LOW-ENERGY POLYMORPHIC TRANSITIONS IN MOLECULAR CRYSTALS OF ENERGETIC MATERIALS: KINETICS AND MECHANISM

A. V. Stankevich

FSUE «RFNC – VNIITF named after Academ. E. I. Zababakhin», Snezhinsk, Russia

Kazan National Research Technological University, Kazan, Russia

Postovsky Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences, Ekaterinburg, Russia

On the phase diagrams for substances and composite materials, it is customary to mark the areas of existence of a particular phase for matter (solid, liquid, gas) and modifications of the solid (α, β, γ …). The boundary lines of existence in the P-T diagrams determine the static characteristics of phase transitions of the first and second kind. Polymorphic transitions, which are phase transitions of the second kind and are characterized by an order parameter, occupy a special place in the classification of phase transitions η [1]. On the one hand, the kinetics and mechanism of polymorphic transitions can be represented as the relaxation value of the order parameter, on the other hand, as the dependence of the velocity constant of movement of molecular fragments under changing external forces. The first part is determined by a function depending on the chemical potential, temperature and pressure, and the second by the dependence of the velocity and trajectory of movement on temperature and pressure.

Considering that various kinds of polymorphic transitions change the degree of order or the packing coefficient of particles in the volume of a solid (unit cell), we note the high probability of a change in the properties of a substance after a phase transition. In addition, polymorphic transitions can cause deformation of crystalline substances, which leads to expansion or compression of the substance in the finished product, an increase in static pressure in them, and the formation of cracks, chips, and other defects in the materials. Therefore, knowledge of the mechanisms of such processes is important.

From the practice of studying polymorphic transitions, we will single out low-energy transitions with a low relaxation coefficient of the order parameter. Such polymorphic transitions are low-energy, i. e. they require a small amount of energy to activate the process of transition from one state to another, moreover, most of these transitions are irreversible under similar influence. The reaction rate constant also has low values of the order of 10^{-2}–10^{-5} c^{-1} in conditions of temperature difference from 10 to 50°C.

In this paper, we analyzed and summarized the results of our previous studies of the kinetics and mechanisms of irreversible phase transitions of the second kind $\beta \rightarrow \alpha$ in 2,4-dinitroanisole (DNAN, 20–80°C) [2], $\beta \rightarrow \alpha$ in cyclotetramethylenetetranitroamine (HMX, 50–150°C), $\beta \rightarrow \alpha$ in 3-nitro-4,5-dihydro-1,2,4-triazol-5-one (NTO, 20–100°C), $\gamma \rightarrow \gamma'$ in 1,1-diamino-2,2-dinitroethylene (FOX-7, 170–200°C), all of these transitions occur with a decrease in density from 1,5 to 8%.

Structural changes were registered by isothermal methods of powder thermorentgenography of the internal standard. Calculations of X-ray diffractometry data were performed using a full-profile analysis method with a quantum modeling cycle of the molecular structure integrated into the algorithm. Kinetic parameters of the polymorphic transition were estimated by isothermal and isoconversion methods based on the Arrhenius equation. The obtained equations of the kinetics of polymorphic transitions made it possible to describe the processes occurring in energetic molecular crystals, as well as to perform thermodynamic calculations to estimate the P-T phase diagrams of mixtures based on them.

The obtained results can be used in constructing a physico-mathematical description of the behavior of condensed matter during thermal exposure, storage, as well as in evaluating the properties of mixed compositions.

References

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