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THERMAL ANALYSIS OF BINARY SYSTEMS
Explosive – lead compound

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Abstract

The thermal decomposition of explosives: pentaerythrol tetranitrate (PETN), 2,4,6-trinitrotoluene (TNT), cyclo-1,3,5-trimethylene-2,4,6-trinitroamine (RDX) and their two-component mixtures with 40% of lead compounds [PbO, Pb_3O_4, $Pb(NO_3)_2$] were performed. The simple method of determination of stability changes in the mixtures described above, in comparison with pure explosives was presented. The lead oxides accelerated significantly the thermal decomposition of explosives. $Pb(NO_3)_2$ acts as a catalyst in the mixture containing TNT degradation, but not in a case of PETN and RDX.

Keywords: compatibility, explosives, lead compounds, thermal decomposition

Introduction

The explosive mixtures consisted of a basic component – sensitiser, as well as other modifiers, changing their physicochemical properties and utility. The lead tetraoxide (Pb_3O_4) is described as a modifier in some patents [1, 2]. The addition of this compound into plastic explosives causes the decrease of detonation velocity. Because of extremely high temperatures and pressure in detonation wave and high dynamics of process, there are some difficulties in investigating the chemical reactions accompanying the process. The information of interaction between the components of a mixture can be obtained by comparison of the thermal stability for pure compounds and their mixtures.

DSC measurements are the good tool for the determination of stability of mixtures because the thermal decomposition of explosives is a strongly exothermic process. There were performed the stability tests for two-component mixtures of explosives like pentaerythrol tetranitrate (PETN), 2,4,6-trinitrotoluene (TNT), and cyclo-1,3,5-trimethylene-2,4,6-trinitroamine (RDX) containing 40% (mass) of lead compounds; PbO, Pb_3O_4, $Pb(NO_3)_2$. The relative thermal decomposition rate was estimated by using the initial stage of thermal decomposition for the small degree of conversion. The method of quick estimation, the influence of lead compounds on the stability of compounds tested, based on the initial stage of thermal decomposition was presented.

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Experimental

The DSC measurements were performed in non-isothermal mode with linear scanning rate β=2 K min^{-1}. The calorimeter was calibrated using the pure In, Sn, Pb, Bi, Zn as a calibrant [3, 4]. The samples of mass about 10 mg were closed hermetically under vacuum in alumina pans. The measurements were performed until the first signs of unsealing appeared. The experimental points before unsealing were used to compare the decomposition rate between pure explosive and its mixture. The unsealing of the sample pan during the measurement is visible on the thermoanalytical curve as a sharp endotherm caused by the relaxation of gaseous products. Our own software was used [3] for the calculation of thermal effects and kinetics parameters. All substances used in the measurements were not less than 99.0%. The explosive mass of the sample used to DSC measurement was always the same.

Results and discussion

The process of decomposition of explosives is complicated [4]. The degradation products could undergo further degradation and possess the catalytic properties. It is considered in the simplest model of decomposition, that the process is the first-order reaction and the products act as catalysts of the decomposition (autocatalytic reaction). The total reaction rate could be expressed by reaction:

$$V=\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k_1(1-\alpha)+k_2(1-\alpha)\alpha \tag{1}$$

where α is a degree of conversion, k_1, k_2 – the rate constants for the first-order and catalytic reactions, respectively. For the very small degree of conversion $\alpha<<1$ the Eq. (1) could be written as:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k_1+k_2\alpha \tag{2}$$

The solubility of volatile products in established temperature is constant. The concentration of catalytic volatile products undergo the relation:

$$\alpha=\alpha^*=\mathrm{const.} \tag{3}$$

Substituting Eq. (3) into (2) we obtained:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k_1+k_2\alpha=k=\mathrm{const.} \tag{4}$$

For the small degrees of conversion we can consider that reaction rate is constant. The kinetics and thermodynamics factors have an influence for this value [5, 6].

The beginning of decomposition of explosive is visible as a deviation of baseline towards the exothermal effect on the thermoanalytical curve. The rate of decomposition is proportional to the deviation of the calorimetric signal from the baseline (b) which is proportional to the released heat (q):

$$\gamma b=\sigma\frac{\mathrm{d}q}{\mathrm{d}t}=\frac{\mathrm{d}\alpha}{\mathrm{d}t}=V \tag{5}$$

where γ and σ are the constants. The equation, describing the relative rate of decomposition ω is:

$$\omega=\frac{b}{b_0}=\frac{V}{V_0}=\frac{k}{k_0} \tag{6}$$

where b is the deviation of the calorimetric signal for the mixture and b_o for the pure explosive. The Eq. (6) is applicable for isothermal and non-isothermal conditions of measurements. When the scanning rate β is linear the relation is given by Eq. (7).

$$\mathrm{d}T=\beta\mathrm{d}t \tag{7}$$

Figure 1 presents DSC curves of melting and the beginning of decomposition of PETN and mixture 60% PETN and 40% $Pb(NO_3)_2$. It can be seen that this lead compound gives no accelerating effect on decomposition process ($\omega\approx1$). The compared curves are very similar.

The DSC curves of melting and the beginning of decomposition of PETN (A), mixtures PETN/Pb_3O_4 60/40 (B) and PETN/PbO 60/40 (C) were presented in Fig. 2. It shows that stability changes according with sequence A>C>B. The rate of thermal decomposition for tested systems was compared for the least temperature, in which the unsealing of the pan is observed (T=439 K). As basic values, the extrapolated values of baseline lead from the linear area before melting until the maximum effect of decomposition was accepted. The ratio of b/b_o at the same temperature (T=439 K) is equal to the relative rate of decomposition. The calculated results of relative rate of

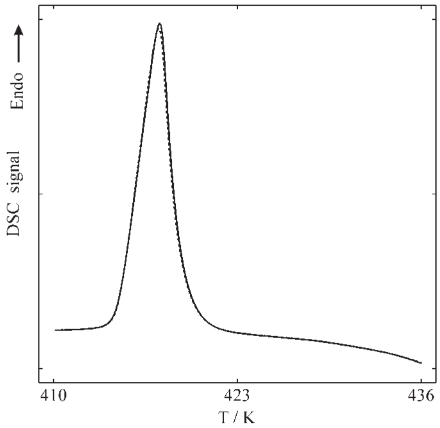

Fig. 1 Comparison of the melting and beginning of thermal decomposition DSC curves for pure PETN — and PETN + 40% $Pb(NO_3)_2$ mixture - - -

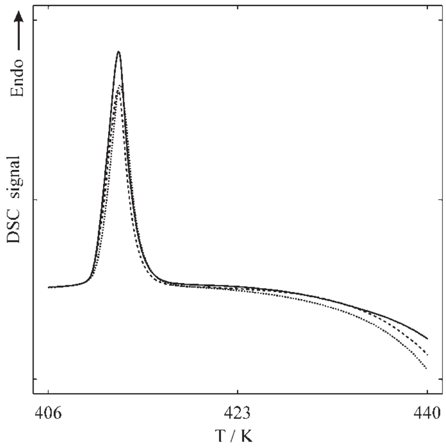

Fig. 2 Comparison of the melting and beginning of thermal decomposition DSC curves for pure PETN —, mixture with 40% PbO - - - and mixture with 40% Pb_3O_4 · · · ·

decomposition (ω) is collected in Table 1. It was proved that lead oxides accelerated the decomposition and the better catalytic properties possess Pb_3O_4.

Table 1 Relative rate of decomposition (ω) at 439 K for mixture containing 60% PETN

Mixture	Relative rate of decomposition (ω)
PETN+$Pb(NO_3)_2$	~ 1
PETN+PbO	1.33
PETN+Pb_3O_4	1.57

Table 2 Relative rate of decomposition (ω) at 511 K for mixture containing 60% TNT

Mixture	Relative rate of decomposition (ω)
TNT+PbO	2.33
TNT+Pb_3O_4	2.66
TNT+$Pb(NO_3)_2$	2.81

The pure TNT and their mixtures of lead compounds were also investigated. The DSC curves of melting and the beginning of decomposition of TNT were present in Fig. 3. The values of relative rate of decomposition (ω) were calculated for the 511 K as the highest temperature of unsealing the pan. Results were presented in Table 2. It is worth mentioning that all investigated lead compounds accelerate the decomposition in the case of TNT. The differences of relative rates of decomposition (ω) for investigated TNT mixtures are low. It is probable that significant growth of ω values for TNT mixtures in comparison with PETN mixtures is caused by the higher value of end temperature of the process. The DSC curves for TNT decomposition the traces of

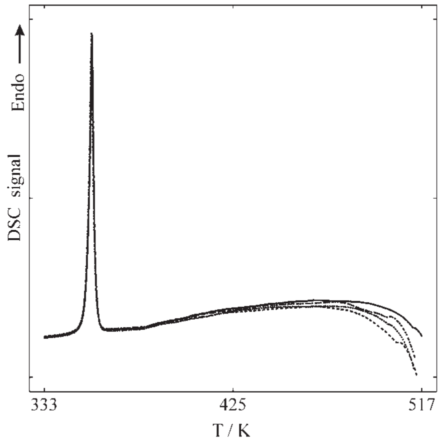

Fig. 3 Comparison of the melting and beginning of thermal decomposition DSC curves for pure TNT —, mixture with 40% $Pb(NO_3)_2$ - - -, mixture with 40% Pb_3O_4 · · · · and mixture with 40% PbO – · · –

degradation were not observed at T=439 K. The rate constant in this temperature is several times lower than in the case of PETN.

The DSC curves of RDX and their mixtures with lead compounds are shown in Fig. 4. The shape of DSC curves of the decomposition of pure RDX and mixtures with $Pb(NO_3)_2$ is similar and it proves that the presence of lead nitrate has no influence on the decomposition of explosive. In both cases one can observe the melting peak and strong decomposition exotherm. The estimated enthalpy of melting of RDX was ΔH_m=20.5 kJ mol^{-1}, melting temperature T_m=476.5 K. The literature parameters [7] were ΔH_m=35.76 kJ mol^{-1}, T_m = 477.2 K respectively. The low values of the melting

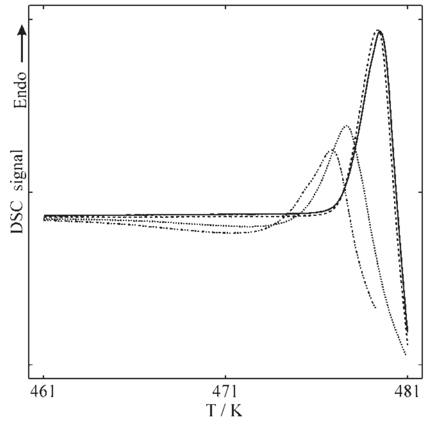

Fig. 4 Comparison of the melting and beginning of thermal decomposition DSC curves for pure RDX —, mixture with 40% $Pb(NO_3)_2$ - - -, mixture with 40% Pb_3O_4 · · · · and mixture with 40% PbO – · · –

enthalpy is the result of the great exothermic effect in the melting process. The results of the comparison of DSC curves of melting and decomposition of pure hexogene and its mixture with PbO (60/40) show that PbO acts as a catalyst for RDX decomposition in the solid phase. The exothermic effects appear before melting and they were overlapping. The enthalpy of this process is $\Delta H_D = -3.8$ kJ mol^{-1} and the melting enthalpy is $\Delta H_m = 7.6$ kJ mol^{-1}. The very low values of melting enthalpy shows that the effect of decomposition, induced by catalytic properties of PbO is great. The comparison of the baselines before the decomposition lead us to the conclusions that this effect appears at much lower temperatures. The mixture RDX/Pb_3O_4 60/40 gives a low exothermic effect $\Delta H_D = -2.0$ kJ mol^{-1} and the value of melting enthalpy is in agreement with expectations and is $\Delta H_m = 8.6$ kJ mol^{-1}. The calculations of relative reaction rates for RDX and mixtures with lead oxides were performed except for mixtures with $Pb(NO_3)_2$. In this case the decomposition does not occur before melting. The relative value of ω for the mixture RDX/PbO, compared with the value for the mixture RDX/Pb_3O_4 is 1.71. The shifting of the melting peak toward the direction of lower temperatures is caused by the presence of dissolved thermal decomposition products of RDX. The dislocation of melting peaks is in agreement with exothermal effects in the solid phase. DSC curve for RDX is very similar to its mixture with $Pb(NO_3)_2$. This results indicate that $Pb(NO_3)_2$ is an inert substance for RDX.

Conclusions

This method of estimation, the relative rate of thermal decomposition of pure explosives allows the quick determination of the thermal compatibility of components. The results lead us to the conclusion that lead oxides have catalytic activity in the process of decomposition of all investigated explosives. Their activity is strongly determined by physicochemical properties of the given explosives. The observations suggest that lead compounds have influence on chemical reactions during detonations. The lead nitrate does not catalyse the decomposition reaction of PETN and RDX, but acts as a catalyst in the decomposition of TNT.

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