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Crystal defects and stability of RDX

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NQR studies demonstrated that structure imperfection of RDX crystals is affected by impurities, the particle size, and the modes of crystallization and pressing of the sample. The initial rate of RDX decomposition depends on the same factors. In pure samples, the rate varies 1.5—2 times and is proportional to imperfection. In spite of crystal destruction, the rate of thermal decomposition in pressed samples decreases due, apparently, to strengthening of the cell effect.

Key words: RDX, thermal decomposition, solid phase, crystal defects.

In studies of the general regularities of solid-phase monomolecular reactions, it has been established[1] that thermal decomposition of organic compounds with m.p. >150 °C proceeds at solid-phase defects and at the surface rather than in the bulk of the ideal lattice. These rather high-melting compounds possess small compressibility, which efficiently hinders the formation of an activated reaction complex. Inhibition in the solid phase, *i.e.*, the ratios of the decomposition constants $k_{\text{liq}}/k_{\text{sol}}$ for these compounds are higher than 100 and depend on the prehistory of the preparation of the sample. Based on abundant data for inorganic compounds,[2] it is commonly assumed that the crystal imperfection and the constant k_{sol} depend on the particle size, the mode of crystallization, and impurities. The effects of these factors on the reactions in molecular crystals of organic compounds have not been adequately studied.[3—5] Previously, it has been demonstrated[3] that the rate of RDX decomposition depends only slightly on the particle size, whereas the stability of HMX increases as the particle size decreases. Grinding of crystals of aromatic compounds also exerts only a slight effect on the stability of these compounds.[4] It is difficult to determine the true values of k_{sol} due to side processes, such as thawing and decomposition through the gas phase as well as decomposition of unstable impurities.[5] Previously,[6] it has been shown that decomposition of RDX crystals was accompanied by the appearance of stresses as well as by generation and motion of dislocations. However, data on a quantitative correlation of the stability with the initial crystal imperfection are lacking. The dependence of defects and the decomposition rate on such standard operation as pressing is also unknown.

In the present work, we studied the role of the above-mentioned factors in solid-phase reactions using thermal decomposition of RDX (cyclotrimethylenetrinitramine) as an example. The latter is a typical compound characterized by the localized mechanism of decomposition in the solid phase.[1] The RDX molecule contains three trivalent nitrogen atoms (^{14}N nuclei possess the quadrupole moment), which made it possible to control the integrated crystal imperfection in various RDX samples using the sensitive nondestructive NQR technique. The NQR flaw detection is a rather new method, and its application to samples of various origin is of interest by itself. In addition to the NQR data, the average sizes of crystallites in powdered samples were determined by the X-ray powder diffraction method.

Experimental

Studies were performed with the use of five RDX samples: *1*, technical product; *2*, technical RDX precipitated with acetone from water at ~20 °C (rapid crystallization); *3* and *4*, samples prepared by recrystallization from hot acetone upon slow (12 h) cooling; and *5*, crystals isolated from the mother liquor remained after complete evaporation of acetone from the solution used for the preparation of sample *3*. The particle sizes of samples *1* and *2* were 0.08—0.12 mm and those of samples *3—5* were 3—5 mm. To examine the effects of grinding and pressing, samples *3* and *4* were ground in a mortar to the particle size of 0.1 mm and then the fine dispersed fraction of samples *3* and *2* was pressed at a pressure of 0.5—2.5 kbar.

The thermal stability was determined from the initial rate of decomposition at 160 °C. No acceleration of the process was observed at this temperature during 6 h. The total imperfection (relative number of molecules located in disordered regions of the crystal lattice) was determined based on broadening of the NQR signal from the amine N atom at 3440 kHz. The NQR studies of the RDX samples were carried out at ~20 °C on a special pulse instrument[7] developed as an attachment for a pulse RI2303 NQR spectrometer; the operating frequency for protons was 60 MHz. The line widths in the pulse NQR spectra were measured according to a standard procedure (at the half-height) in units of frequency. The average size of the crystallites (L) was determined (with an accuracy of 1—2 mm) by the X-ray powder diffraction method[8] based on broadening of the reflection [131] with the diffraction angle θ = 12.68°. This line

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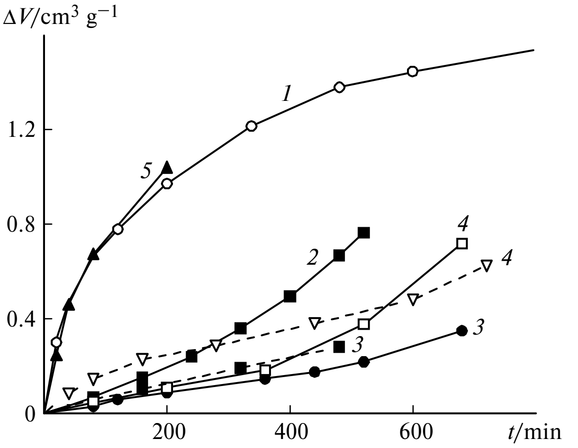

Fig. 1. Initial regions of the kinetic curves of decomposition of various RDX samples (*1—5* are the numbers of the samples; the ground samples are indicated by dashed lines).

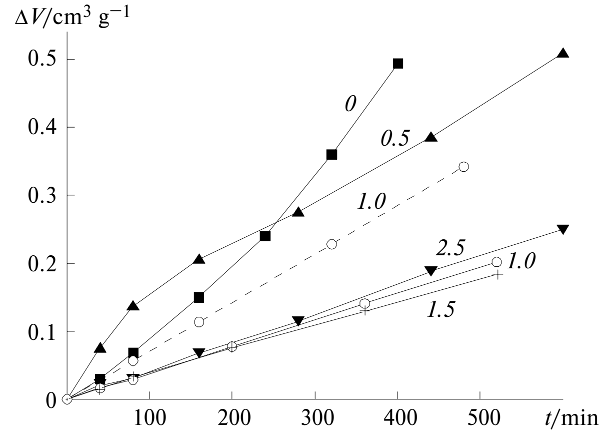

Fig. 2. Effect of pressing on decomposition of sample *2* (the pressing pressure is denoted by figures (in kbar); the curve for the sample ground after pressing to the size of 0.3 mm is indicated by a dashed line).

is located rather far from the adjacent reflections and is not distorted by overlapping.

Results and Discussion

Examples of kinetic curves for the initial stages of gas evolution at 160 °C for the starting, ground, and pressed samples are shown in Figs. 1 and 2. The initial rates of gas evolution, the half-widths of the NQR lines, and the crystallite size perpendicular to the [1.3.1] plane are given in Table 1.

The largest crystallites were present in technical RDX (sample *1*). At the same time, NQR study demonstrated that this sample had a larger number of defects resulting, apparently, from the presence of an impurity. The impurity reaction was pronounced in the initial stage of gas evolution (see Fig. 1), but the resulting defects were not reflected in RDX decomposition as such. This is evident from the fact that the initial region of the kinetic curve was completely reproduced in sample *5*, which contained a small number of defects and which was obtained after evaporation of acetone from a solution of technical RDX. As a result of crystallization according to this procedure, the impurity was formed as an individual phase and deposited on the surface of RDX crystals without distortion of the structure of the latter. Apparently, the "impurity defect" detected by the NQR method is actually associated with stresses in the RDX crystals, which cause distortion of the gradient of the electric field strength, but do not lead to crystal destruction. After completion of the impurity reaction, decomposition of technical RDX proceeded more slowly than that in the case of purified samples, which corresponds to a more perfect crystal structure.

In samples, which were purified from impurities and were not subjected to mechanical treatment, the rate of decomposition was dependent on the mode of crystallization, and the directly proportional dependence was observed between ω, δ, and L^2.

Grinding of large crystals of samples *3* and *4* led to narrowing of the NQR line; however, the initial rate did not decrease, and even, on the contrary, increased. This is attributable to the fact that grinding of crystals occurs along dislocations to form small crystals. The latter have a small number of defects, but possess a large surface on which decomposition readily proceeds; however, this

Table 1. Initial rate (ω) of decomposition at 160 °C, the half-width of the NQR line (Δ/Hz), and the crystallite size (L) for different RDX samples

Sample	Δ/Hz		L/nm		ω/cm^3 g^{-1} min^{-1}		
	I	II	I	II	I	II	III
1	750	—	61.5	—	0.02 ($3.5 \cdot 10^{-4}$)*	—	
2	450	—	38.9	—	$8 \cdot 10^{-4}$	—	$4 \cdot 10^{-4}$
3	330	200	—	48.1	$4 \cdot 10^{-4}$	$6 \cdot 10^{-4}$	$4 \cdot 10^{-4}$
4	300	200	—	47.5	$5 \cdot 10^{-4}$	$7 \cdot 10^{-4}$	—
5	200	—	—	—	0.02	—	—

Note. Samples: I, initial, II, ground, III, pressed at p = 1 kbar, conversion of samples *1—5* δ > 15000.

* The rate in the linear region after completion of the impurity reaction.

surface is not manifested in the NQR spectra as a defect. The particle sizes in ground samples *3* and *4* are identical to those in sample *2*, but microblocks in the former samples are larger, and, correspondingly, they are more stable than sample *2*.

An unexpected effect was found in the studies of the pressed samples. Thus, pressing led to substantial broadening of the NQR line and to a change in its position. However, the rate not only was increased, but even sometimes was decreased. The crystallite size also remained unchanged upon pressing. Thus, it was found that L = 37.9 nm for pressed sample *2*. Apparently, elastic stresses, which appearred upon pressing and which did not relax after removal of the pressure, affected substantially the width of the NQR line (but not the ω and L values). Decomposition of RDX is reversible, and insignificant deceleration of decomposition upon pressing may be associated merely with the effect of a decrease in the unit cell volume occupied by the molecule (the "cell" effect) in a compressed interblock substance. It is also possible that the number of defects in the pressed sample is somewhat increased due to crystal destruction upon pressing, but these changes are compensated by the cell effect.

A typical pattern of a change in the rate upon pressing of sample *2* is shown in Fig. 2. At a pressing pressure of 0.5 kbar (the relative density is 0.9), the initial rate of gas evolution was higher than that observed before pressing. However, even at a pressure of 1 kbar at which the relative density was 0.925, the rate became smaller than that in the case of a powdered sample. A further increase in the pressing pressure to 2.5 kbar did not lead to a change in the relative density and the decomposition rate. The rate was doubled upon grinding of the pellet (6 mm in diameter and 2 mm in thickness) to the particle size of 0.3 mm; however, the rate was still smaller than that in the initial sample *2*. It should be noted that gas evolution was not observed upon dissolution of partially decomposed pellets 2—4 mm thick in Me_2CO. Therefore, gaseous products were not retained in pressed pellets and the manometric measurements for these products were not correct.

The results of our study demonstrated that the most substantial change (ten times) of the initial rate of gas evolution occurred when the compound was purified from unstable impurities. The crystal imperfection and the decomposition rate depended only moderately (changed by a factor of 1.5—2) on the mode of crystallization (rapid or low deposition) and the crystal size (grinding under conditions, which did not lead to mechanical destruction). A slight increase in stability upon pressing was observed for the first time. Pressing would be expected to exert a noticeable effect, but only in reversible reactions and only in highly imperfect samples.

Previously,[6] it has been suggested that products of RDX decomposition can create substantial stresses in the crystals even at the initial stages of the reaction (0.06%), which should lead to cleavage of microblocks and an increase in the decomposition rate. The dynamics of the change of L in the course of decomposition, which was measured for the finely ground fractions of sample *4*, did not confirmed the above suggestion. Thus, the degrees of conversion δ at 160 °C were 0, 0.005, 0.07, and 0.32% and L = 47.5, 50.0, 51.0, and 42.3 at the moments 0, 2, 10, and 20 h, respectively (see Fig. 1, curve *5*). Only at δ = 0.32%, when the rate was already higher than the initial value by a factor of 8, fragmentation of microblocks became noticeable. Therefore, the crystallite size was initially increased on the background of acceleration of decomposition due, apparently, to recrystallization. Then, at the stage of substantial acceleration, the crystallite size was decreased, but this decrease was not proportional to a change in the rate. It can be concluded that acceleration of RDX decomposition at the inital stages is caused primarily by autocatalysis or thawing, but not by an increase in crystal imperfection.

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