



## Prognosis of Energetic Compounds Stability in Solid Phase

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**Abstract:** Results of the analysis and specification of phenomenological models of the monomolecular reactions running homogeneously in volume of undisturbed crystal lattice or localized on its defects are presented. It is shown, that within the limits of these models it is possible to calculate with satisfactory accuracy the ratio of rate constants in liquid and solid phases  $K_T = k_{liq}/k_{sol}$ , and thus on known  $k_{liq}$  to predict  $k_{sol}$ , describing stability of substance.

**Keywords:** monomolecular reactions, crystal state, retarding

### Introduction

There is a big group of the technologically important substances and materials for which the opportunity of a preliminary estimation of stability has an actual meaning. The energetic condensed systems (explosives, gun powders, propellant components, including ecologically pure oxidizers), gas forming compositions, the medicinal preparations, functionally substituted polymers, initiators and inhibitors of chain reactions, curing agents of polymeric system concern to them.

Such prognosis gives essential advantage including economic one:

- At a stage of planning of synthesis of new target compounds,
- At a stage of drawing up of compounding compositions with required stability,
- For an estimation of safe modes of storage and processing of new materials.

Necessity in prognosis spring up more often at investigation of energetic materials. A quantitative measure of stability is the rate constant of the first noncatalytic stage of decomposition which in overwhelming majority of cases represents monomolecular process. Therefore the prognosis of stability can be constructed on the basis of the general theory of monomolecular reactions. This theory is very well developed for gas and liquid conditions, but not for solid state reactions. Therefore naturally to establish quantitative relation between rate constants in liquid and solid phases,  $k_{\text{liq}}$  and  $k_{\text{sol}}$  is represented for a long time, and to use it for a finding  $k_{\text{sol}}$  on known  $k_{\text{liq}}$ . The greatest successes in calculation of ratio  $K_T = k_{\text{liq}}/k_{\text{sol}}$ , which can be named a retarding factor of reaction in a solid phase (as always  $K_T > 1$ ), are achieved within the limits of models of phenomenological type, the analysis, specification and possibility of practical use are considered in the given work.





## Results and Discussion

**Liquid condition.** For a liquid condition (melt or solution) the problem of prognosis of stability of organic compounds as a whole is substantially already solved. This prognosis is based on a huge experimental material on kinetic studying reactions of thermal transformation practically all classes of compounds (over 1000 reactions with known parameters of Arrhenius equation) to which not less extensive data from adjacent areas – on bond dissociation energies of compounds and thermal effects of processes are added, effective RRKM method of calculation of preexponential factor and quantum chemical methods of calculation of heats of formation of free radicals and estimations of activation energy. The obtained help material allows to estimate a stability level of a new substance using a method of analogies and the structural formula of compound with a sufficient error for practice, or to classify substances as certainly stable or, on the contrary, low stable for application in concrete conditions. All this system of the prognosis is specified and extends continuously owing to involving in it new types of structures or new classes of compounds, especially having practical importance. In Table 1, for an example, the comparative estimation of stability in a liquid condition of the basic classes of energetic-intensive compounds is presented. Introduction of substituents leads, as a rule, to down of stability of base structural group. More details on influence of a structure on stability of compounds of various types can be found in the works quoted in Table 1.

**Solid phase.** In comparison with a liquid for which there is a full arsenal of methods and techniques for an establishment of the mechanism of reaction and separation of monomolecular stages from complex process, the experimental

material on kinetic research of monomolecular reactions in a solid phase looks much more poorly. Being limited by the temperature of fusion, these reactions run slowly and, as a rule, become complicated by a lot of side factors which account demands carrying out special researches. For example, reliable values of rate constants in a solid condition are received only for few compounds. There is, however, an opportunity to solve all problems of the solid state reactions connected with a finding and prognostication of rates, by means of theoretically calculated retarding factor  $K_T = k_{liq}/k_{sol}$ .

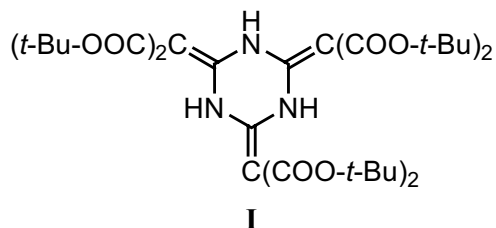
**Table 1.** Characteristic values of the kinetic parameters of decomposition of groups X in the compounds R—X or R-X-R, where R = Et

Group X	E kJ mol <sup>-1</sup>	logA [s <sup>-1</sup> ]	150 °C		Ref.
			k s <sup>-1</sup>	ω <sub>rel</sub>	
-CNF <sub>2</sub> ) <sub>2</sub> -	199	16.0	2.9E-9	1.0	[1]
-C(NO <sub>2</sub> )F	199	17.0	2.9E-8	10	[1]
-C(NO <sub>2</sub> ) <sub>2</sub> —	199	17.1	3.7E-8	13	[1]
-N(NO <sub>2</sub> )- (planar)	172	14.5	2.1E-7	72	[2]
-ONO <sub>2</sub>	168	14.7	1.0E-6	2.4E3	[3]
-CH <sub>3</sub> N <sub>3</sub>	163	14.4	1.8E-6°	630	[4]
-C(NO <sub>2</sub> ) <sub>3</sub>	180	17.2	1.0E-5	3.4E3	[1]
-NF <sub>2</sub> <sup>b</sup> (shielded)	126	9.0	3.2E-7	110	[1]
-N(NO <sub>2</sub> )- <sup>c</sup> (pyramidal)	159	14.5	7.4E-6	2.5E3	[2]
-C(NO <sub>2</sub> ) <sub>2</sub> NF <sub>2</sub>	168	16.0	2.2E-5	7.5E3	[5]
—C(NO <sub>2</sub> ) <sub>2</sub> N <sub>3</sub>	163	15.5	2.2E-5	8.0E3	[1]
-NF <sub>2</sub> <sup>d</sup> (open)	111	8.3	4.1E-6	1.4E3	[1]
-NHNO <sub>2</sub>	111	10.1	2.6E-4	1E5	[6]
-N(NO <sub>2</sub> )F	126	15.0	0.3	1E9	[1]
-N(NO <sub>2</sub> ) <sub>2</sub>	121	15.0	1.0	3E8	[7]
	193	14.5	6.0E-11	0.01	[1]
	188	14.8	3.2E-9	1.1	[1]
	197	14.9	4.2E-9	1.4	[1]
	176	15.0	2.6E-7	70	[1]

**Homogeneous reaction in volume of a crystal.** For a case of volumetric reaction within the limits of a method of a transitive condition in representation of a crystal as isotropic elastic continuum [8] for  $K_T$  formula (1) is received:

$$RT \ln K_T = \Delta E = (\Delta V_{\text{sol}}^\ddagger)^2 / 2\beta V_M \quad (1)$$

Where  $\Delta E$  – a difference activation energy  $E_{\text{sol}} - E_{\text{liq}}$ ,  $\beta$  – factor of isothermal compressibility,  $V_M = M/\rho$  – molar volume of substance,  $\Delta V_{\text{sol}}^\ddagger$  – the additional volume of activation in a solid phase which is treated, how an increment of volume of the cavity occupied by a molecule, till the sizes of this cavity in which a breakage of all intermolecular bonds occurs and a molecule receives the same free rotational-vibrational movement, as in a liquid. In the expanded cavity reaction runs with a rate constant  $k_{\text{liq}}$ , and the retarding effect of a solid phase is determined by work  $\Delta E$ , a cavity spent for elastic deformation. Such treatment  $\Delta V_{\text{sol}}^\ddagger$  means independence  $K_T$  from microscopic details of a structure of a crystal, and also of volumetric characteristics of the reaction. At any size and a sign on true volume of activation  $\Delta V_{\text{liq}}^\ddagger$  reaction rate in a solid phase should decrease. This conclusion following from model, has been confirmed experimentally [9] by direct measurement of  $\Delta V_{\text{liq}}^\ddagger$  and  $K_T$  values for olefin elimination reaction from ester **I**. This ester is the only compound from an ester class which thermal decomposition can be observed in a solid condition.



It has appeared, that in chloroform solutions this reaction has negative volume of activation  $\Delta V_{\text{liq}}^\ddagger = -13.7$  ccm/mole and at the same time is retarded by a solid phase,  $K_T = 7$  at 150 °C. Other examples on this theme can be malonic and oxalic acids. Their decomposition rate also decreases at transition in a solid condition (see Table 2), and should have negative value since reactions go through a cyclic transitive condition. However, direct measurements  $\Delta V_{\text{liq}}^\ddagger$  for these compounds were not made.

**$\Delta V_{\text{liq}}^\ddagger$  calculation.** Thus, the main condition of reaction proceeding in a solid phase is unlocking mobility of molecules and consequently the parameter  $\Delta V_{\text{sol}}^\ddagger$  can be calculated through cavity volume in which the molecule makes

free three-dimensional rotation. Such cavity should have the form close to spherical. Therefore an estimation  $\Delta V_{\text{sol}}^{\ddagger}$  it is spent as follows. The molar volume of substance reduced by 25% (that corresponds to free volume in a crystal at dense packing of molecules), we divide into number of molecules and we find the volume occupied by one molecule. Using sphere form for this volume, we calculate radius  $r$  and increase it on  $\Delta r$  in order to find required enlargement of volume  $\Delta V_{\text{sol}}^{\ddagger}$  of a molecule.  $\Delta r$ , having key value for calculation, it is possible to calculate by reverse calculation from  $\Delta V_{\text{sol}}^{\ddagger}$  using the formula (1), using reliable experimental data on  $K_T$  which are available for reactions of thermal decomposition of some explosives. For hexanitroethane and tetryl (see Table 2) values  $K_T$  are equal 7 [10] and 50-100 [11], the factor of compressibility is equal accordingly  $5 \cdot 10^{-10}$  and  $1.0 \cdot 10^{-10} \text{ Pa}^{-1}$ , whence we find  $\Delta r = 0.22 \text{ \AA}$  for hexanitroethane and  $0.21\text{-}0.23 \text{ \AA}$  for tetryl. Decomposition of hexanitroethane, having plastic crystals, undoubtedly, runs in volume of a lattice, reaction on surface and defects is more probable for tetryl. In this case observable  $K_T$  should approximate to a limit of retarding in volume and consequently the  $\Delta r$  value should appear underestimated. In the independent way, from the analysis of an increment of activation energy  $\Delta E$  of volumetric reactions of reorientation hexafluorine complex  $\text{KPF}_6$  and  $\text{KIrF}_6$  in work [12] within the limits of the dynamic theory reorientation it is found  $\Delta r \approx 0.2 \text{ \AA}$ . The expanded cavity should contain the activated complex of bond dissociation reactions, having positive volume of activation. At calculation by method RRKM preexponential factor the decomposition *t*-butoxy radical is found [13], that bond C-C in this radical, having dissociation energy about  $62.7 \text{ kJ}\cdot\text{mole}^{-1}$ , is elongated at breakage on  $0.3 \text{ \AA}$ . From activation volume  $\Delta V_{\text{liq}}^{\ddagger}$  calculations it is found [14], that the length of O-O bond ( $125.4 \text{ kJ}\cdot\text{mole}^{-1}$ ) increases on  $0.4 \text{ \AA}$  at decomposition of benzoyl peroxide. It is possible to suppose, that for bonds with average dissociation energy ( $170\text{-}250 \text{ kJ}\cdot\text{mole}^{-1}$ ), such as C-N, N-N, N-O, O-O, an increment of length in transition state of semihard type will reach  $0.5 \text{ \AA}$ . By that radius of a cavity will increase on  $0.25 \text{ \AA}$ . Thus, different estimations give enough narrow  $0.2\text{-}0.25 \text{ \AA}$  interval of  $\Delta r$  values. At such expansion of a cavity the intermolecular bonds restricting rotation of a molecule as of whole will be destroyed as breakage of these weak bonds occurs at 3-4% increasing in distance between molecules. For carrying out the further calculations we have chosen a constant  $\Delta r = 0.23 \text{ \AA}$ . The maximal possible deviation thus equal  $\pm 0.03 \text{ \AA}$ , that will give the maximal error in  $K_T$  value at  $150 \text{ }^\circ\text{C}$  in 3-4 times at  $V_M = 100 \text{ ccm}\cdot\text{mole}^{-1}$  and 4-5 times at  $V_M = 500 \text{ ccm}\cdot\text{mole}^{-1}$ .

**$\beta$  Calculation.** For calculations  $K_T$  under the formula (1) it is necessary to have data on factor of compressibility. In view of extreme scantiness of

experimental data for the HCNO-compounds having density  $> 1$  g/ccm, a unique accessible opportunity of a finding calculation under the formula  $\beta = 1/C_0^2\rho$ , connecting compressibility with a sound velocity. In turn,  $C_0$  is possible to calculate on semiempirical Rao formula (see [8]), considering a chemical structure of substance,  $C_0^{1/3}M/\rho = \sum z_i B_i$ . Here  $z_i$  – is a number of chemical bonds of the given kind, and  $B_i$  – increments these bonds. The list of known increments, cited in work [15], includes following bonds: N-H 90; C-H 95.2; C-C 4.25; C-O 34.5; C-O (ether) 44.5; C=C 129.0; C=O 186.0; C-N 20.7; O-H 99.0; C-NO<sub>2</sub> 302.5; O-NO<sub>2</sub> 360.0; N-NO<sub>2</sub> 330.0; C-C (aromatic) 67.2. This set of increments does not allow to calculate  $C_0$  for a lot of nitrogen compounds, in particular, for nitriles, azides and azo compounds. Therefore, using laws of change increments  $B_i$  in a number of ordinary and double bonds C-C, C-N, C-O, C=C, C=O, we have deduced approached values  $B_i$  for following bonds: N-N 15; N=N 150; C=N 170; C≡N 250; C-N<sub>3</sub> 250. At presence in a multinuclear molecule of single bonds of such type the error in the calculation, connected with increment inexactness, will be insignificant. Change  $C_0$  on 10% leads to change  $K_T$  on 30%. Increments  $B_i$  for calculation of sound velocity of a under Rao scheme are found for a liquid condition of substance. The increase  $C_0$  at transition in a solid phase with good accuracy is considered at calculation through change of density. As shown in [15] on separate examples, the rates of a sound calculated for solid substances under Rao scheme and found experimentally, coincide within the accuracy limits of experiment. The accuracy requirement of measurement of density is more essential. In view of very strong  $K_T$  dependence from  $r$ , this value should be known about accuracy not below 2%.

**Relation additional activation parameters  $\Delta E$  and  $\Delta V_{sol}^\ddagger$  with characteristics of fusion of substance.** The estimation  $\Delta V_{sol}^\ddagger$  in the way described above shows, that for the majority of real explosives  $\Delta V_{sol}^\ddagger$  is connected with  $V_M$  by relation  $\Delta V_{sol}^\ddagger = (0.1-0.2) \cdot V_M$ . On the same value (10-20%) there is an increase in volume at fusion of organic substances. This fact shows conformity of model of free volume to terms “the fused cavity” or “virtual fusion” which are sometimes used for treatment of physical and chemical processes in a solid phase [16].

Still in 1921 Hinshelwood has assumed, that the degree of slowing-down of decomposition reaction of tetryl in a solid phase is defined by the latent heat of fusion of substance  $Q_{fus}$  [11]. Having an opportunity of calculation  $\Delta E$  on the equation (1), we have lead comparison  $\Delta E$  with  $Q_{fus}$ . At calculation  $\Delta E$  those compounds for which the density is certain with accuracy of 1-2% are used only. Generally the ratio  $\delta = \Delta E/Q_{fus}$  varies over a wide range, from 0.1 up to 0.9. However for big group HCNO- or HCNOF-compounds the narrow interval of change is observed, and

$$\Delta E = (0.6 \pm 0.1) \cdot Q_{\text{fus}} . \quad (2)$$

This ratio can be used for the fast approached estimation  $\Delta E$  and  $K_T$ , and also for a finding the reverse calculation on the equation (1) values  $\beta$  and then increments  $B_i$  in formula Rao for new structural elements.

**Estimation of limits of  $K_T$  change for homogeneous reaction in volume.** At combinations of parameters of  $M$ ,  $\rho$  and  $\beta$ , meeting in real molecules,  $\Delta E$  changes from 2.1 up to 20.9 kJ/mole, an interval of change  $K_T$  at 150 °C is about 2-500. The maximal error of  $K_T$  evaluation does not exceed 5 times. It is natural, that the same result, but in more evident form, the formula (2) gives. Heats of fusion  $Q_{\text{fus}}$  are equal 2.1-4.2 kJ/mole in most cases of organic molecules. According to (2),  $\Delta E$  changes will be made with 5.0-25.1 kJ/mole and  $K_T$  at 150-200 °C can change from 4 up to 1000. In these limits, experimental data on  $K_T$  range all (see Table 2). This fact confirms adequacy of model of volumetric reactions and an opportunity of quantitative estimations  $K_T$ , despite of the approaches, in the formula (1) and  $\Delta V_{\text{sol}}^\ddagger$  calculations.

**The reactions localized on defects of a crystal lattice.** According to the representations developed originally by the S. Bon [17] still in 1951, for the description of reactions on defects the model which is based following postulates can be formulated:

1. The basic type of defects in molecular crystals is the rows of dislocations forming borders of crystal grain (CG). Reaction goes on a surface of CG.
2. All molecules on a surface of CG have identical reactionary ability.
3. The increment of activation energy  $\Delta E = E_{\text{sol}} - E_{\text{liq}} = 0$ , therefore decrease in reaction rate in a solid phase is connected, basically, with formal reduction of a preexponent because of reduction of number reactionary molecules.

At performance of these conditions the factor of retarding of reaction in solid phase  $K_T$  will vary in inverse ratio to a part of the molecules located on a surface of CG, and absolute value  $K_T$  for CG of the cubic form is equal

$$K_T = L/6l \quad (3)$$

where  $L$  and  $l$  - the linear sizes of CG and a molecule respectively.

The first postulate follows from independence of reaction rates of the crystal sizes. This fact is noted by Bon [10], however literature data on this question are poor and contradictory. Therefore we have studied influence of the sizes of crystals on decomposition rate of three nitramines – trimethylene trinitramine, octogen and ketohexogen (K-6). It is found, that the initial decomposition rate

$\omega_{ini}$ , measured when all side factors masking solid state process (see below) were considered, does not change at crushing monocrystals from 2 up to 0.05 mm. The surface area of particles thus increases in 40 times; the internal surface practically does not change. At the same time rate depends on a mode of crystallization from a solution, as the sizes of CG, apparently, vary. So, for example, octogen particles in the size 0.02 mm received in conditions supersaturating (strong dilution of acetone solution by water) and at slow crystallization from viscous solvent, differ on  $\omega_{ini}$  in 2 times. About the same difference it is observed for hexogen and ketohexogen samples, using slow and fast crystallization from solutions.

As movement of molecules on a surface is hindered, the requirement of creation of additional activation volume  $\Delta V_{sol}^\ddagger$ , following on model of the fused cavity, stands also for the localized reactions. However  $\Delta E$  on a surface of CG or in amorphous substance can be, at least, in 2 times below, than in volume, i.e. generally  $\Delta E$  may about 7.5-12.5 kJ/mole. Such difference between  $E_{sol}$  and  $E_{liq}$  very difficult to observe experimentally and consequently it is possible to conclude, that within the limits of experiment accuracy the third Bon postulate will be satisfied always. This conclusion proves to be true on experience. Examples can be found in works [1, 2].

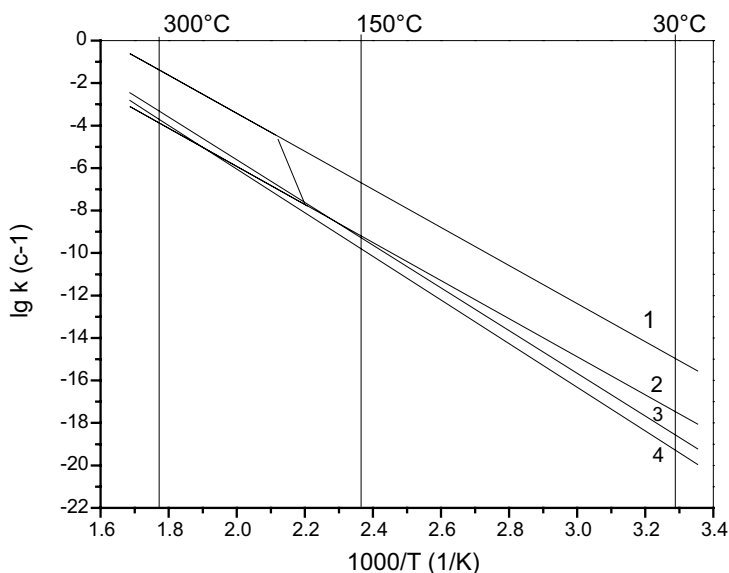
Because of absence of data on  $L$  for concrete compounds and samples it is impossible to estimate absolute  $K_T$  values under the formula (2) and thus to check up the second postulate of the model, concerning uniformity of CG surface. It is possible, that the hindrance of reaction in places of CG contacts will be compensated by increase (in comparison with volume) to reactivity of near-surface layer and amorphous substance. Irrespective of a condition 2 realization,  $K_T$  on defects should depend linearly from  $L$ .

Absence of data on  $L$  is connected with methodical difficulties of measurement of this size. The accessible method of X-ray powder diffraction allows to find the sizes of the fine CG having  $l < 100$  nm. Larger CG which prevail in molecular crystals, do not give line broadening on powder pattern, but only at  $L > 100$  nm normal Laue patterns are obtained, allowing to determine structure of a crystal. Using these two features it is possible to establish easily conditional limit,  $L = 100$  nm dividing CG on small and large. In view of this limit and accepting a postulate 2, it is possible to make general estimations useful to the prognosis. At extreme values  $L = 10-10^3$  nm and typical values  $l = 0.5-1.0$  nm  $K_T$  on defects can vary from units up to hundreds, i.e.  $K_T$  for the localized reactions should lay inside of interval  $K_T$  of volumetric reactions. For typical cases of real molecules at  $L = 100$  nm even if  $\Delta E \neq 0$ ,  $K_T$  value will not exceed 50, accordingly for maximum large CG ( $L = 1000$  nm) it is possible to expect increase  $K_T$  up to 500 times. Thus, threshold value  $L = 100$  nm, which has



arisen for the methodical reasons for division of samples into two groups – small and large CG, it is possible to use for separating macro samples with an expected insignificant or expected high degree of stabilization in a solid phase.

**Limits of  $K_T$  change.** Near outside values of  $K_T$  are obtained for volumetric reaction at  $\Delta E$  20-25 kJ/mole and for reaction, localized on defects, at  $L = 1$  micron and  $l = 5 \text{ \AA}$ . In Figure 1 temperature dependence of a rate constant  $k_{sol}$  for these cases by example of simulated reaction having parameters of liquid phase decomposition  $E = 171.4 \text{ kJ mole}^{-1}$  and  $\lg A = 14.5 \text{ (s}^{-1}\text{)}$ .



**Figure 1.** Comparison of retarding effect of a solid phase for the reactions running in volume of not disturbed crystal and reactions, localized on defects. 1 – a liquid phase, simulated reaction,  $E = 171.4 \text{ kJ mole}^{-1}$ ,  $\lg A = 14.5 \text{ (c}^{-1}\text{)}$ . 2 – a solid phase, reaction on defects.  $L = 1$  microns,  $l = 5 \text{ \AA}$ .  $E = 171.4 \text{ kJ mole}^{-1}$ ,  $\lg A = 12.0 \text{ (c}^{-1}\text{)}$ . 3 – Reaction in volume for  $E = 192.3 \text{ kJ/mole}$  ( $\Delta E = 20.9 \text{ kJ mole}^{-1}$ ),  $\lg A = 14.5 \text{ (c}^{-1}\text{)}$ . 4 – Reaction in volume for  $E = 196.5 \text{ kJ mole}^{-1}$  ( $\Delta E = 25.1 \text{ kJ mole}^{-1}$ ),  $\lg A = 14.5 \text{ (c}^{-1}\text{)}$ .

At room temperature outside  $K_T$  values of volumetric reaction exceed 1000 and never reach this value due to competition with reaction localized on defects, for which at all temperatures  $K_T$  is near 300. At the higher temperatures the rates ratio varies. At 250 °C  $K_T$  in volume becomes less than on a surface of large CG. At temperature near 150 °C lines 4 (volumetric reaction  $\Delta E = 20.1 \text{ kJ/mol}$ )

and 2 (reaction on defects) are crossed. At approach to melting point (m.p. about 200 °C) because of increasing of compressibility Arrhenius dependence for  $k_{\text{sol}}$  of volumetric and local reactions is broken, and  $k_{\text{sol}}$  draws near to  $k_{\text{liq}}$ . The deviation from linear dependence  $k_{\text{sol}}$  from  $1/T$  begins 10-20 °C below m.p. At  $\Delta E$  and  $L$  decreasing  $\lg k_{\text{sol}} = f(1/T)$  lines are displaced upwards and various variants of their relative positioning and crossing are possible.

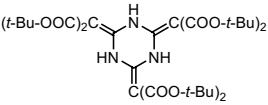
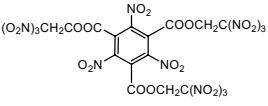
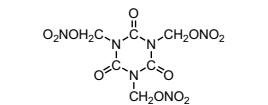
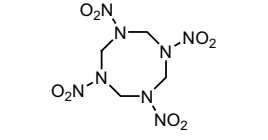
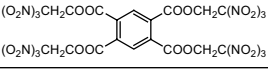
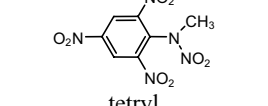
**Experimental  $K_T$  definition.** Decomposition reactions in a solid phase are complicated due to a lot of by-effects which are necessary to consider for determining correct  $k_{\text{sol}}$  values. Below the major factors influencing decomposition rate of solid substance, and ways of their elimination are listed. The analysis of literature data shows, that conditions of determination of correct values  $k_{\text{sol}}$  are satisfied not always. Therefore we execute revision and additional  $K_T$  definition for several compounds, including not explosives. As a result representative list of compounds for experimental testing of theoretical models was formed.

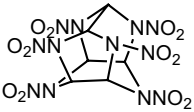
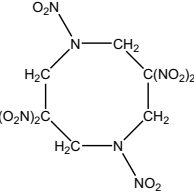
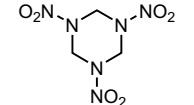
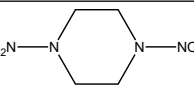
Factors, have an influence on kinetics solid-state reaction	Clearing methods by-factors
Submelting effects	Investigation of reaction 20 °C below m.p.
Vaporization and vapours decomposition	Investigation of reaction under large degree of reactor filling by compound (0.1-0.3 g $\text{ccm}^{-1}$ ), so vapour part below 0.1%.
Formation of liquid phase, and dilution of substance in products	Measuring of rate at initial (linear) parts of kinetic curves (usually below 1.0% conversion)
Sorption of solvent, water and air (at manometer measurements)	Vacuum desiccation above experimental temperature and glass capsulation without air

**Comparison of the theory with experiment.** In Table 2 comparison of  $K_T$  values calculated on the equation (1), with experimental data is presented. Comparison is executed for all substances at which it has appeared possible to calculate the parameters entering into the formula (1), and having available correct  $k_{\text{sol}}$ . These substances – representatives of different classes of compounds, have the greatest possible difference on such parameters, as  $M$  (100-900  $\text{g mole}^{-1}$ ),  $\rho$  (1.1-2.0  $\text{g ccm}^{-1}$ ) and  $\beta$  (0.5-5.0)  $10^{-10} \text{ Pa}^{-1}$ . For compounds 1-4, 6,7 resulted in Table 2, calculated  $K_T$  values lay considerably below 100 and will be correlated with experimental data. CG of these substances, by the X-ray analysis, have big sizes, reaction at dislocations runs slowly and consequently it is possible to consider, that in these cases the processes going homogeneously in all volume

of a crystal are observed. In compounds **8-19** calculated  $K_T$  are close to 100 or in some times more than 100 and in compounds with significant retarding in volume it is possible to expect display the dislocation mechanism of decomposition. This mechanism, undoubtedly, is carried out at compounds **8, 10** at which experimental  $K_T$  much less calculated, and the sizes of CG are small. In all other cases greater calculated  $K_T$  are combined with greater sizes of CG, and again distinction between experimental and calculated sizes is insignificant. This result sustains a conclusion that calculated  $K_T$  always gives the top limit of the experimental retarding, and this limit is realized, if the CG sizes are great.

**Table 2.** Calculated and experimental  $K_T$  values for different compounds

No.	Compound	M, G mole <sup>-1</sup>	$\rho$ , g ccm <sup>-1</sup>	$T_{fus}$ , °C	$10^{10}\beta$ , Pa <sup>-1</sup>	$\Delta E$ , kJ mole <sup>-1</sup>	$K_T$ calc	$K_T$ exp	CG sizes
1	(NO <sub>2</sub> ) <sub>3</sub> CC(NO <sub>2</sub> ) <sub>3</sub>	300	1.85	150.0	2.715	6.7	8	6 [10]	Large
2	HOOC-CH <sub>2</sub> -COOH	104	1.63	135	2.003	7.1	9	40[17]	Large
3		723	1.15	200	2.625	10.5	17	10 [9]	Large
4	(CH <sub>3</sub> ) <sub>2</sub> (CN)CN=NC(N)(CH <sub>3</sub> ) <sub>2</sub>	164	1.11	97	2.268	7.9	20	50	Large
5		834	1.78	176	2.256	11.3	24	8 [18]	Small
6	<i>m</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> C(O)N <sub>3</sub>	192	1.547	77	1.864	9.2	29	36	Large
7	C[(OCH <sub>2</sub> C(NO <sub>2</sub> ) <sub>3</sub> ) <sub>3</sub> ] <sub>4</sub>	732	1.84	162	2.038	11.7	32	20	Large
8		354	1.77	148	1.382	14.2	73	10 [19]	Small
9		296	1.78	281	0.584	20.3	97	90 [20, 21]	Large
10		906	1.82	171	1.593	16.3	102	5 [18]	Small
11		287	1.73	129	1.263	14.6	106	50-100 [11]	Large

No.	Compound	M, G mole <sup>-1</sup>	$\rho$ , g ccm <sup>-1</sup>	T <sub>fus</sub> , °C	10 <sup>10</sup> · $\beta$ , Pa <sup>-1</sup>	$\Delta E$ , kJ mole <sup>-1</sup>	K <sub>T</sub> calc	K <sub>T</sub> exp	CG sizes
12		438	2.04	250	0.971	20.9	144	100 [22]	Large
13	HOOC <sup>+</sup> COOH	90	1.9	189	0.698	18.8	167	122	Large
14		384	1.891	250.0	2.204	22.2	200	500 [10]	Large
15		222	1.816	201	0.804	21.3	230	300 [23, 24]	Large
16	O <sub>2</sub> NN[CH <sub>2</sub> C(NO <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub> ] <sub>2</sub>	326	1.721	185.0	0.978	20.1	236	230 [10]	Large
17	C(CH <sub>2</sub> ONO <sub>2</sub> ) <sub>4</sub>	316	1.778	143	1.035	18.4	271	100 [25]	Large
18		176	1.64	195	0.777	21.3	299	200	Large
19	[CH <sub>2</sub> N(NO <sub>2</sub> )CH <sub>2</sub> C(NO <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub>	476	1.88	179.2	1.026	20.9	314	92 [10]	Large

## Conclusions

Reduction of rate of monomolecular reactions and, accordingly, increase of stability of substance at transition from a liquid condition in solid one is determined by heat of fusion of substance  $Q_{\text{fus}}$  and the linear sizes  $L$  of CG. These sizes cannot be calculated in advance, however methods of preparation of crystals with big CG and the tendency of change  $Q_{\text{fus}}$  depending on compound structure are known. The greatest possible increase of stability of organic compounds in a solid phase is equal about 300 times and is observed at  $Q_{\text{fus}} \approx 40$  kJ mole<sup>-1</sup> and  $L = 1$  microns. The limit of increase of stability for each concrete compound can be estimated with the maximal error which is not exceeding 5 times, under the formula of model of free volume for all cases when the X-ray density of substance is known and the factor of volumetric compression can be by calculated.

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