

Проведенный анализ экспериментальных данных по разложению ГНС в статических и динамических условиях нагрева, до и после температуры плавления позволяет предложить более простую модель, применимую как для разложения в твердом состоянии, так и в расплаве.

Закономерности разложения ГНС в статических и динамических условиях нагрева при разложении ниже и выше температуры плавления удастся объяснить в рамках одной модели, автокатализа первого порядка с бимолекулярной промежуточной стадией, необходимо только учитывать фазовые переходы, проходящие в ГНС при динамическом нагреве.

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THE MODEL OF HEXANITROSTILBENE DECOMPOSITION

P.N. Stolyarov

SSC RF GOC Central Research Institute Of Chemistry And Mechanics, Moscow, Russia

In solving many practical and theoretical problems it is necessary to know the kinetics of decomposition of energetic materials. At the same time it is necessary to predict the stability over the temperature limits of the study. It is necessary for determine the temperature-time safe conditions of operation with the EM products. It requires the selection of a mathematical model, understanding of its forecasting capabilities, as well as the physical and chemical features of the reactions, often limits by the possibility of the forecast.

Decomposition of a number of molecular crystals proceeds with the formation of liquid compounds in which the original material is dissolved, and which causes the acceleration of the decomposition of these compounds. In the context of this process it is easy to explain the transition from the decomposition of the first order in the gas phase to the decomposition of the solid state to the liquid intermediate or final products, are subject to the laws of the first order autocatalysis [1] or autocatalytic second order [2-3].

However, to describe the experimental curves of nitro compounds decomposition the equations obtained during the development of the theory of solid-state processes in ionic crystals are often used.

Features of the development of the theory of homogeneous and heterogeneous reactions considered in [4].

A classification and theory of reactions in solids are considered in [5]. The reactions which flow from the formation of nuclei (seeds) of a new phase, growth of seeds, and the formation of a new phase structured.

The authors provide the following interpretation of the curve shape - if the free activation energy of the reaction of growth on the phases interface is less than the formation activation energy of the seed, the growth of existing seeds supersede formation of new and the type of decomposition curves is autocatalytic. If the energies are not differing greatly, then a large number of seeds appeared, the period until the acceleration is reduced or non-existent (Figure 1 - b, c). It is assumed that, for formation of a stable seed takes part $n-1$ particles, and the number of seeds increases as $N=A \cdot \tau^n$.

It is easy to see that in the usual symbols $n = 1-N/N_0$ (η - decomposition degree N_0 - the original number of molecules), the mathematical expression is $\eta = 1-A \cdot \tau^n$. Or in differential form $d\eta/d\tau = B(1-\eta)^{(n-1)/n}$. For the seed in a ball shape $n = 3$ and $d\eta/d\tau = B(1-\eta)^{2/3}$, for the cylinder - $d\eta/d\tau = B(1-\eta)^{1/2}$, for the plane - $d\eta/d\tau = B$.

In processing the experimental curves due to the technical difficulties of observation of nucleation of the initial period of nucleation, were seen only part of the curve. In [6] one-step reaction $d\eta/d\tau = k\eta(1-\eta)$ has been introduced for the curves treatment of silver oxide decomposition. In this case η determined by external parameters being measured. In view of the large number of works devoted to the consideration of possible ways of reactions in the solid phase and the equations describing this process, in this article the analysis of the work carried out previously and the resulting equations are not presented.

Currently for the processing of the experimental data used an equation of Avrami-Erofeev $d\eta/d\tau = k\eta^n(1-\eta)^m$ or its multiple modifications. Unlike the autocatalysis equation which is often used to describe the curves of the decomposition of organic crystals, the equation Avrami-Erofeev not include the decomposition process at an early stage.

In [7-8] developed a methodical approach to experimental models to processing decomposition data of organic matter. Using the proposed method for solving the kinetic equations, an attempt was made to develop a kinetic model for the analysis of experimental data, based on the first stage of decomposition. In the book [11] provides a summary of the thermal stability data of nitro compounds research by the authors in a few years. There are equations of formal kinetics used for the processing of experimental data. In this case, a lot of attention is paid to the first stage of decomposition and its accounting.

In [9] experimental data of aromatic compound hexanitrostilbene (HNS) decomposition was processed using the equations of heterogeneous reactions. HNS [10] has a melting point 319°C - 323°C used as the heat-resistant explosive.

The decomposition of the aromatic compound HNS in [9] was carried out under in static and dynamic conditions of heat above and below the melting temperature. The authors used a multi-step kinetics. For the decomposition in the liquid state 4 successive stages ($A \rightarrow B \rightarrow C \rightarrow D \rightarrow E$), the first two and the fourth stage as η^n , the third - the catalytic $\eta^n(1 + k_c x)$, where x - catalyst. For solid state proposed a three-step model ($A \rightarrow B \rightarrow C \rightarrow D$), where the first stage is a three-dimensional grain growth of a new phase $n^{2/3}$, the second and third catalytic reaction are reactions of n -th order.

Table 1 summarizes the data obtained for the reaction constants.

The activation energy of the first step in the melt is more than two times higher than that for the solid state, usually aromatic compounds such difference is not observed. Unfortunately, the authors do not provide an explanation of the data obtained.

Melting point of HNS as was said is 319°C - 323°C and to describe decomposition in melt or in curve of material whose decomposition starts in the solid phase, and ends after melting temperature, equation of heterogeneous reactions are used.

Table 1. Kinetic parameters of HNS decomposition

Constant	Melt A→B→C→D→E	Solid A→B→C→D
log k ₁ , s ⁻¹	31,62	11,75
E ₁ , kJ/mol (kcal/mol)	389,6 (93,2)	175,9 (42,8)
n ₁	0,4	
log k ₂ , s ⁻¹	0,79	19,53
E ₂ , kJ/mol (kcal/mol)	28,4 (6,8)	261,7 (62,6)
n ₂	0,55	0,35
log k _{2c} , s ⁻¹		0,61
log k ₃ , s ⁻¹	17,78	5,39
E ₃ , kJ/mol (kcal/mol)	233,8 (55,9)	108,3 (25,9)
n ₃	0,91	1,64
log k _{3c} , s ⁻¹	0,028	
log k ₄ , s ⁻¹	22,5	
E ₄ , kJ/mol (kcal/mol)	296,0 (70,8)	
n ₄	2,46	

The experimental curve of HNS decomposition in isothermal conditions in temperature range 304°C – 274°C were process by easier autocatalysis equation of first and second order and by autocatalysis equation of first with bimolecular transitional stage.

In figure 1 there are calculation and experimental data for the model of autocatalysis equation of first order A→B A+B→2B (a),

$$d\eta/d\tau = 10^{14.546} \exp(-50000/RT)(1-\eta) + 10^{15.48} \exp(-50000/RT)(1-\eta)\eta$$

autocatalysis of second order A→B+B A+2B→4B (b)

$$d\eta/d\tau = 10^{14.7} \exp(-50000/RT)(1-\eta) + 10^{15.8} \exp(-50000/RT)(1-\eta)\eta^2$$

autocatalysis of first order with bimolecular intermediate stage A→B+B→C A+C→2B+C (c)

As it seen from the present data satisfactory explanation of experimental curves was obtained by using the first order model of autocatalysis with bimolecular intermediate stage

$$d\eta_1/d\tau = 10^{14.78} \exp(-50000/RT)(1-\eta_1) + 10^{17.45} \exp(-50000/RT)(1-\eta_1)\eta_2$$

$$d\eta_2/d\tau = 10^{14.0} \exp(-50000/RT)(\eta_1 - \eta_2)^2$$

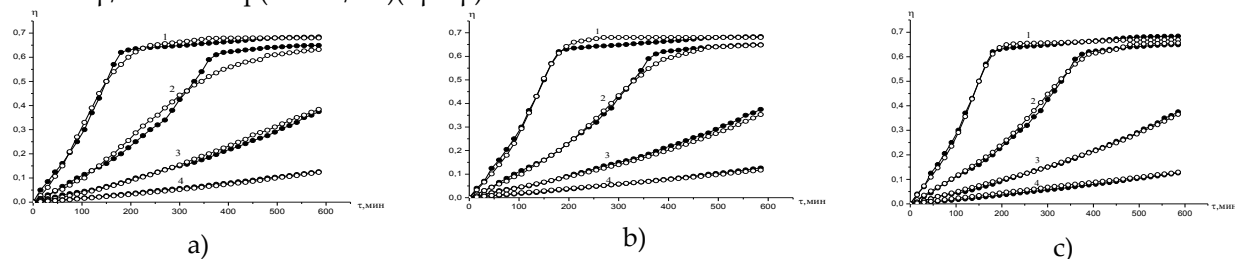


Figure 1. Experimental (●) and calculation (○) decomposition curves of HNS

Experimental data obtained in a dynamic heating, can be divided into two groups. Some obtained at heating rates of 0.05°C/min to 0.4°C/min, terminated to the melting temperature. Other obtained at heating rates of 2.5°C/min to 40°C/min, and then decomposed to the melting temperature.

As is in the case with the expansion in static conditions, a satisfactory description of the experimental curves for the expansion of the melting temperature is observed for the autocatalytic model with first order bimolecular intermediate stage (Figure 2, a-0.4°C/min, b-0.2°C/min, c-0.05°C/min).

$$d\eta_1/d\tau = 10^{14.8} \exp(-50000/RT)(1-\eta_1) + 10^{17.0} \exp(-50000/RT)(1-\eta_1)\eta_2$$

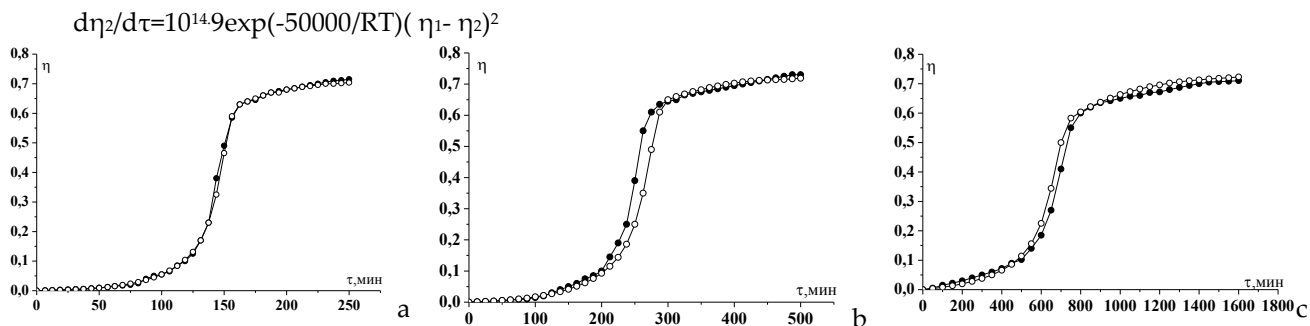


Figure 2. Experimental (●) and calculation (○)decomposition curves of HNS

Kinetic parameters during the decomposition to melt temperature under static and dynamic conditions of heating is similar.

Kinetics of HNS decomposition at heating rates of 2.5°C/ in to 40 °C/min is considered by the authors as decomposition in the melt. However, analysis of these curves reveals that the decomposition begins to the melting point and ends above the melting point. Figure 3 shows the calculated and experimental data using the model of the first order with autocatalysis bimolecular intermediate stage. In this case, even the complexity of the model ($A \rightarrow B + B \rightarrow C$ $A + B \rightarrow 2B$ $A + C \rightarrow 2B + C$ $B + B + C \rightarrow 2C$) does not lead to a satisfactory agreement between the experimental and calculated curves.

The autocatalysis model of first order with bimolecular intermediate stage

$$d\eta_1/d\tau = 10^{15.45} \exp(-50000/RT) (1 - \eta_1) + 10^{15.5} \exp(-50000/RT) (1 - \eta_1) (\eta_1 - \eta_2) + 10^{16.4} \exp(-50000/RT) (1 - \eta_1) \eta_2$$

$$d\eta_2/d\tau = 10^{15.5} \exp(-50000/RT) (\eta_1 - \eta_2)^2 + 10^{15.5} \exp(-50000/RT) (\eta_1 - \eta_2)^2 \eta_2$$

For experimental data at rates 2.5°C/min (a), 10°C/min (b), 20°C/min (c), 40°C/min (d) (figure 3) simple models do not allow to satisfactorily describe the experimental data, due to the fact that decomposition starts in the solid state and continues to melt.

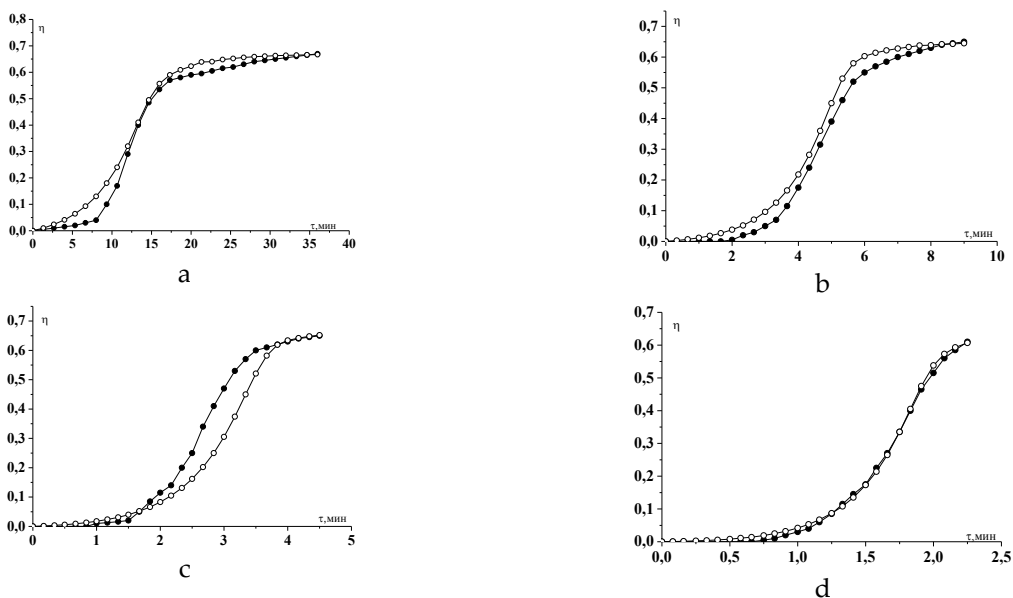
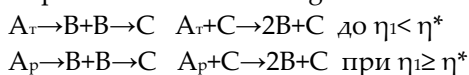


Figure 3. Experimental (●)and calculation (○)decomposition curves of HNS

Lack of DTA data may not accurately determine the melting beginning, and the process of its course. However it is possible to propose a model which takes into account the expansion in the solid and molten phases, selecting formal decomposition depth at which a transition occurs from decomposition in the solid phase in the melt to degrade.



where η^* - decomposition depth at which no solid phase.

Acceleration in the solid phase may be due to the fact that part of the final products is liquid and dissolves the starting material. The experimental and calculated curves obtained using this model are shown in Fig.3

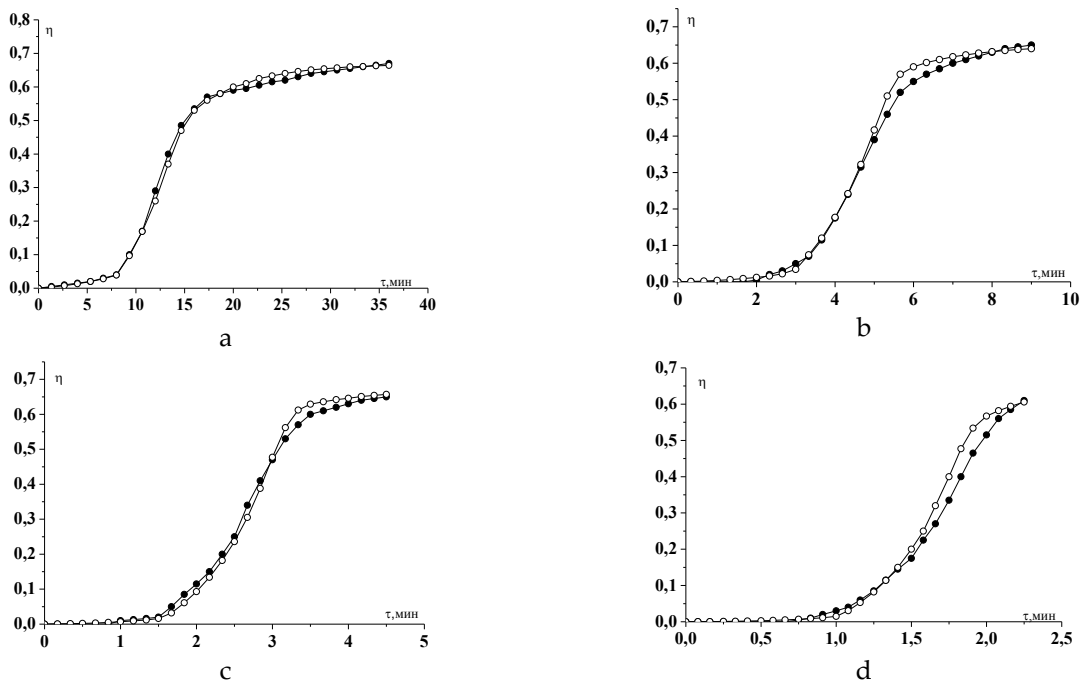


Figure 4. Experimental (●) and calculation (○) decomposition curves of HNS, heating rate a: a - 2.5°C/min; b - 10°C/min; c - 20°C/min; d - 40°C/min

The autocatalysis model of first order with bimolecular intermediate stage

$A \rightarrow B + B \rightarrow C$ $A + C \rightarrow 2B + C$ taking to account the melt of sample during heating process

Systems of equations before melting:

$$d\eta_1/d\tau = 10^{15.0} \exp(-50000/RT) (1 - \eta_1) + 10^{17.0} \exp(-50000/RT) (1 - \eta_1) \eta_2$$

$$d\eta_2/d\tau = 10^{14.9} \exp(-50000/RT) (\eta_1 - \eta_2)^2$$

Systems of equations after melting:

$$d\eta_1/d\tau = 10^{15.7} \exp(-50000/RT) (1 - \eta_1) + 10^{16.8} \exp(-50000/RT) (1 - \eta_1) \eta_2$$

$$d\eta_2/d\tau = 10^{15.5} \exp(-50000/RT) (\eta_1 - \eta_2)^2$$

The analysis of experimental data on the decomposition of HNS in static and dynamic conditions of the heating before and after melting temperature allows to offer a more simple model applicable for decomposition in the solid state or in the melt.

Laws of decomposition of HNS in static and dynamic conditions of heat during the decomposition of below and above the melting point can be explained in the framework of a model autocatalytic first order bimolecular intermediate stage, it is only necessary to consider phase transitions taking place in the HNS in dynamic heating.

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К ВОПРОСУ О ВОЗМОЖНОСТИ ИСПОЛЬЗОВАНИЯ ТЕПЛОТЫ ВЗРЫВЧАТОГО ПРЕВРАЩЕНИЯ ДЛЯ ОЦЕНКИ ДЕЙСТВИЯ ВЗРЫВА. ИНДИВИДУАЛЬНЫЕ ВВ И ИХ СМЕСИ ДРУГ С ДРУГОМ

A. Smirnov¹, Maija Kukla²

¹ГосНИИмаш имени В.В.Бахирева, Дзержинск, Россия

²Университет Мериленда, США,

Рассмотрены методические вопросы определения теплоты взрыва в детонационном калориметре. Определено время реализации теплоты взрыва. Представлены уравнения для расчета теплоты взрыва, скорости и давления детонации, относительной метательной способности индивидуальных ВВ и их смесей друг с другом. Определение времени реализации теплоты взрыва, а также проведенный статистический анализ связи взрывчатых характеристик позволяют обосновать применимость теплоты взрыва для расчета детонационных параметров и характеристик действия взрыва.

Введение

В течение последних пятидесяти лет найдены и экспериментально подтверждены пути синтеза достаточно широкого набора новых энергоемких соединений из самых различных классов органических веществ. Поиск новых ВВ остается стихийным, несмотря на появление доступных методов расчета, позволяющих осуществлять прогнозирование некоторых свойств ВВ. Оценка перспектив энергоемкого вещества для решения конкретных технических задач предполагает проверку соответствия комплекса физико-химических, термохимических и взрывчатых характеристик набору требований, вытекающих из условий применения. Однако, ввиду того, что отсутствует общепринятая практика совместного анализа набора взрывчатых характеристик, широко принято вместо комплексной оценки использовать какой-либо один параметр взрывчатого превращения. При этом предполагается наличие прямой связи между используемым параметром и остальными характеристиками взрыва. В принципе это правильно, так как все взрывчатые характеристики связаны друг с другом. Однако для оценки свойств следует руководствоваться