Kinetics of the β→δ structural reorganization in 1,3,5,7-tetranitrooctahydro-1,3,5,7-tetrazocine

V. V. Zakharov and B. L. Korsunskii*

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (496) 515 3538. E-mail: vzakh@icp.ac.ru

Kinetics of the β→δ thermal phase transition in the polycrystalline mono- and polydispersed samples of 1,3,5,7-tetranitrooctahydro-1,3,5,7-tetrazocine (octogen, HMX) was studied by the isothermal calorimetry. Effects of different factors on the transition kinetics were investigated.

Key words: 1,3,5,7-tetranitrooctahydro-1,3,5,7-tetrazocine (HMX, octogen), kinetics, isothermal calorimetry, phase transition.

Studies of the dynamic behavior of energetic materials is one of the most important fields of chemical physics. Existence of several structural phases in many crystalline materials complicate these studies. 1,3,5,7-Tetranitrooctahydro-1,3,5,7-tetrazocine (octogen, HMX) is one of such materials. It should be also noted that octogen is one of the most powerful explosives and in this connection is of significant interest.

The polymorphic transition in octogen occurs at considerably lower temperatures than its thermal decomposition, therefore, its thermal stability in many cases is not determined by the chemical reactivity, but by the disposition to polymorphic transformation. The β-phase is practically the most important out of four earlier known phases of octogen. It is thermodynamically stable under normal conditions and, in addition, has the highest density as compared to the other phases. The β→δ polymorphic transition is observed around 160 °C, therefore, the δ- rather than β-phase very often undergoes thermal decomposition.[1]

From the point of view of practical significance, it seems important to in details study dynamics of the β→δ phase transition in octogen within as wide temperature range as possible. There are just few publications on this subject and they are often contradictory. In particular, the earlier performed works studied polymorphic transformations in octogen by IR Fourier-spectroscopy and by methods of nonlinear optics.[2,3] In addition, the β→δ phase transition was studied by DSC, and the values of effective activation energy and preexponential factor were determined assuming that this process proceeds as the first order reaction.[4] However, our already initial experiments on the studies of kinetics of the solid phase β→δ transition by isothermal calorimetry showed that the indicated process is much more complicated.

In this work, we present results of our first studies on the kinetics of β→δ polymorphic transformation (PT) by isothermal calorimetry. The most important task consisted in determination of kinetic laws of the phase transition and in the studies how different factors affect the transition kinetics.

Experimental

Isothermal studies of kinetics of the PT β→δ in HMX were carried out in the temperature range 159.4—169.0 °C on DAK-1-1a and DAK-1-1 differential colorimeters constructed in the IPChPh of RAS and made in the Scientific and Technical Association "Experimental Factory for Science Instrumentation". Experiments were carried out with polycrystalline monodispersed (the particle sizes 5 and 20 μm) and polydispersed (20—3000 μm) samples of octogen in the sealed evacuated tubes ($m \approx 1$ mmol, $m/V \approx 10^{-1}$ g cm^{-3}).

Results and Discussion

In the first stage, kinetics of PT β→δ was studied in the monodispersed sample of octogen (the fraction of 20 μm) within the temperature range 159.4—169.0 °C. Figure 1 shows the differential and integral kinetic curves of thermal absorption for the PT β→δ at 159.4 °C, whereas Fig. 2 shows the integral kinetic curves of thermal absorption for the transition β→δ within the whole temperature range under study.

The data given clearly indicate that the PT β→δ occurs with a pronounced self-acceleration. The works cited above suggested the first order kinetics for this process. However, most likely, this is due to the fact that most experiments were carried out either under nonisothermic condi-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1413—1416, July, 2011.

1066-5285/11/6007-1436

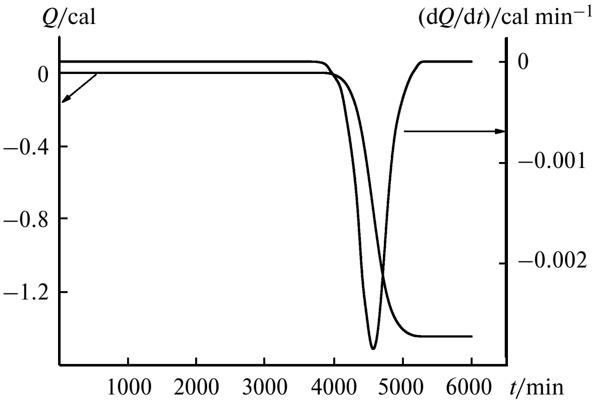

Fig. 1. The kinetic curves of thermal absorption during PT β→δ in octogen (20 μm) at 159.4 °C.

tions, or at too high temperatures, when a kinetic law of transition cannot be clearly tracked down.

As it is known, polymorphic transition includes two macroscopic steps: nucleation and growth of a new phase. Earlier, taken other explosive, *viz.*, hexanitrohexaazaisowurtzitane, as an example, it was shown[5] that polymorphic transformation of crystals of the same size occurs very fast, within few minutes. Therefore, the induction period in the Figures given above corresponds to the nucleation and can be explained by fact that different crystals due to the different degree of imperfection are characterized by different time of nucleation.

Kinetics of PT is described by the equation for autocatalysis, in which the order of the reaction on the catalyst increases from the first to the second with elevation of temperature. In this case, the maximum rate of the reaction obeys the Arrhenius equation with the energy of activation E_a equal to 102.9±11.6 kcal mol^{-1}, that agrees with the value 103.6±3.1 kcal mol^{-1} determined[4] by DSC. This value itself is apparently an effective one and reflects a combination of processes, in particular, a collective character of interactions during nucleation.

The endothermic effect for the β→δ transition of the samples under study is 2.1±0.2 kcal mol^{-1} and is characteristic of the thermal effects of PT in molecular crystals (the DSC method gave[6] the value 2.3±0.2 kcal mol^{-1}).

Due to the possibility of the reverse transition δ→β at lower temperatures[4] (~120 °C), we studied kinetics of several cycles of PT β→δ for the same sample of octogen. The differential kinetic curves of thermal absorption for PT β→δ at 161 °C are given in Fig. 3.

For repeated recurrence ("cycling") of PT, a considerable shortening of the induction period and increase in the rate of PT β→δ with the increase in the number of the PT cycles are observed, that is possibly due to the physical processes related to the decomposition of crystals resulting from the mechanical stresses during the solid phase PT. Apparently, such a decomposition causes an increase in imperfections of the crystal and the corresponding increase in the reactivity, that results in the reduction of the induction period.

Comparative studies of kinetics of PT β→δ in two monodispersed samples (5 and 20 μm) (Fig. 4) demonstrated more rapid proceeding PT β→δ in the sample with smaller particle sizes, that is apparently due to the higher specific surface of the fine-dispersed sample, since imperfections, which initiate nucleation, can be concentrated on the particle surface. It cannot be excluded either that the lower diffusion hindrance play a defining role in the fine-dispersed sample as compared to the coarse-dispersed one.

Kinetics of PT β→δ in the polydispersed sample of octogen (20—3000 μm) was studied in the temperature range 161.0—169.0 °C. The differential and integral kinetic curves of the thermal absorption during PT β→δ in this sample are given in Fig. 5.

As it is seen from Fig. 5, the process of PT β→δ in the polydispersed sample is more complicated, namely, at

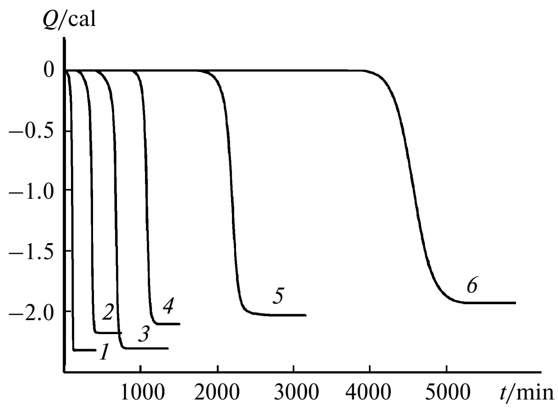

Fig. 2. The integral kinetic curve of thermal absorption during PT β→δ in octogen (20 μm) at various temperatures (°C): 169.0 (*1*), 167.0 (*2*), 165.4 (*3*), 164.0 (*4*), 162.0 (*5*), 159.4 (*6*).

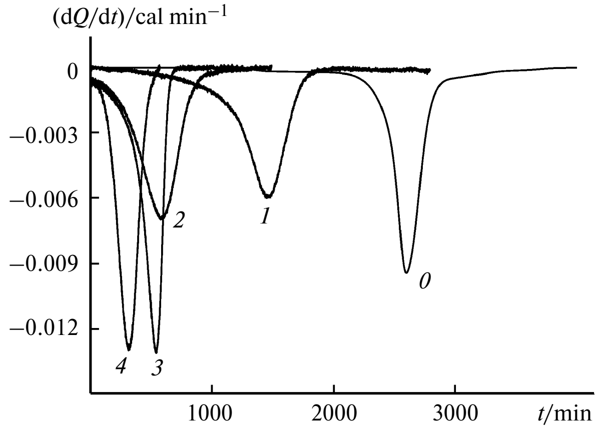

Fig. 3. The integral kinetic curve of thermal absorption during several cycles of PT β→δ in octogen (20 μm) at 161.0 °C; the numbers at the curves correspond to the number of the PT cycle.

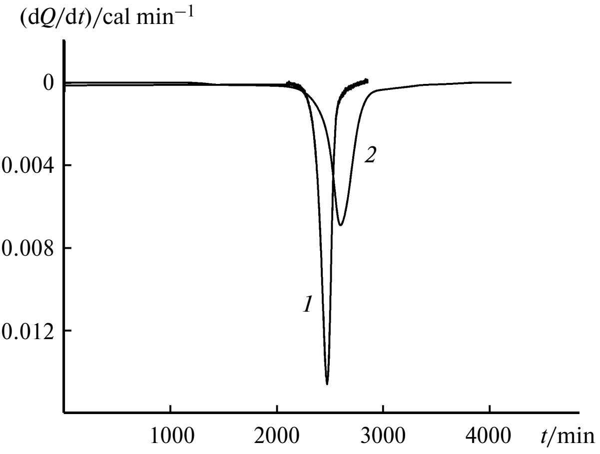

Fig. 4. The differential kinetic curve of thermal absorption during PT β→δ in octogen at 161.0 °C: 5 (*1*) and 20 μm (*2*).

higher temperature the calorimetric curve acquires a "fine structure" (it can be seen more illustrative in Fig. 6, where it is compared with the monodispersed sample), whereas at lower temperature (lower 164 °C), the differential curve already has several maxima.

Similar structure has been observed earlier for the already mentioned hexanitrohexaazaisowurtzitane[5] and it is apparently due to the different reactivity of crystals having different sizes.

In addition, comparison of the kinetic curves of thermal absorption during PT β→δ in this polydispersed sample and the monodispersed (5 and 20 μm) samples studied by us earlier indicates that the process proceeds much slower in the polydispersed sample with larger sizes of octogen particles (Fig. 7). This is also in good agreement with the results given above for the monodispersed octogen: the smaller the crystal size, the faster is PT. When kinetics of thermal decomposition of octogen was studied,[7] the similar effect of the crystal sizes on the rate of the process was observed.

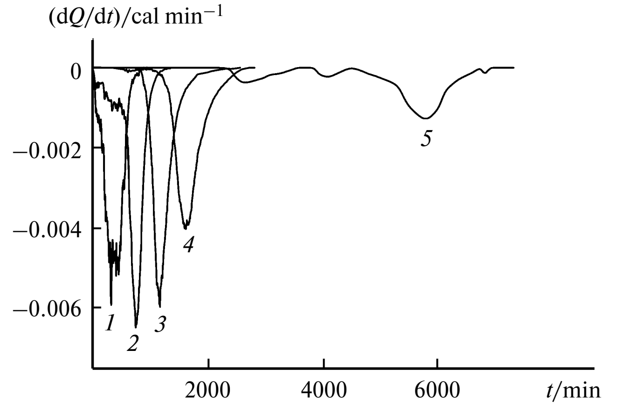

Fig. 5. The differential kinetic curve of thermal absorption during PT β→δ in the polydispersed samples of octogen (HMX_{techn}) at various temperatures (°C): 169.0 (*1*), 167.0 (*2*), 165.4 (*3*), 164.0 (*4*), 161.0 (*5*).

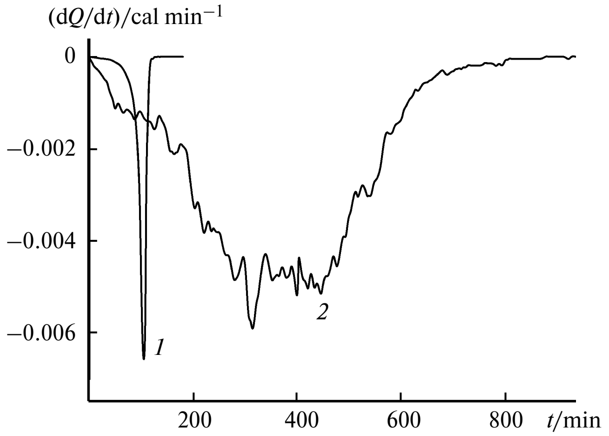

Fig. 6. The differential kinetic curve of thermal absorption during PT β→δ in the monodispersed (20 μm) (*1*, 0.05(d*Q*/d*t*)) and polydispersed (*2*, d*Q*/d*t*) samples of octogen at 169.0 °C.

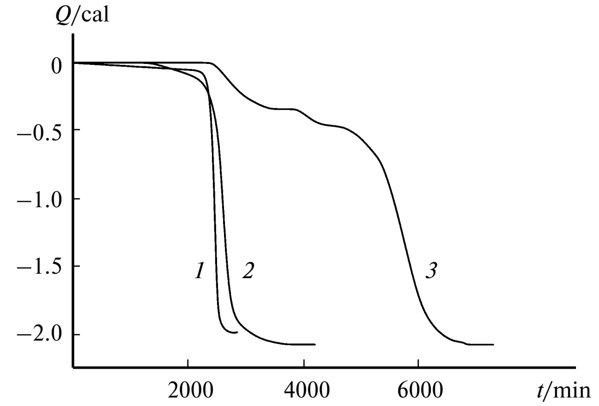

Fig. 7. The integral kinetic curve of thermal absorption during PT β→δ at 161.0 °C in different samples of octogen: monodispersed (5 (*1*) and 20 μm (*2*)) and polydispersed (*3*) samples.

At the present time, we develop a polychronic kinetic model of polymorphic transitions for molecular crystals, which is based on the hypothesis of independent proceeding PT in the ensemble of isolated crystals-microreactors by the mechanism of the first order autocatalysis. In our opinion, this model will allow us to explain, in particular, a very complicated structure of kinetics of PT β→δ in the polydispersed samples of octogen, which varies depending on the crystal dispersities and includes numerous peaks for the rate of the process.

In conclusion, the isothermal calorimetry method established that kinetics of the thermal PT β→δ in the monodispersed samples of octogen is described by the autocatalysis equation. The activation energy of the process is equal to 102.9±11.6 kcal mol^{-1}. The endothermic effect is 2.1±0.2 kcal mol^{-1}. When the particle sizes of the monodispersed octogen decrease, PT β→δ occurs faster. At "cycling" of the PT β→δ, the induction period becomes significantly shorter, whereas the rate of the process increases. In the polydispersed octogen, the PT is very complicated: at low temperatures, the differential kinetic curve has several maxima, whereas a "fine structure" is observed for it at high temperatures.

References

1. B. F. Henson, B. W. Asay, R. K. Sander, S. F. Son, J. M. Robinson, P. M. Dickson, *Phys. Rev. Lett.*, 1999, **82**, 1213.
2. T. B. Brill, R. J. Karpowicz, *J. Phys. Chem.*, 1982, **86**, 4260.
3. L. Smilowitz, B. F. Henson, B. W. Asay, P. M. Dickson, *J. Chem. Phys.*, 2002, **117**, 3789.
4. R. K. Weese, J. L. Maienschein, C. T. Perrino, *Thermochimica Acta*, 2003, **401**, 1.
5. N. V. Chukanov, V. A. Dubovitskii, V. V. Zakharov, N. I. Golovina, B. L. Korsunskii, S. A. Vozchikova, V. V. Nedel´ko, T. S. Larikova, A. V. Raevskii, S. M. Aldoshin, *Khim. Fiz.*, 2009, **28**, 98 [*Russ. J. Phys. Chem. B* (*Engl. Transl.*), 2009, **3**, 486].
6. P. G. Hall, *Trans. Faraday Soc.*, 1971, **67**, 556.
7. M. Fathollati, S. M. Pourmortazavi, S. G. Hosseini, *J. Energetic Materials*, 2008, **26**, 52.

Received March 4, 2011