Models for unimolecular reactions in the solid phase and stability prediction of energetic compounds in the condensed state

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The results of analysis and refinement of phenomenological models for unimolecular reactions proceeding homogeneously in the bulk of undistorted crystal lattice or localized on the lattice defects are presented. It is shown that, within the framework of these models, the ratio of the rate constants for reactions in the liquid and solid phases, $K = k_l/k_s$, can be calculated with satisfactory accuracy and thus the known k_l values can be used to predict the rate constant k_s characterizing the stability of the materials.

Key words: unimolecular reactions, solid phase, additional volume model.

Thermal stability is an important characteristic of explosives and other energetic compounds. A quantitative measure of stability is the rate constant for the first noncatalytic step of decomposition (in the vast majority of cases, this is a unimolecular process). The theory of unimolecular reactions, which has been well developed for the gas- and liquid-phase processes, was to the full extent used in the studies of decomposition reactions of energetic compounds in the liquid phase. In particular, this theory was used to establish the reaction mechanisms and to reveal structure—stability correlations for a large number of compounds from various classes. In turn, thanks to these works the stability prediction for new compounds became possible.

Experimental data on the decomposition in the solid phase are scarce. Below the melting point, solid-phase reactions usually proceed slowly and are complicated by some side factors; taking them into account requires particular studies. Suffice it to say reliable values of the rate constants for solid-phase reactions were obtained only for a few tens of compounds. Therefore, attempts to establish quantitative relationships between the rate constants for reactions in the liquid and solid phases (k_l and k_s, respectively) and to use these relationships for the determination of k_s values from the known k_l constants seem to be natural. The greatest advances in calculations of the ratio $K = k_l/k_s$, which can be called the retardation factor of a solid-phase reaction (because always one has $K > 1$), were made within the framework of some phenomenological models that are analyzed, refined, and tested for applicability in the present study.

Liquid state. The problem of stability prediction for energetic compounds in the liquid state (melts, solutions) is to a great extent solved. The prediction is based on a large array of experimental data on the kinetics of thermal transformations of almost all classes of organic compounds (more than 1000 reactions with the known Arrhenius parameters) augmented with an array of auxiliary data on the bond dissociation energies and thermal effects of processes. The latter data array is at least comparable with the former in size. Prediction can be made using a simple method of analogies (comparison with structurally similar substances) or numerous reactivity indices relating the rate constant for the initial step of a reaction to the induction and steric constants of substituents, to spectroscopic characteristics of substances, or to thermal effects of reactions. In addition to these empirical calculations, theoretical computations of the pre-exponent A using the Marcus—Rice theory and quantum chemical methods of evaluation of the bond dissociation energies and activation energies of elementary steps are possible. Taken altogether, these methods allow one to assess the stability of a new substance in the liquid phase with practically admissible accuracy or to classify a number of substances as undoubtedly stable or, *vice versa*, unstable for being used under specified conditions based on the structural formulas of the compounds studied. This system of prediction is continuously refined and extended owing to inclusion of new types of structures or new classes of compounds depending on their practical importance. As an example, in Table 1 the stabilities of main classes of energetic compounds in the liquid state are compared. The introduction of substituents usually reduces the stability of the basic structural group. More detailed information on the effect of the structure on the stability of different types of compounds can be found in the references cited in Table 1.

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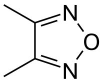
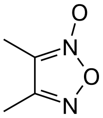
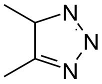
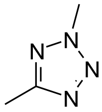
Table 1. Characteristic values of the kinetic parameters of decomposition of groups X in compounds R—X or R—X—R with R = Et

X	E/kJ mol^{-1}	log(A/s^{-1})	150 °C		Reference
			k/s^{-1}	W_{rel}	
$—(CNF_2)_2—$	199	16.0	$2.9 \cdot 10^{-9}$	1.00	1
$—C(NO_2)F$	199	17.0	$2.9 \cdot 10^{-8}$	10.00	1
$—C(NO_2)_2—$	199	17.1	$3.7 \cdot 10^{-8}$	13.00	1
$—N(NO_2)—$ (planar)	172	14.5	$2.1 \cdot 10^{-7}$	72.00	2
$—ONO_2$	168	14.7	$1.0 \cdot 10^{-6}$	$2.40 \cdot 10^{3}$	3
$—CH_3N_3$	163	14.4	$1.8 \cdot 10^{-6}$	630.00	4
$—C(NO_2)_3$	180	17.2	$1.0 \cdot 10^{-5}$	$3.40 \cdot 10^{3}$	1
$—NF_2$ (eclipsed)	126	9.0	$3.20 \cdot 10^{-7}$	110	1
$—N(NO_2)—$ (pyramidal)	159	14.5	$7.40 \cdot 10^{-6}$	$2.5 \cdot 10^{3}$	2
$—C(NO_2)_2NF_2$	168	16.0	$2.2 \cdot 10^{-5}$	$7.50 \cdot 10^{3}$	5
$—C(NO_2)_2N_3$	163	15.5	$2.2 \cdot 10^{-5}$	$8.00 \cdot 10^{3}$	1
$—NF_2$ (open)	111	8.3	$4.1 \cdot 10^{-6}$	$1.40 \cdot 10^{3}$	1
$—NHNO_2$	111	10.1	$2.6 \cdot 10^{-4}$	$1.00 \cdot 10^{5}$	6
$—N(NO_2)F$	126	15.0	0.3	$1.00 \cdot 10^{9}$	1
$—N(NO_2)_2$	121	15.0	1.0	$3.00 \cdot 10^{8}$	7
	193	14.5	$6.0 \cdot 10^{-11}$	0.01	1
	188	14.8	$3.2 \cdot 10^{-9}$	1.10	1
	197	14.9	$4.2 \cdot 10^{-9}$	1.40	1
	176	15.0	$2.6 \cdot 10^{-7}$	70.00	1

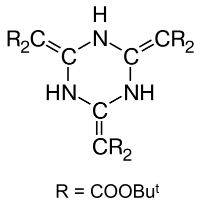
A homogeneous reaction in the bulk of a crystal

The model for the description of reactions proceeding in the bulk of undistorted crystal lattice gives the upper limiting value of the expected retardation factor of a unimolecular process on going from the liquid to solid state. In addition, the bulk model facilitates the interpretation of reactions on the surface of a crystal and on defects.

Using the transition state method and assuming that the crystal is an isotropic elastic continuum, the retardation factor of a bulk reaction K is given by[8]

$$RT\ln K = \Delta E_{add} = \Delta V^{\neq}{}_{add}{}^{2}/2\beta V_m, \qquad (1)$$

where $\Delta E_{add} = E_s - E_l$ is the activation energy difference between reactants in the solid and liquid phases, respectively; β is the isothermal compressibility factor; $V_m = M/\rho$ is the molar volume of the substance; and $\Delta V^{\neq}{}_{add}$ is the additional activation volume in the solid phase (this parameter is treated as the increase in the volume of the cell occupied by the molecule to the volume of a cavity in which all intermolecular bonds are broken and the molecule executes the same free rotational-vibrational motion as in the liquid). The reaction in the extended cell is characterized by the rate constant k_l and the retardation effect of the solid phase is determined by the work ΔE_{add} neeeded for elastic deformation of the cell. This interpretation of a unimolecular process is identical to the "molten cell" model developed to describe recombination reactions of free radicals in the solid phase.[9] This interpretation of the parameter $\Delta V^{\neq}{}_{add}$ means that K is independent of the microscopic details of the crystal structure and of the sign of the true activation volume $\Delta V^{\neq}{}_{l}$. At any $\Delta V^{\neq}{}_{l}$ value, the reaction rate in the solid phase should decrease. This conclusion follows from the model and was confirmed experimentally[10] by direct measurements of $\Delta V^{\neq}{}_{l}$ and K for the reaction of isobutylene elimination from *tert*-butoxycarbonyl hexahydrotriazine ester, the only ester compound whose decomposition in the solid state was observed.



The elimination proceeds *via* the formation of a six-membered cyclic transition state with the loss of three free internal rotations and has a negative activation entropy. This mechanism is typical of esters. The activation volume of this reaction in a chloroform solution is $\Delta V^{\neq}_{l} = -13.7$ cm^3 mol^{-1}; retardation of the reaction in the solid phase is characterized by $K = 7$ at 150 °C. Yet another example is the decomposition of malonic acid

$$\mathrm{HOOCCH_2COOH} \longrightarrow \mathrm{CH_3COOH + CO_2},$$

which proceeds *via* a four-membered cyclic transition state with the loss of two internal rotations. The decomposition rate of malonic acid decreases[11] by a factor of 40 at 110 °C on going to the solid state; and $\Delta V^{\neq}_{l} = -7$ cm^3 mol^{-1}.[12] The absolute value of true activation volume $\Delta V^{\neq}_{l}$ will influence $\Delta V^{\neq}_{\mathrm{add}}$. Reactions characterized by zero or negative $\Delta V^{\neq}_{l}$ values should also be characterized by the smallest $\Delta V^{\neq}_{\mathrm{add}}$ values. An increase in $\Delta V^{\neq}_{l}$ should be accompanied by an increase in $\Delta V^{\neq}_{\mathrm{add}}$.

$\Delta V^{\neq}_{\mathrm{add}}$ Calculations. Since the general condition for a reaction in the solid phase to proceed is the release of the molecular mobility, the parameter $\Delta V^{\neq}_{\mathrm{add}}$ can be calculated taking into account the volume of the cavity in which the molecule executes free three-dimensional rotation. Such a cavity should have a nearly spherical shape. Therefore, it was proposed[13] to estimate $\Delta V^{\neq}_{\mathrm{add}}$ as follows. The molar volume of a substance reduced by 25% (this corresponds to the free volume in a crystal at close packing of molecules) is divided by the number of molecules and thus one gets the volume occupied by one molecule. Assuming a spherical shape of this volume, the radius, r, of the sphere can be calculated and then it can be increased by an increment Δr in order to obtain the additional molecular volume $\Delta V^{\neq}_{\mathrm{add}}$. The Δr value is of paramount importance for calculations. It can be determined by back calculations of $\Delta V^{\neq}_{\mathrm{add}}$ using expression (1) based on reliable experimental data for K which are available for the thermal decomposition reactions of some energetic compounds. Hexanitroethane[14] and tetryl (*N*-methyl-*N*,2,4,6-tetranitroaniline)[15] are characterized by K values equal to 7 and 50—100 and by the compressibility factors β equal to $5.0 \cdot 10^{-10}$ and $1.0 \cdot 10^{-10}$ Pa^{-1}, respectively. It follows that $\Delta r = 0.22$ Å for hexanitroethane and 0.21—0.23 Å for tetryl.

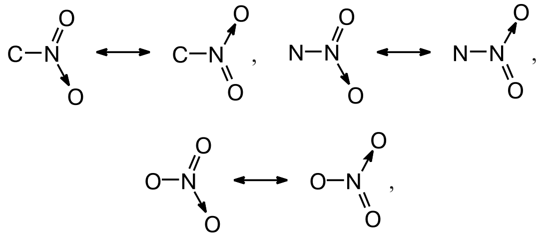
Decomposition of hexanitroethane having plastic crystals undoubtedly occurs in the bulk of the crystal lattice; for tetryl, the reactions on the surface and defects are more probable. In this case, the observed K value can only approach the limiting value for the bulk reaction and therefore the Δr value may be underestimated. An independent analysis of the increase in the activation energy ΔE_{add} of bulk reorientation reactions of hexafluorocomplexes $\mathrm{KPF_6}$ and $\mathrm{KIrF_6}$ within the framework of the dynamic theory of reorientation gave $\Delta r \approx 0.20$ Å.[16] For widespread bond dissociation reactions characterized by positive activation volumes, the extended cell should be large enough to accomodate not only a single molecule but also the activated complex. According to the RRKM calculations of the preexponent for the decomposition of *tert*-butoxyl radical,[17] the C—C bond in this radical (bond dissociation energy of about 62 kJ mol^{-1}) elongates by 0.3 Å upon dissociation. Calculations[17] of the activation volume $\Delta V^{\neq}_{l}$ for the decomposition of benzoyl peroxide showed that the C—C bond in the benzoyl radical (bond dissociation energy of is 125 kJ mol^{-1}) elongates by 0.4 Å upon dissociation. One can admit that elongation of moderate-strength bonds (170—240 kJ mol^{-1}), such as C—N, N—N, N—O, and O—O in semirigid transition states may reach a value of 0.5 Å. Consequently, the cell radius will increase by 0.25 Å. Thus, various estimates give a rather narrow interval of values (0.2—0.25 Å) for Δr. In this case, intermolecular bonds that preclude rotation of the entire molecule (dissociation of these weak bonds is accompanied by a small increase in the intermolecular distances) will be broken. Further calculations were carried out using a constant value $\Delta r = 0.23$ Å. In this case, the maximum possible deviation is ±0.03 Å, which gives for K values a maximum deviation of 300-400 per cent ($V_{\mathrm{m}} = 100$ cm^3 mol^{-1}) and 400—500 per cent ($V_{\mathrm{m}} = 500$ cm^3 mol^{-1}) at 150 °C. This is a relatively low cost for the possibility of carrying out calculations for molecules with different molecular mass and for reactions with different activation volumes using the same computational scheme.

Estimation of $\Delta V^{\neq}_{\mathrm{add}}$ by the method described above shows that for most energetic compounds the parameter $\Delta V^{\neq}_{\mathrm{add}}$ is related to V_{m} as follows: $\Delta V^{\neq}_{\mathrm{add}} = (0.1—0.2)V_{\mathrm{m}}$. Melting of organic substances is accompanied by an increase in their volume to the same extent (10—20%). This fact confirms that the free volume model corresponds to the terms "molten cell" or "virtual melting" which are sometimes used for the interpretation of physicochemical processes in the solid phase.[19] At $V_{\mathrm{m}} = 100—300$ cm^3 mol^{-1}, the volume $\Delta V^{\neq}_{\mathrm{add}}$ can be approximately calculated using the relation $\Delta V^{\neq}_{\mathrm{add}} = 0.1V_{\mathrm{m}} + 10$ that can be used for fast evaluation of $\Delta V^{\neq}_{\mathrm{add}}$.

Calculation of the compressibility factor β. To calculate K using expression (1), one should know the compressibility factor β. Since relevant experimental data for the HCNO compounds with densities $\rho > 1$ g cm^{-3} are scarce, the only way to determine β is to use the expression $\beta = 1/(C_0{}^2\rho)$ relating the compressibility to the speed of sound C_0. In turn, C_0 can be determined from the semiempirical Rao formula (see Refs 20 and 21) which takes into account the chemical structure of the substance:

$$C_0^{1/3}M/\rho = \Sigma z_i B_i, \tag{2}$$

where $R = C_0^{1/3}M/\rho$ is the temperature-independent quantity usually called the molecular speed of sound; z_i is the number of chemical bonds of a given type, and B_i are the increments of these bonds. The list of the known increments[20,21] includes the following bonds: B(N—H) = 90, B(C—H) = 95.2, B(C—C) = 4.25, B(C—O) = 34.5, $B(\text{C—O}_{\text{ester}})$ = 44.5, B(C=C) = 129.0, B(C=O) = 186.0, B(C—N) = 20.7, B(C=N) = 145, B(C≡N) = 285, B(O—H) = 99.0, $B(\text{C—NO}_2)$ = 302.5, $B(\text{O—NO}_2)$ = 360.0, $B(\text{N—NO}_2)$ = 330.0, and $B(\text{C—C}_{\text{Ar}})$ = 67.2. Using the additivity of the molecular speed of sound in the Rao scheme and representing the C—NO_2, O—NO_2 and N—NO_2 fragments as



from the relations $B(\text{C—NO}_2) = B(\text{C—N}) + B(\text{N=O}) + B(\text{N}\rightarrow\text{O}) = 302.5$, $B(\text{N—NO}_2) = B(\text{N—N}) + B(\text{N=O}) + B(\text{N}\rightarrow\text{O}) = 330.0$, and $B(\text{O—NO}_2) = B(\text{O—N}) + B(\text{N=O}) + B(\text{N}\rightarrow\text{O}) = 360.0$, one gets the increments of the N—N and N—O bonds, namely, B(N—N) = 48.2 and B(O—N) = 78.2.

This set of increments is insufficient for calculations of C_0 for many compounds, in particular, heterocyclic energetic compounds for which it is first of all desired to experimentally determine the B_i values for the N=N, N=O, N→O, C—N_3 bonds and other structural elements. Some progress in this field can be achieved using the relation between the additional activation energy ΔE_{add} and the heat of fusion of a substance (see below), which allows one to calculate ΔE_{add} from expression (1).

As early as 1921, in a study on tetryl decomposition it was assumed[15] that the degree of retardation of the reaction in the solid phase is related to the heat of fusion of the substance Q_{m}. Using the possibility of calculating ΔE_{add} from Eq. (1), the ΔE_{add} values were compared[22] with Q_{m}. The ΔE_{add} values were calculated for those compounds whose densities were determined with an accuracy of 1—2%. Generally, the ratio $\delta = \Delta E_{\text{add}}/Q_{\text{m}}$ varies over a wide range from 0.1 to 0.9. However, for a large group of HCNO or HCNOF compounds, δ varies in a narrow interval:

$$\Delta E_{\text{add}} = (0.6\pm0.1)Q_{\text{m}}. \tag{3}$$

Having measured the heat of fusion of 1,1,3,5,5-pentanitro-1,5-bis(difluoroamino-3-azapenthane (Q_{m} = 38.9 kJ mol^{-1}, ρ = 2.045 g cm^{-3}) and using relationships (3), (1), and (2), it was found that $B(\text{C—NF}_2)$ = 330. By analogy, taking into account the reference data on the heat of fusion and density of azobenzene (Q_{m} = 21.2 kJ mol^{-1}, ρ =1.203 g cm^{-3}) and azoxybenzene (Q_{m} = 17.8 kJ mol^{-1}, ρ =1.150 g cm^{-3}), it was found that B(N—N) = 220 and B(N→O) = 220. Using the evaluation scheme of B(N—N) and B(N—O) given above, we obtained B(N=O) = 61.8.

The increments B_i for calculations of the speed of sound in the Rao scheme correspond to experimental data for the liquid state. An increase in C_0 on going to the solid phase is to a good accuracy taken into account by calculations based on the density changes. There are a few examples[21] that the speeds of sound calculated for solid substances using the Rao scheme and those determined experimentally are equal to one another within the limits of experimental accuracy. A more significant requirement is imposed on the accuracy of the density measurements. Owing to a very strong dependence of K on ρ this quantity should be known with an accuracy of at least 2%.

Limits of changes in *K* for a bulk homogeneous reaction. The ΔE_{add} values calculated using expression (1) and the parameters M, ρ, and β of real molecules lie in the range 2—20 kJ mol^{-1} and the K values lie between 2 and 500 at 150 °C. The maximum error in the determination of K is at most 500 per cent. The same result in a more clear form can be obtained from relation (3). The heats of fusion of most organic molecules are in the range 8—40 kJ mol^{-1}. Then, according to Eq. (3), the changes in ΔE_{add} will be from 5 to 25 kJ mol^{-1}, and the K factors can vary from 4 to 1000 at 150—200 °C. It is this range of values that covers all experimental data on K (Table 2). This fact confirms the correctness of the bulk reaction model and the possibility of evaluating K values in spite of the approximations made in deriving expression (1) and methods of calculations of $\Delta V^{\neq}_{\text{s}}$ and β.

Reactions localized on lattice defects. According to the concept developed in Ref. 11, one can construct a model for the description of reactions on defects. The model is based on the following postulates.

1. The main type of defects in molecular crystals includes rows of dislocations that form the microblock boundaries. The reaction proceeds on the surface of microblocks.

2. All molecules on the surface of microblocks have identical reactivities.

3. The additional activation energy is equal to zero ($\Delta E_{\text{add}} = E_{\text{s}} - E_{\text{l}} = 0$); therefore, retardation of solid-phase reactions is mainly due to the formal decrease in the pre-exponent owing to a decrease in the number of reactive molecules.

If these retardation conditions are met, the retardation factor, K, of the solid-phase reaction will change as the inverse of the fraction of molecules arranged on the sur-

$(NO_2)_3CC(NO_2)_3$

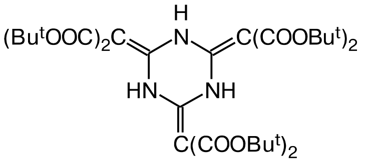
1

$HOOC{-}CH_2{-}COOH$

2

$(CH_3)_2(CN)CN{=}NC(CN)(CH_3)_2$

3



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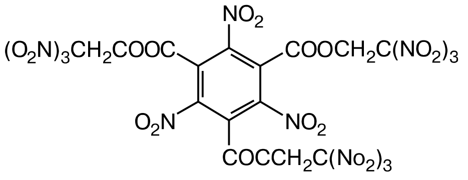

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$\mu\text{-}O_2NC_6H_4C(O)N_3$

6

$C[(OCH_2C(NO_2)_3]_4$

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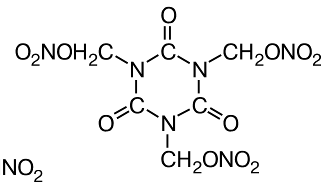

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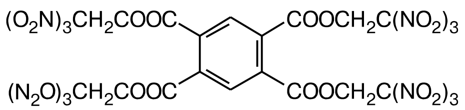

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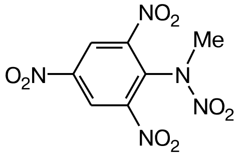

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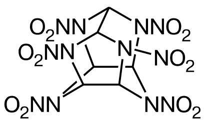

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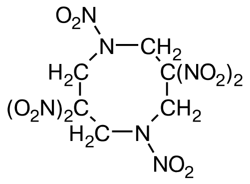
$HOOCCOOH$

12



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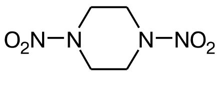
$O_2NN[CH_2C(NO_2)_2CH_3]_2$

14

$C(CH_2ONO_2)_4$

15



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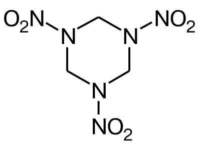
$[CH_2N(NO_2)CH_2C(NO_2)_3]_2$

17



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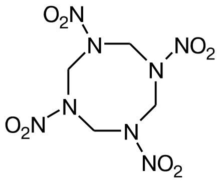

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Table 2. Calculated and experimental values of retardation factor *K* for various classes of compounds

Compound	*M* /g mol^{-1}	ρ /g cm^{-3}	T_m /°C	β • 10^{10} /Pa^{-1}	ΔE_{add} /kcal mol^{-1}	*K*		Microblock size*
						Calculations	Experiment	
1	300	1.850	150.0	2.715	1.6	8	6	A
2	104	1.630	135.0	2.003	1.7	9	40	A
3	164	1.110	97.0	2.268	1.9	20	50	A
4	723	1.150	200.0	2.625	2.5	17	10	A
5	834	1.780	176.0	2.256	2.7	24	8	B
6	192	1.540	77.0	0.964	4.1	29	36	A
7	732	1.840	162.0	2.038	2.8	32	20	A
8	354	1.770	148.0	1.382	3,4	73	10	B
9	906	1.820	171.0	1.593	3.9	102	5	B
10	287	1.730	129.0	1.263	3.5	106	100	A
11	438	2.040	250.0	0.971	5.0	144	100	A
12	90	1.900	189.0	0.698	4.5	167	122	A
13	384	1.891	250.0	2.204	5.3	200	500	A
14	326	1.721	185.0	0.978	4.8	236	230	A
15	316	1.778	143.0	1.035	4.4	271	100	A
16	176	1.640	195.0	0.777	5.1	299	200	A
17	4762	1.880	179.2	1.026	5.0	314	92	A
18	222	1.840	201.0	0.731	5.6	484	300	A
19 (δ-Form)	296	1.780	281.0	0.584	7.5	97	90	A

* A and B stand for large and small, respectively.

face of a microblock, and the K value for cubic microblocks is

$$K = L/(6l), \tag{4}$$

where L and l are the linear dimensions of the microblock and molecule, respectively.

The first postulate follows from independence of the reaction rate on the crystal size. This was reported as early as in Ref. 11. The external surface area of the smallest 20-nm crystals is by a factor of 10 and more smaller than the internal surface area of these crystals even if they are comprised of the largest microblocks (1 μm in size). The second and third postulates are partially met. The molecules on the edges and at the vertices of microblocks, as well as the molecules in the interstices or in the near-surface layer vibrationally excited by a reflected phonon wave have increased reactivity. These factors cause an increase in the rate of decomposition on defects. But this effect is compensated by the unfulfilment of the condition $\Delta E_{\text{add}} = 0$, *i.e.*, by violation of the third postulate. Since molecular motion on the surface is hindered, the requirement of creating an additional activation volume $\Delta V^{\neq}_{\text{add}}$, as follows from the "molten cell" model, still holds for the localized reactions. However, the difference ΔE_{add} on the surface of microblocks or in the interstitials should be at least two times lower than in the bulk (generally, ΔE_{add} can be 3 to 12 kJ mol^{-1}). This difference between E_s and E_l is hard to observe experimentally, and therefore one can suggest that the second and third Bon postulates[11] are met within the limits of experimental accuracy. Irrespective of rigorous fulfilment of the second postulate, the K value for the reaction on defects should be a linear function of L.

The lack of data on L is due to methodological difficulties in measurements of this parameter. Using X-ray powder diffraction, one can determine the size of small blocks ($L < 100$ nm). Larger microblocks (main units in molecular crystals) give no line broadening in the Debye powder patterns. Only at $L > 100$ nm one can obtain well defined X-ray patterns suitable for crystal structure determination. Using these two indicators, one can easily determine the conditional boundary between small and large microblocks, *viz.*, $L = 100$ nm. Now we can make some useful estimates. At the limiting values $L = 10$—10^3 nm and typical values $l = 5$—10 Å, the K values for the reaction on defects can vary from a few units to a few hundreds, *i.e.*, the K values for localized reactions should be within the range of K values for bulk reactions. For typical cases of real molecules ($L = 100$ nm) even if the condition $\Delta E_{\text{add}} = 0$ is not met, the K value is at most 50. Correspondingly, for the largest microblocks ($L = 1000$ nm) one can expect an increase in K to a value of 500. Thus, the threshold value $L = 100$ nm appeared for methodological reasons can be used for classification of samples into two groups, namely, samples with expected low or high degree of stabilization in the solid phase.

Limits of changes in *K*. The temperature dependences of the rate constants k_s for the maximum possible retardation in the case of bulk and localized reactions are shown in Fig. 1. The limit is attained at $\Delta E_{\text{add}} = 25$ kJ mol^{-1} for the bulk reaction and at $L = 1$ μm for $l = 5$ Å for the reaction on the surface of microblocks. At low temperatures, the bulk reaction proceeds slower than the reaction on defects. But at 150 °C, the K values for the reactions in the bulk and on the surface of large microblocks become equal to each other and the lines are crossed. As the melting point is approached, the Arrhenius dependence for k_s of the bulk reaction is violated owing to an increase in the compressibility factor and k_s tends to k_l. The deviation from the linear dependence $\log k_s$—$1/T$ begins 10—20 °C below the melting point. As the parameters ΔE_{add} and L decrease, the lines for k_s are shifted upward and various cases of their mutual position and crossing become possible.

Evaluation of changes in the reaction rate upon a polymorphous phase transition. Changes in the rate of unimolecular decomposition reaction on going from one polymorph to another can be estimated using expression (1) provided that the densities of the polymorphs are known. Usually, the density changes only slightly upon the polymorphous transition; however, taking into account a very strong dependence of K on ρ, one can expect a significant acceleration of the reaction on going to the high-temperature phase. Such estimates can be compared with experimental data only for 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (octogene). The densities of the octogene α- and β-polymorphs are equal to 1.87 and 1.78 g cm^{-3}, respectively.[23] Then, from expression (1) for a bulk homogeneous reaction at 180 °C one gets a value of 8.0 kJ mol^{-1} for the difference between the ΔE_{add} values for the δ- and

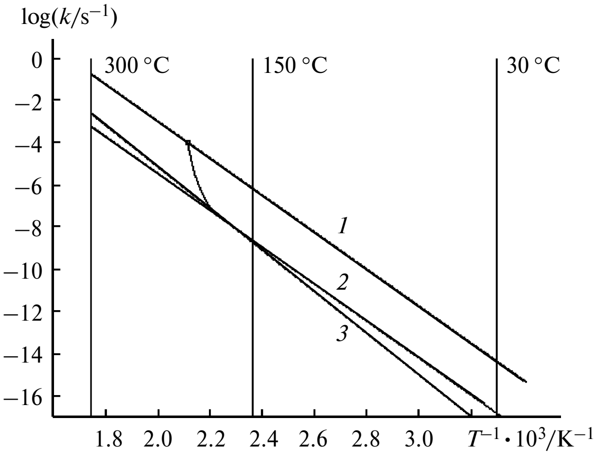

Fig. 1. Limiting value of retardation effect of the solid phase for reactions in the bulk of undistorted crystal and for reactions localized on defects: *1* – liquid phase, $E = 170$ kJ mol^{-1}, $\log A = 14.5$ (s^{-1}); *2* – solid phase, reaction on defects, $L = 1$ μm, $l = 0.5$ nm, $E = 170$ kJ mol^{-1}, $\log A = 12.0$ (s^{-1}); *3* – reaction in the bulk, $E = 195$ kJ mol^{-1}, $\log A = 14.5$ (s^{-1}).

α-polymorphs and the ratio $k_s(\delta)/k_s(\alpha) = 8.2$ (*cf.* 3.3 for the experimental value[24]). The latter value is smaller than the calculated one and, probably, characterizes a reaction on dislocations.

Experimental determination of *K*. Solid-phase decomposition reactions are complicated by various side phenomena which should be taken into account in order to obtain correct k_s values. Below, we present a list of key factors affecting the decomposition rates of solid substances and relevant methods of their elimination.

Factors affecting the kinetics of a solid-phase reaction	Remedies for the side factors
Premelting effects	Investigation of reactions at temperatures 20 °C below the melting point
Vaporization and decomposition of vapours	Conducting reactions at high degree of reactor filling with substances (0.1—0.3 g cm^{-3}) that provide a fraction of vapors of less than 0.1%
Formation of liquid phase and dissolution of substance in products	Measurements of reaction rates at initial linear portions of the kinetic curves (usually, below 1.0% conversion)
Sorption of solvent, water, and air (in the case of manometric measurements)	Vacuum desiccation at the experiment temperature and glass capsulation without air

An analysis of published data shows that the conditions needed to obtain correct k_s values are not always met. Therefore, the available data were re-checked[3,14] and the *K* values were additionally determined for some new substances including non-energetic compounds. The results of these studies are listed in Table 2.

Comparison of the results of calculations with experimental values. *K* values calculated using Eq. (1) are compared with experimental data in Table 2. The comparison was carried out for all substances for which (i) we succeeded in calculating the parameters appeared in expression (1) and (ii) correct k_s values were available. These substances belong to different classes of compounds and have maximum possible differences for such parameters as *M* (100—900 g mol^{-1}), ρ (1.1—2.0 g cm^{-3}), and β $(0.5—5.0) \cdot 10^{-10}$ Pa^{-1}. The *K* values calculated for compounds **1**—**4**, **6**, and **7** are much smaller than 100 and agree with experimental data. Crystals of these substances have large microblocks and reactions on dislocations proceed slowly. Consequently, this suggests homogeneous reactions in the bulk of the crystals. Compounds **5**, **8**, and **9** have small microblocks, the apparent *K* values are much smaller than the calculated ones and therefore it is probable that the reactions are localized on defects. In other cases, the calculated *K* values approach a value of 100 or are multiples of 100; in connection with significant retardation in the bulk, one can expect manifestation of the dislocation mechanism of decomposition. However, the experimental and calculated values differ insignificantly. The results obtained confirm the conclusion that calculations always give the upper bound of the retardation factor observed in the experiment and this limit is attained for large microblocks.

Summing up, the additional volume model based on the fundamental principle according to which the reactivity is related to molecular mobility and on the concept of the free volume gives a simple but correct description of retardation of unimolecular reactions in the solid phase. In spite of the approximations made in deriving the general expression for calculations and in estimating its parameters, the results of calculations using this model agree with the experimental data. The model relates the retardation factor $K = k_l/k_s$ to the common physicochemical properties of substances (molecular mass, density, compressibility, heat of fusion, linear dimension of microblocks in the crystal) and thus makes it possible to calculate the limits of changes in *K* for molecular crystals and to estimate this value for any crystalline compound. The maximum possible *K* value for a reaction in the bulk of an undistorted crystal approaches a value of 300 and corresponds to $Q_m = 40$ kJ mol^{-1}. This limit can be attained in the case of low-defect crystals with large microblocks ($L = 1$ μm), where the rate of the reaction on defects becomes lower than the rate of homogeneous reaction in the bulk.

The problem of stability prediction for organic substances both in the liquid and solid state is first of all topical for energetic compounds. In this case, the estimates obtained from prediction may appear to be useful for the design of synthetic routes to novel compounds with specified properties. Establishment of the applicability range of the model calculations requires targeted kinetic studies of energetic compounds including thorough investigations of liquid-phase reactions, determination of the mechanism of the initial step and rate measurements in impurities or in inert solvents, taking into account side factors that mask solid-phase reactions, and determination of correct values of the rate constants k_s. In addition to new experimental data on *K*, the development of the bulk model requires elaboration of effective theoretical methods of calculation of the densities and compressibility factors of substances.

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