kinetic scheme may be

$$A_1 + D \longrightarrow B, \quad (Ic)$$

$$A_2 + D \longrightarrow B + A_1. \quad (IIc)$$

It can be demonstrated that the rate constant k_{ef} is related to the equilibrium constant of step (III) (K_1) and to the rate constants of steps (Ic) and (IIc) by Eqs. (3) and (4).

If the overall process includes two parallel reactions yielding different products B and C,

$$A_1 + D \longrightarrow B, \quad (Id)$$

$$A_2 + D \longrightarrow C, \quad (IId)$$

then, as in the case of the first-order reaction, the rate constant k_2 in Eqs. (3) and (4) should be replaced with $2k_2$ because two molecules of A, not one, disappear in

step (IId), as distinct from step (II). The ratio of the product B and C formation rates (w_B/w_C) is given by Eq. (6).

If the reactants A and D form the heteroassociation species AD, the second-order reaction will include the following steps:

$$A + D \longrightarrow B, \quad \text{(Ie)}$$
$$AD \longrightarrow C, \quad \text{(IIe)}$$
$$A + D \longleftrightarrow AD. \quad \text{(IIIe)}$$

Again, a comparatively simple general solution can be obtained only under the assumption that the concentrations of the reactants A and D are equal. Note that this case is the most important in practice. The effective rate constant of the reaction will then be

$$k_{ef} = A_0^{-2}(1-\alpha)^{-2}(K_1k_1 + k_2)\{[0.25K_1^{-2} + A_0(1-\alpha)K_1^{-1}]^{0.5} - 0.5K_1^{-1}\}^2,$$

where k_1 and k_2 are the rate constants of steps (Ie) and (IIe), respectively, and K_1 is the equilibrium constant of step (IIIe).

At $K_1k_1 \gg k_2$ this relation will appear as

$$k_{ef} = k_1A_0^{-2}(1-\alpha)^{-2}\{[0.25K_1^{-1} + A_0(1-\alpha)]^{0.5} - 0.5K_1^{-0.5}\}^2.$$

In the general case of unequal concentrations of A and D under the condition that K_1 is small (the equilibrium is strongly shifted toward the heteroassociation species), the effective rate constant of the reaction is $k_{ef} \approx K_1k_1 + k_2$.

Radical chain reactions. The radical chain mechanism is observed for some liquid-phase EM synthesis and decomposition processes and for the oxidation of organic compounds [17, 18, 31, 33, 34]. The simplest kinetic scheme of a radical chain process initiated by the initiator I introduced into the system (the initiator concentration will be designated I) includes the following elementary steps: initiation ($I \longrightarrow 2R^\bullet$), chain propagation ($R^\bullet + A_1 \longrightarrow R^\bullet$), and chain termination ($R^\bullet + R^\bullet \longrightarrow P$). The rate constants of these steps will be designated k_i, k_1, and k_t, respectively. In view of the formation of the dimer A_2, this scheme should be supplemented with a reactant association step ($2A_1 \longleftrightarrow A_2$, equilibrium constant K_1) and with a chain propagation step involving the dimer ($R^\bullet + A_2 \longrightarrow R^\bullet + A_1$, rate constant k_2). In the quasi-steady-state approximation with respect to the concentration of radical $R^\bullet$, i.e., under the assumption that $R^\bullet \approx (k_iI/k_t)^{0.5} = \text{const}$, the process obeys the first-order kinetic laws and the effective rate constant k_{ef} is given by Eq. (3). The rate of the radical chain process is

$$w = k_{ef}R^\bullet A = k_1(k_iI/k_t)^{0.5}\{[0.0625K_1^{-2} + 0.5K_1^{-1}A_0 \times (1-\alpha)]^{0.5} - 0.25K_1^{-1}\} + K_1k_2(k_iI/k_t)^{0.5}\{[0.0625K_1^{-2} + 0.5K_1^{-1}A_0(1-\alpha)]^{0.5} - 0.25K_1^{-1}\}^2.$$

If the chain carrier radical results from the decomposition of the reactant A ($A_1 \longrightarrow 2R^\bullet$), then k_{ef} is again given by Eq. (3) and the rate of the radical chain process is $w = k_{ef}R^\bullet A$, where $R^\bullet = \{k_i[(0.0625K_1^{-2} + 0.5K_1^{-1}A^{0.5} - 0.25K_1^{-1}]/k_t)\}^{0.5}$.

RESULTS AND DISCUSSION

In this study, we have carried out a mathematical modeling of the kinetics of the parallel reactions occurring in a structured liquid medium and involving reactants capable of association and interconversion. The results demonstrate that the effective rate constant in the monomer–dimer system can increase or decrease as the reactant concentration is varied, depending on the equilibrium constant and on the ratio of the rate constants of the reactions involving the unassociated molecules and association species. The analytical expression relating the effective rate constant of the reaction to the rate constants of the elementary steps, equilibrium constants, and reactant and solvent concentrations is nonlinear, is independent of the reaction order and depends on the association species type (autoassociation or heteroasscoiation). The results of our analysis (Figs. 1–7) are in qualitative agreement with the experimental data available on the kinetics of liquid-phase reactions.

The $\alpha(t)$ curves and the temperature dependences of k_{ef} for the monomer–dimer reaction system are qualitatively similar to those observed for unassociated systems. We demonstrated for the first time that the ratio of the rates of the parallel reactions depends on the reactant concentration and that, as the temperature is varied, the rates of the parallel reactions can change in opposite ways. Thus, an efficient way of investigating the kinetics and mechanisms of reactions in associated systems is by analyzing the dependence of k_{ef} on the reactant concentration, and particularly on the reaction temperature, because temperature variations change both the reactivity of the association species and the ratio of their concentrations in the reaction medium.

For quantitative characterization of the kinetic features of a structured liquid-phase reaction medium and for determination of the true rate constants for the initial step of the reaction, it is necessary to know not only the effective initial rate constant k_{ef}, but also the type of reactant association species and the equilibrium constant. The association of molecules can be quantitatively characterized by spectroscopic methods (NMR and IR spectroscopy). It is more difficult to determine k_{ef} for the thermal decomposition of an EM. The decomposition of an EM is known to be a complicated process consisting of tens or even hundreds of elementary steps and to be accompanied by the formation of numerous intermediates, including fairly stable ones [18]. However, a formal kinetic approach is typically used in kinetic studies of EM

thermal decomposition [17]. The experimental kinetic curves are usually described in terms of a single rate constant, k_{app}, which is taken to be the rate constant of the initial step; that is, it is assumed that the initial step limits the rate of the overall process. The experimental data that are in conflict with this assumption, such as the existence of parallel initial steps, the formation of stable intermediates, and the reversibility of many elementary steps, are ignored. The assumption that k_{app} is identical to the true rate constant of the initial step of EM decomposition is contrary the fundamentals of the dynamics of physical and chemical processes in structurally complicated systems.

At present, because of lack of equilibrium constant and association species type data (and lack of overall rate constant data for the initial steps in the case of EM decomposition), calculated and experimental data can be compared only in terms of the dependence of k_{ef} or k_{app} on A_0. Quantum chemical calculations make it possible to determine the rate constants of the initial steps involving both unassociated molecules and their association species; that is, they provide a means to compare the results of theoretical calculations with the numerical values of these constants calculated from experimental data using the above formulas.

The approach suggested here enables one to determine the rate constants of elementary steps of reactions involving both unassociated molecules and associated species. This is essential for establishing a correlation between the reactivity and the state of aggregation for EMs. As was noted in a monograph by Denisov et al. [35], the liquid state in a certain sense is intermediate between the gaseous and solid states of matter. For a structured liquid, it is natural to compare the reactivity of unassociated molecules to the reactivity of the same molecules in the gas phase. At the same time, it can be assumed that the rate constant of the elementary step involving the association species characterizes the reactivity of the defect zones in molecular crystals of the EM at a given temperature and that determination of this rte constant is of fundamental significance. This assumption is substantiated, in particular, by quantum chemical data indicating a similarity between the supramolecular structures of the crystal lattice and dimers of 1,1-diamino-2,2-dinitroethylene [36].

Practically, the results of our analysis will be of use in the prediction of EM stability and in the determination of EM synthesis conditions maximizing the yield of the desired product.

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