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Abstract

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FORMAL-KINETIC REGULARITIES OF THE THERMAL DECOMPOSITION OF EXPLOSIVES IN THE LIQUID PHASE

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In the isothermal decomposition of most explosives, self-acceleration of the reaction is observed. In the scientific and educational literature on explosives, the classical equation of autocatalysis is used to describe the kinetics of these reactions:

$$\frac{d\eta}{dt} = k_1(1-\eta) + k_2\eta(1-\eta), \tag{1}$$

where η is the degree of conversion, and k_1 and k_2 are kinetic constants. However, in many cases the kinetic curves do not fit this equation. Significant discrepancies are obtained between the calculated and experimental curves both in the form of the kinetic curves themselves and in the position of the maximum reaction rate. These discrepancies to a certain extent introduce confusion into the question of the mechanism by which the reaction itself proceeds. In the literature (1), for example, cases are cited in which the self-acceleration of the thermal decomposition of explosives is explained by the presence of branched chain or consecutive reactions, although no experimental facts confirming the existence of such reactions are given. At the same time, the predominant number of experimental results shows that the thermal decomposition of condensed explosives proceeds with autocatalysis by the final products of the reaction (2).

A detailed consideration of the thermal decomposition of explosives leads to the conclusion that, in terms of the conditions under which the process proceeds, these reactions differ substantially from ordinary reactions for which the classical equation of autocatalysis was obtained (reactions in gases and solutions). The point is that, during the decomposition of condensed explosives, as a rule, a large part of the products consists of gases. The removal of gaseous products from the reaction zone leads to a decrease in the reaction volume in the course of decomposition, which affects the kinetics of the reaction.

In the present work we consider the formal-kinetic regularities of the thermal decomposition of explosives in the liquid phase, taking into account the change

Fig. 1

Figure 1: Fig. 1

in volume. Since in the overwhelming majority of cases, when two or several components are mixed, practically no change in volume occurs, then, as a first approximation, it may be assumed that the volume of the condensed phase is an additive function of the volumes of the unreacted substance and the condensed residue formed by a given moment of time. Thus, the volume of the liquid phase may be regarded as a linear function of the degree of conversion:

$$v = v_0(1 - \mu\eta),$$

where

$$\mu = \frac{v_0 - v_{\text{res}}}{v_0}$$

is the degree of volume change upon complete decomposition,

v_0 is the initial volume of the substance, and v_{res} is the volume of the condensed residue.

The kinetic equation obtained for a reaction of the n-th order proceeding under conditions of variable volume has the form

$$\frac{d\eta}{dt} = k\,\frac{(1-\eta)^n}{(1-\mu\eta)^{\,n-1}}. \tag{2}$$

If the change in volume during the decomposition process is sufficiently large ($\mu \approx 1$), then equation (2) is transformed into the equation of a simple monomolecular reaction. This indicates that first-order reactions, which are often observed in the decomposition of explosives, may in reality proceed according to either a monomolecular or a bimolecular law.

Taking into account the change in volume in autocatalysis by the final condensed decomposition products also leads to a change in the character of the kinetic curves. In this case our kinetic equation has the form:

$$\frac{d\eta}{dt} = k_1(1-\eta) + k_2\alpha(1-\mu)\,\frac{\eta(1-\eta)}{1-\mu\eta}, \tag{3}$$

where α is the fraction of catalyst in the condensed residue.

Fig. 1. Dependence of the reaction rate $w = \dfrac{d\eta}{dt}$ on the degree of conversion according to equation (3). $\eta_0 = 0.1$

Fig. 2

Figure 2: Fig. 2

Fig. 2. Dependence of the specific rate $w_{\text{sp}} = \dfrac{1}{1-\eta} \cdot \dfrac{d\eta}{dt}$ on the degree of conversion. *I*—first-order reaction, *II*—first-order autocatalysis (equation (1)), *III*—curve according to equation (3)

At $\mu = 0$ (the limiting case: no change in volume occurs in the course of the reaction), equation (3) is transformed into the classical equation of autocatalysis (1). Integration of (3) gives

$$[1 + (1-\mu)\eta_0]\, k_2\alpha(1-\mu)t = \frac{1}{1-\mu\eta_0} \ln\left(1 + \frac{1-\mu\eta_0}{\eta_0}\eta\right) - (1-\mu)\ln(1-\eta),$$

where

$$\eta_0 = \frac{k_1}{k_2\alpha(1-\mu)}.$$

Figure 1 presents the calculated dependence of the reaction rate on the degree of conversion for a specified η_0 and various μ. As is evident from this figure, the magnitude of the maximum rate and the degree of conversion $\eta_{\max}$ at which it is reached depend strongly on the value of μ. At large μ,

$\eta_{\max}$ is close to unity, i.e., the maximum rate is found at the end of decomposition. The value $\eta_{\max}$ can be calculated from the formula:

$$\eta_{\max} = \frac{(1-\mu\eta_0) - \sqrt{(1-\mu)(1-\mu\eta_0)}}{\mu(1-\mu\eta_0)}.$$

The difference between equations (1) and (3) is especially clearly manifested in the curves of the dependence of the specific rate $\frac{1}{1+\eta}\frac{dn}{dt}$ on the extent of conversion (Fig. 2).

When carrying out the thermal decomposition of explosives in the presence of relatively large amounts of strong catalysts, a simple catalytic reaction takes place. The kinetic equation, taking account of the change in volume, in this case has the form

$$\frac{d\eta}{dt} = k\beta\frac{1-\eta}{1-\mu\eta},$$

where β is the fraction of added catalyst in the mixture.

Fig. 3. Dependence of the specific reaction rate on the extent of conversion during decomposition of ethylenediamine dinitrate. Points—experimental Robertson data (^{3}). The curve was calculated from equation (3). $k_1 = 4 \cdot 10^{-3}$ min^{-1}; $k_2 \alpha (1 - \mu) = 58.1 \cdot 10^{-3}$ min^{-1}; $\mu = 0.90$; $t = 238$°C.

Figure 3: Fig. 3. Dependence of the specific reaction rate on the extent of conversion during decomposition of ethylenediamine dinitrate. Points—experimental Robertson data (^{3}). The curve was calculated from equation (3). $k_1 = 4 \cdot 10^{-3}$ min^{-1}; $k_2 \alpha (1 - \mu) = 58.1 \cdot 10^{-3}$ min^{-1}; $\mu = 0.90$; $t = 238$°C.

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The change in the volume of the reacting substance plays no role in autocatalysis by gaseous products, since the concentration of dissolved gases is determined only by pressure and temperature and does not depend on the volume of the liquid phase. In this connection, decomposition of explosives carried out in a closed system, when the pressure of the gaseous products is proportional to the extent of conversion, should obey the classical equation of autocatalysis.

Thus, taking account of the change in volume in the course of decomposition has made it possible to obtain an expression describing the kinetics of thermal decomposition of explosives under autocatalysis by the final condensed products of the reaction. Experimental data obtained in the decomposition of a number of substances in the liquid phase are in good agreement with the proposed equation. This may be illustrated by the following example. Figure 3 presents the dependence of the specific rate on the extent of conversion in the thermal decomposition of ethylenediamine dinitrate (according to Robertson' s data (^{3})), at $T = 238$°C. The agreement of the calculated curve with the experimental points indicates the validity of equation (3).

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Note: Figure translations are in progress. See original paper for figures.