Retardation of monomolecular reactions in the solid phase

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The rate constants of initial monomolecular stages of thermal decomposition in the solid phase were measured for 22 organic compounds. The ratio of rate constants of decomposition in the melt and solid state, characterizing the reaction retardation in the crystal lattice, was determined. The retardation effect was compared to the physical properties of the crystal.

Key words: monomolecular reactions, solid phase, retardation effect.

Decomposition of organic compounds in the solid phase occurs much more slowly than in the liquid phase.[1–3] The retardation effect of the crystalline lattice (REL), which can be defined as the ratio of rate constants of decomposition in the liquid phase to that in the solid phase (k_{liq}/k_s), is often the only factor that causes the stability of the substance and its suitability for use after prolong storage. This situation is characteristic of medicines, explosives, and initiators of chain processes. Experimental determination of REL and development of methods suitable to predict the properties of new substances are an important aspect of the general theory of the stability of organic compounds. Development in this field is restricted because the data on k_s values are limited and the theoretical models of monomolecular reactions in the solid phase cannot be verified.

Solid-phase decomposition reactions are usually accompanied by several side processes, such as evaporation and fast decomposition of compounds in the gas phase, melting on admixtures and products, autocatalysis at the early stages of the process, effects of premelting near points of phase transitions, and others. Due to side reactions, the observed k_s values often exceed the true values by one and even two orders of magnitude. The methods for taking into account secondary factors[2] are quite simple, but are used to a full extent only for several compounds.

Therefore, the purpose of this work is to obtain, first, a sufficiently representative array of correct k_s and k_{liq}/k_s values and, second, the dependence of REL on the physical properties of the crystal and on other parameters used in theoretical models.

Experimental

Decomposition rates were measured by the manometric method. The reaction course was monitored at conversions of 0.01—1.00%, which allowed one to avoid the influence of autocatalytic processes and topochemical regime of the reaction. To eliminate unstable or catalytic admixtures, the substances were purified by sublimation onto a heated support or by recrystallization from different solvents with thorough drying. The purification was carried out until a constant decomposition rate was achieved.

To increase the sensitivity of the method, we used such loadings of the substance that the ratio of the sample weight to the volume of the reaction vessel was ~0.5 g cm^{-3}. Thus, the amount of substance in the vapor phase was insignificant as compared to the weight of the solid sample, and the reaction in vapor could be neglected even at the highest possible difference in the rates in the gas and solid phases (four orders of magnitude).[4]

The k_s values were calculated from the time of achievement of a degree of decomposition of 0.1%. For calculation of the conversion, the stoichiometric coefficient of gas release determined by the decomposition of the substance in melt was used.

Results and Discussion

The REL values for 22 compounds calculated using the correct k_s values are presented in Table 1. The kinetic data used for composing Table 1 are presented in Table 2. The rate constants obtained for the decomposition in melt (noncatalytic stages) or in inert solvents were used as k_{liq}. When several data were available, the minimum k_s and k_{liq} values were taken for the calculation of REL. For compounds **21** and **22**, the constants were chosen from the published data.[2,17,18]

The REL values were calculated at temperatures 20 °C lower than the melting point of the substance when pre-melting effects do not affect the k_s value. The melting points of the substances and the volume compressibility (β) (the parameter characterizing the force of interatomic interaction in the crystal) are also presented in Table 1. The β values were calculated by the Rao method,[19] and the group increments were borrowed from the literature data.[20]

The mechanisms of initial monomolecular stages of decomposition are known for all compounds presented

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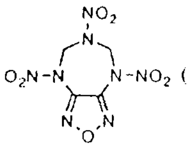
Table 1. Retardation effect of the crystalline lattice and physical properties of the substances

Compound	k_{liq}/k_s	m.p./°C	$\beta \cdot 10^{10}$/Pa^{-1}	V_0/cm^3 mol
$[FC(NO_2)_2CH_2]_2NNO_2$ (**1**)	4	86	3.530	173.9
$[F_2NC(NO_2)_2CH_2]_2NNO_2$ (**2**)	4	102	—	198.0
$C(NO_2)_3C(NO_2)_3$ (**3**)	6	140	5.500	169.4
PhN=N—NHPh (**4**)	6	101	—	—
$[C(NO_2)_3CH_2]_2NNO_2$ (**5**)	10	95.5	1.050	199.0
$F_2NC(NO_2)_2CH_2NNO_2(CH_2)_2C(NO_2)_2NF_2$ (**6**)	10	120	—	—
$[NF_2(NO_2)_2CCH_2N(NO_2)CH_2]_2$ (**7**)	20	158	—	—
 (**8**)	25	148	—	—
1,3,5-Trinitro-2,4,6-triazidobenzene (**9**)	28	131	—	—
1,3,5-Tris(trinitromethyl)benzene (**10**)	38	113	—	—
$N_3(CH_2NNO_2)_4CH_2N_3$ (**11**)	87	177	—	—
$HOOCCH_2COOH$ (**12**)	90	135	—	—
$[(NO_2)_3CCH_2N(NO_2)CH_2]_2$ (**13**)	92	180	1.060	254.5
2,4,6-$(NO_2)_3C_6H_2N(NO_2)Me$ (**14**)	100	130	1.200	164.5
HOOC—COOH (**15**)	122	189	—	—
1,4-Dinitro-1,4-diazacyclohexane (**16**)	210	213	1.310	107.3
$[MeC(NO_2)_2CH_2]_2NNO_2$ (**17**)	230	177	0.968	189.5
$C(CH_2ONO_2)_4$ (**18**)	360	142	—	178.5
1,1,3,5,5,7-Hexanitro-1,4-diazacyclohexane (**19**)	500	250	0.925	203.2
1,4,6,9-Tetranitro-1,4,6,9-tetraazadecalin (**20**)	1000	236	—	—
1,3,5-Trinitro-1,3,5-triazacyclohexane (**21**)	1400	201	0.809	122.0
1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (**22**) (β-modification)	8380	277	0.547	155.8

in Table 1: bond cleavage of C—NO_2 (**2**, **3**, **5**—**7**, **10**, **13**), N—NO_2 (**1**, **14**, **16**, **17**, **19**—**22**), O—NO_2 (**18**), and N—N (**4**) and elimination of N_2 (**11**) *via* the formation of the linear transition state or elimination of N_2 (**9**) and CO_2 (**12**, **15**) molecules through the cyclic transition state.

The majority of reactions are characterized by a positive activation volume, *i.e.*, they occur with a volume increase in the transition state ($\Delta V^{\ne}$). For compounds **9** and **11**, one can expect $\Delta V^{\ne}$ values close to zero, whereas for **12** and **15**, they can even be negative.

It is seen from the data in Table 1 that the REL values vary within very wide limits from 4 to 10^4. To explain such a broad interval of REL variation, the theory of solid phase reactions should be considered.

Based on the published data,[1,21—23] a generalized physical model of monomolecular reactions in the solid phase can be envisaged. A reaction can proceed in the bulk of the crystal or on its surface and on defects of the crystalline lattice. The reaction occurring on defects has the same activation energy (E) as in the liquid phase (or close to it), but the pre-exponential factor includes the coefficient that takes into account the fraction of molecules in disordered sites of the lattice. According to estimates[1,24,25] based on the calculation of the number of molecules arranged on the network of dislocations that separate microblocks of the crystal (the linear sizes of the microblocks are 10^{-3}—10^{-5} cm), the fraction of such reactive molecules is 0.01—1.00%. Thus, the reaction on defects limits the k_{liq}/k_s ratio to 10^4, and the reaction in the bulk can be observed only if REL does not exceed 100.

Reaction in the bulk of the crystal requires additional energy $\Delta E = E_s - E_{liq}$ necessary for the formation of a cavity with a volume exceeding the activation volume $\Delta V^{\ne}$, so that the leaving group does not experience forces of interatomic attraction. The pre-exponential factor of the reaction occurring in the bulk should be the same as that for the reaction in the liquid phase. It is difficult to calculate ΔE by the molecular dynamics method.[26] The macroscopic approach,[22] considering the crystal as an elastic continuous medium, leads to the equation

$$2.303RT\log(k_{liq}/k_s) = \Delta E = (\Delta V^{\ne}_s)^2/(2\beta V_0), \qquad (1)$$

where V_0 is the molar volume of the substance, and $\Delta V^{\ne}_s$ is the activation volume in the solid phase. This volume is not equal to the true value $\Delta V^{\ne}$. According to the published data,[23] it can be estimated as an increase in the volume of the cell occupied by a molecule due to elongation (by 10—15%) of the cleaving bond in the

Table 2. Kinetic parameters of decomposition of organic compounds in liquid and solid states

Compound	Medium[a]	T /°C	E [b]	log$A$ [c]	k [d] /s^{-1}	References
1	Solution in TNT	170—210	40.0	14.92	$1.3 \cdot 10^{-11}$	4
	Solid phase	66			$3.0 \cdot 10^{-12}$	[e]
2	Melt	105—120	38.5	15.70	$3.5 \cdot 10^{-8}$	[e]
	Solid phase	82			$8.8 \cdot 10^{-9}$	[e]
3	Gas	90—135	35.8	16.52	$4.0 \cdot 10^{-4}$	2
	Solid phase	120			$6.6 \cdot 10^{-5}$	[e]
4	Melt	100—160	39.9	17.50	$7.2 \cdot 10^{-8}$	5
	Solid phase	80			$1.2 \cdot 10^{-8}$	[e]
5	Melt	110—150	36.8	15.59	$2.9 \cdot 10^{-8}$	4
	Solution in DNB	110—165	36.1	15.06	$2.4 \cdot 10^{-8}$	4
	Solid phase	75			$2.4 \cdot 10^{-9}$	[e]
6	Solution in TNT	100	—	—	$1.3 \cdot 10^{-7}$	[e]
	Solid phase	100	—	—	$1.3 \cdot 10^{-8}$	[e]
7	Solution in TNT	130—170	40.3	16.9	$30 \cdot 10^{-5}$	[e]
	Solid phase	100—140	42.6	16.4	$1.5 \cdot 10^{-6}$	[e]
8	Solution in NB	114	—	—	$3.3 \cdot 10^{-4}$	[e]
	Solid phase	114	—	—	$1.3 \cdot 10^{-4}$	[e]
9	Solution in xylene	70—115	26.0	12.10	$1.6 \cdot 10^{-3}$	6
	Solid phase	50—100	28.8	12.20	$5.7 \cdot 10^{-5}$	[e]
10	Solution in TNT	95	—	—	$1.2 \cdot 10^{-3}$	[e]
	Solid phase	95	—	—	$3.5 \cdot 10^{-5}$	[e]
11	Solution in DNB	120—180	36.3	14.59	$1.4 \cdot 10^{-4}$	7
	Solid phase	120—175	36.7	12.86	$1.6 \cdot 10^{-6}$	[e]
12	Melt	136—160	32.2	13.50	$2.3 \cdot 10^{-5}$	[e]
	Solid phase	115	—	—	$2.6 \cdot 10^{-7}$	[e]
13	Solution in DNB	130—180	40.7	16.80	$2.6 \cdot 10^{-4}$	4
	Solid phase	158			$2.8 \cdot 10^{-6}$	[e]
14	Melt	140—160	35.2	13.50	$2.6 \cdot 10^{-7}$	8
	Melt	131—155	36.0	13.80	$1.8 \cdot 10^{-7}$	9
	Melt	150—175	35.9	13.50	$1.0 \cdot 10^{-7}$	10
	Solid phase	80—120	38.9	13.20	$1.0 \cdot 10^{-9}$	2
15	Gas	150—190	35.2	13.80	$2.5 \cdot 10^{-4}$	[e]
	Solid phase	120—180	38.6	13.40	$2.1 \cdot 10^{-6}$	[e]
16	Melt	135—200	37.1	13.90	$1.5 \cdot 10^{-8}$	11
	Solution in TNB	120—260	37.9	14.00	$8.1 \cdot 10^{-8}$	12
	Solution in NB	225—245	37.1	12.00	$2.0 \cdot 10^{-6}$	12
	Solid phase	185			$9.5 \cdot 10^{-9}$	[e]
17	Solution in DNB	145—170	39.7	15.7	$3.3 \cdot 10^{-5}$	13
	Solid phase	150			$2.3 \cdot 10^{-7}$	[e]
18	Melt		40.0	15.8	$4.7 \cdot 10^{-7}$	14
	Solid phase	120—130	39.0	12.7	$1.3 \cdot 10^{-9}$	2
19	Solution in TNT	170—210	38.0	14.5	10^{-2}	[e]
	Solid phase	230	—	—	$2 \cdot 10^{-5}$	[e]
20	Gas	216	—	—	$2 \cdot 10^{-3}$	[e]
	Solid phase	216	—	—	$2.1 \cdot 10^{-5}$	[e]
	Solid phase	204—234	50.1	18.9	$3.2 \cdot 10^{-4}$	15
21	Solution in DNB	160—200	39.7	14.3	$1.4 \cdot 10^{-5}$	16
	Solid phase	140—190	39.8	11.2	10^{-8}	17
22	Solution in DNB	171—215	44.9	16.0	$3.1 \cdot 10^{-3}$	16
	Solid phase	130—180	37.9	9.2	$3.7 \cdot 10^{-7}$	18

[a] The following designations were used: DNB is *m*-dinitrobenzene, NB is nitrobenzene, TNB is 1,3,5-trinitrobenzene, and TNT is trotyl.
[b] In kcal mol^{-1}.
[c] The pre-exponential factor A is expressed in s^{-1}.
[d] At T = m.p. − 20 °C.
[e] Data of this work.

transition state,[27] *i.e.*, approximately by 0.2 Å. Extension of the cell by 0.2 Å results in weakening of intermolecular interactions and allows atoms of the molecule to converge freely, forming cyclic transition states. Thus, the $\Delta V^{\neq}_{s}$ value depends slightly on the reaction type and on the value and sign of the true activation volume.

The calculation of REL by Eq. (1), assuming that the cell volume is $V_0/(6.02 \cdot 10^{23})$ and its expansion is 0.2 Å, gives values that often coincide by an order of magnitude with the experimental values. For compounds **1**, **3**, **5**, **13**, **14**, **16**, **17**, **19**, **21**, and **22**, *i.e.*, when kinetic data for calculations were available, the calculated REL value was 8, 3, 100, 386, 10, 453, 31, 250, 400, and 3040, respectively. The highest deviations from the experimental values (see Table 1) are observed for molecules with a long chain. In this case, local motions of, not the whole molecule, but only of its fragments containing the reaction center have a substantial effect on the REL values.

The absence of a method of exact estimation of $\Delta V^{\neq}_{s}$ restricts the possibility of using Eq. (1) for practical calculations, although there is some doubt that the macroscopic model adequately reflects the real pattern. Equation (1) is important because it predicts, first, low REL, *i.e.*, the possibility of the reaction occurring purely in the bulk of the sample, and, second, the dependence of REL on the elastic properties of the crystal. Both predictions agree with the experimental data. Only the nonconstant character of the $\Delta V^{\neq}_{s}$ values disturbs the linearity of the dependence of REL on $1/(\beta V_0)$, which is demonstrated by the data in Table 1.

The dependence of REL on the melting point of the substance, which is also a good measure of forces of intermolecular interaction, especially for short-chain molecules,[28] is presented in Fig. 1. This dependence represents the curve with saturation. All the experimental points are located inside the interval limited by two dashed lines in Fig. 1, and points for substances with a high molecular weight lie closer to the lower boundary in Fig. 1. For compounds with m.p. <150 °C, the REL values are mainly lower than 100 and, hence, we may consider that the reaction in the volume predominates in this case as well.

For the substances with higher melting points, the reaction in the volume is changed by the decomposition on crystal defects, which, as shown above, can limit

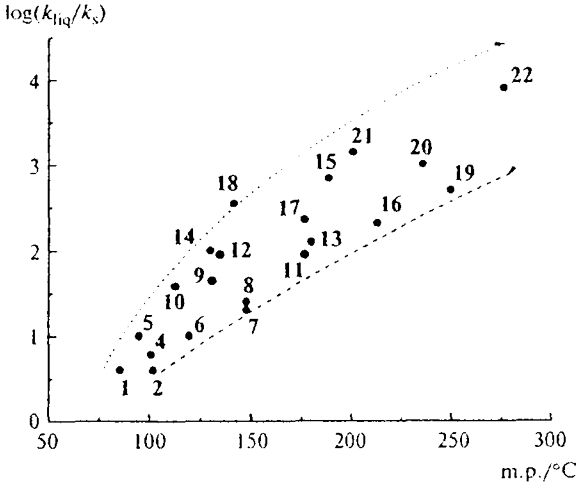


Fig. 1. Dependence of the retardation effect of the crystalline lattice on the melting point of the substance. Numeration of points corresponds to the numbers of compounds in Table 1.

REL by the interval of 10^2—10^4, which is experimentally observed. Compound **3** (it is not shown in Fig. 1), which represents plastic crystals, falls out of the general dependence. For long-chain compounds **6** and **7**, according to the absolute REL value, decomposition in the bulk is also possible, despite sufficiently high melting points.

The experimentally determined ΔE value is low and does not usually exceed the measurement error, which is 3—4 kcal mol^{-1}. Therefore, it is difficult to use this value to estimate REL at different temperatures and to separate volume and local reactions. The latter can be performed using absolute values of REL or melting points of the substances. The experimental data in Table 1 agree with the macroscopic model and suggest that for organic compounds with m.p. ~100 °C the irreversible monomolecular reaction occurs in the ideal part of the crystal lattice with REL < 10, and at m.p. >200 °C the reaction proceeds on defects only. Within the interval m.p. = 150—200 °C, REL is equal to 10^2—10^3, and the indicated reactions compete with each other. These conclusions give a clear semi-quantitative pattern of changing REL; however, they need further verification. It is necessary to obtain new data on REL, including those for reactions with a negative activation volume, as well as to identify directly localized reactions and to compare the decomposition rate with the defectiveness of the crystal.

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