

**THERMAL DECOMPOSITION OF PETN AND HMX  
OVER A WIDE TEMPERATURE RANGE  
(#258)**

V.N. German, S.E. Grebennikova,  
L.Ye. Kornilova, S.P. Lobanova,  
L.V. Fomicheva  
Institute of Physics of Explosion,  
RFNC-VNIIEF  
Sarov, Russia

Using the manometric method, thermal decomposition of HMX, PETN and explosives based on them has been studied over the temperature range from 80 to 220°C. The generated experimental results are not subject to the linear law in  $\ln K - 1/T$  coordinates. This testifies to the fact that the activation energy of thermal decomposition is not a constant, but changes greatly as the temperature changes.

For HMX it has been shown that the specific values of activation energy of thermal decomposition at low temperatures are much lower than the same parameters generated at high temperatures. The relation between the activation energy of PETN thermal decomposition and the temperature has a more complicated form:

-in the temperature range from 100 to 135°C the activation energy increases as the temperature decreases;

-at the temperatures below 100°C the activation energy reduces as the temperature of experiments decreases.

Based on the experimental relations, the equations have been sorted out and used to determine the effective activation energy of thermal decomposition of recrystallized HMX and HMX plasticized with fluoroplastic (in the Arrhenius – Franck-Kamenetsky model).

Comparison of  $E = f(T)$  relations for recrystallized HMX and HMX plasticized with fluoroplastic has shown that the catalyzing effect of fluoroplastic on HMX thermal decomposition makes itself evident at the temperatures over 120°C. At the temperatures below 120°C which are the main operational temperatures of explosive devices (ED) containing HMX or HMX-based compositions this influence is missing.

It has been found out that the activation energies of HMX, PETN and compositions based on them become comparable at the temperatures below 90°C. This points to the fact that the chemical stability of the tested HES is almost the same at low temperatures.

## INTRODUCTION

The knowledge of regularities of thermal decomposition of energetic materials (of explosives, in particular) over a wide temperature range is of great practical importance. Over the period of their life cycles HEs and charges containing these HEs are subject to various temperature and time effects. These are temperature and time effects produced on HEs by production processes and those caused by HE storage prior to its application. Specific application environments for some charges of HEs are also related to effects produced on them by elevated temperatures (for example, application of shooting apparatus in oil and gas boreholes, etc.). Finally, in emergency situations caused by fires HE charges are subject to very high temperatures, which may lead to their unauthorized cook-off. Knowing HE thermal decomposition regularities allows the extent of its thermal decomposition under given temperature and time conditions to be estimated thus making it possible to predict possible guarantee periods of charges and probability of unauthorized explosion in abnormal situations.

## EXPERIMENTAL RESULTS

Currently, a few methodical approaches to studies into thermal decomposition of high explosives are being used. As a rule, investigators determine a HE thermal decomposition rate at a given temperature (more often it is a number of temperatures) and extrapolate the generated experimental

data to the temperature range for which the behavior of charges from this HE should be estimated. To extrapolate the experimental data to the required temperature range, the Arrhenius equation is generally used:

$$K = B * \exp(-E / RT), \quad (1)$$

where:  $K$  is the reaction rate constant at  $T$ ,  $s^{-1}$ ;

$B$  is the pre-exponential factor,  $s^{-1}$ ;

$E$  is the activation energy, J/mole (cal/mole);

$R$  is the gas constant.

In most cases the experiments for determining the activation energy in the Arrhenius equation are made over a narrow temperature range that is rather far away from both the HE charge storage and operation temperature range and from the probable range of temperature effects produced on charges in abnormal situations. The question is whether such an extrapolation is rightful.

Based on the studies into HMX thermal decomposition over the temperature range from 120 to 220°C, work [1] shows that the reaction rate constant is not subject to the linear law in  $\ln K - 1/T$  coordinates. This testifies to the fact that the activation energy is not a constant, but changes greatly as the temperature changes.

The objective of this work was to study thermal decomposition of some HEs over a rather wide temperature range (80...220°C). This was done to reduce the probable extrapolation errors resulting from estimation of the changes in operation properties and the safety of handling the charges containing these HEs

over the period of their life cycles and in abnormal situations.

HMX and PETN were chosen for the studies. These two HEs belong to different classes of nitro compounds (nitramine and nitroester) and are known as the substances having highly different thermal stability. In addition, such HE-based explosive compositions as HMX plasticized with fluoroplastic (HE of LX-14 type) and a plastic PETN and polyisobutylene-based composition (HE of XTX type) were studied.

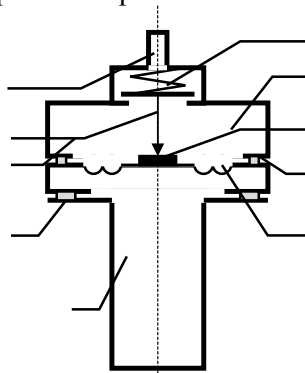
To look into thermal decomposition of explosives, a manometric method was used [1].

The manometric method is more preferable because it allows determining the extent of HE thermal decomposition over a shorter period of time and with much lower error than other methods. The studies with this method were carried out using the measurement and computation complex (MCC) "Vulkan". A compensation transducer whose simplified diagram is shown in figure 1 is the main MCC "Vulkan" part.

Membrane (9) of stainless steel 80  $\mu\text{m}$  thick serves as a sensing element of the transducer. It leans against contact (4) isolated from the whole transducer body with rigid center (8) welded to it. Together they form an electric circuit that can be used to control the measurement process. In beaker (10) under the membrane the transducer reaction volume is located where the tested substance is placed.

Above the membrane there is compensation volume (7) where to compressed air is fed to balance the membrane deflection caused by pressure of gaseous products of the tested substance decomposition. The moment of the

membrane and contact opening specifies the equilibrium between the measured and compensation pressures.



**FIGURE 1. TRANSDUCER DIAGRAM**

**1-Reaction volume; 2-Seal; 3-Membrane assembly; 4-Contact needle; 5-Vacuum line; 6-Contact spring needle; 7-Compensation volume; 8-Rigid center; 9-Membrane.**

Hermiticity of the reaction volume is provided by seal (2) between the beaker and membrane head and by sealing nut (1).

The permissible  $\Delta P_t/P_t$  pressure measurement error is  $\pm 1\%$  of the measured value.

The temperature measurement, regulation and stabilization system of the MCC "Vulkan" maintains the specified temperature in thermostats with the absolute error no more than  $\pm 0.2^\circ\text{C}$ .

The specimen mass error is determined by the balance weight and makes up  $\pm 0.0005$  g.

The reaction volume  $V_r$  was measured with  $\pm 0.1$   $\text{cm}^3$  error using a volume buret. The pressure measurement time was controlled with  $\pm 10$  s error by MCC automatics.

The maximum errors of the main measured quantities V, K and E were  $\Delta V_t/V_t = \pm 2\%$ ;  $\Delta K/K = \pm 3\%$  and  $\Delta E = \pm 300 \text{ cal/mole}$ , respectively.

Manometric experiments were conducted in the following order. The specimen of the tested HE ( $\approx 0.5 \dots 1.0 \text{ g}$ ) was placed in the reaction area of MCC transducer, evacuated to  $\sim 0 \dots 5 \text{ mm Hg}$  residual pressure and put in the thermostat heated to the experiment temperature.

The thermal decomposition kinetics of HMX and HMX-based composition was studied over the temperature range from 80 to 220°C. The experimenting time at 80°C was as much as 600 hours. The experimenting time at 220°C was limited by fast attaining of  $\sim 1500 \text{ mm Hg}$  limiting value in the transducer and made up 300 minutes. The thermal decomposition kinetics of PETN and PETN-based composition was studied over 80...135°C temperature range. As in the experiments with HMX, the experimenting time made up 600 hours at low temperatures (80°C) and 300 minutes at high temperatures (135°C).

The pressure of gaseous thermal decomposition products was measured every 12 hours at low temperatures. As the temperature increased, measurements were made each 10 minutes. Four independent experiments were conducted for each temperature.

Using the measured pressure values, the volumes of released gases were calculated.  $V_t^n = f(t)$  relation is much more convenient than  $P_t = f(t)$  since it applies to normal conditions and is normalized to the mass unit. Thus, it allows the experiments conducted under different conditions (the experiment temperature, the reaction

vessel volume, the specimen weight, etc.) to be compared. A large statistical collection of experimental points of  $V_t^n = f(t)$  relations was processed for each temperature in  $\ln ( V_c^n / ( V_c^n - V_t^n ) )$ , t coordinates using the least-squares technique.

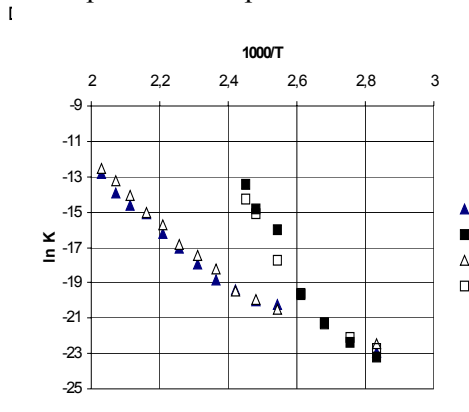
Table 1 gives the thermal decomposition rate constants derived from the experimental data for various temperatures.

**TABLE 1. THERMAL DECOMPOSITION RATE CONSTANTS OF HMX, PETN AND COMPOSITIONS BASED ON THEM AT VARIOUS TEMPERATURES**

Temperature (°C)	Thermal decomposition rate constant ( $s^{-1}$ )			
	HMX	PETN	HMX-based composition	PETN-based composition
80	$4.21 \cdot 10^{-11}$	$8.55 \cdot 10^{-11}$	$2.78 \cdot 10^{-10}$	$1.34 \cdot 10^{-10}$
90		$1.95 \cdot 10^{-10}$		$2.5 \cdot 10^{-10}$
100		$5.79 \cdot 10^{-10}$		$5.39 \cdot 10^{-10}$
110		$2.95 \cdot 10^{-9}$		$3.17 \cdot 10^{-9}$
120	$1.68 \cdot 10^{-9}$	$3.68 \cdot 10^{-7}$	$1.24 \cdot 10^{-9}$	$1.96 \cdot 10^{-8}$
130	$2.03 \cdot 10^{-9}$	$1.1 \cdot 10^{-7}$	$2.13 \cdot 10^{-9}$	$2.83 \cdot 10^{-7}$
135		$1.51 \cdot 10^{-6}$		$6.37 \cdot 10^{-7}$
140	$3.77 \cdot 10^{-9}$		$3.56 \cdot 10^{-9}$	
150	$6.46 \cdot 10^{-9}$		$1.19 \cdot 10^{-8}$	
160	$1.63 \cdot 10^{-8}$		$2.64 \cdot 10^{-8}$	
170	$3.9 \cdot 10^{-8}$		$5.06 \cdot 10^{-8}$	
180	$9.38 \cdot 10^{-8}$		$1.47 \cdot 10^{-7}$	
190	$2.71 \cdot 10^{-7}$		$2.94 \cdot 10^{-7}$	
200	$4.42 \cdot 10^{-7}$		$7.86 \cdot 10^{-7}$	
210	$9.31 \cdot 10^{-7}$		$1.82 \cdot 10^{-6}$	
220	$2.81 \cdot 10^{-6}$		$3.67 \cdot 10^{-6}$	

In figure 2 the same values are presented in  $\ln K, 1000/T$  coordinates. According to [2], the experimental points must be on the straight line whose slope determines the value of thermal

decomposition activation energy. As can be seen from the figure, the experimental points for all tested HEs fail to follow this statement. Hence, the activation energy is not a temperature independent constant.



**FIGURE 2. LOGARITHM OF THE THERMAL DECOMPOSITION RATE CONSTANT FOR THE TESTED HES AS A FUNCTION OF INVERSE TEMPERATURE**

**1 – HMX; 2 – HMX-based composition;  
3 – PETN  
4 – PETN-based composition**

Table 2 gives the thermal decomposition activation energies of the tested HEs for various temperatures. They were calculated from equation (1) using the pre-exponential factor as had been proposed earlier in [3].

It equals  $4.71 \cdot 10^{13} \text{ s}^{-1}$  for HMX and HMX-based composition and  $4.5 \cdot 10^{13} \text{ s}^{-1}$  for PETN and PETN-based composition. The same data are shown in figure 3.

As the measurements show (table 2), the activation energy of HMX, PETN and the compositions based on them is a function of temperature. As the temperature increases, the relation  $E=f(T)$  of HMX and HMX-based composition

approaches the constant value  $E_{\text{max}} \approx 43,400 \text{ cal/mole}$ . For  $T < 160^\circ\text{C}$  it depends on  $T$  almost linearly.

**TABLE 2. TEMPERATURE DEPENDENCE OF THE ACTIVATION ENERGY (CAL/MOLE) OF HMX THERMAL DECOMPOSITION**

Temperature (°C)	Activation energy of thermal decomposition (cal/mole)			
	HMX	PETN	HMX-based composition	PETN-based composition
80	38,100	38,300	37,800	38,000
90		38,800		38,700
100		39,100		39,200
110		38,900		38,800
120	40,400	37,300	40,600	38,400
130	41,300	37,100	41,200	37,100
135		36,400		37,100
140	41,800		41,800	
150	42,300		41,800	
160	42,800		42,100	
170	42,800		42,500	
180	43,000		42,500	
190	42,900		42,800	
200	43,200		42,800	
210	43,400		42,900	
220	43,400		43,100	

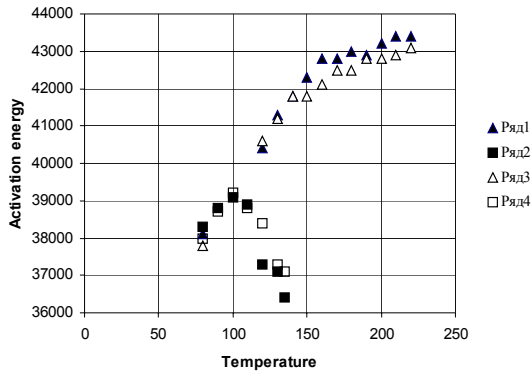
The relation  $E=f(T)$  for PETN is more complicated:

-over the temperature range from 100 to 135°C the activation energy value grows as the temperature decreases;

-at the temperatures below 100°C the activation energy decreases as the experiment temperature reduces.

It should be noted that the thermal decomposition rate constants of all tested HEs become comparable at the temperatures below 90°C while at 130°C

the difference between them makes up two orders of magnitude. Figure 2 shows that at higher temperatures this difference becomes greater.



**FIGURE 3. TEMPERATURE DEPENDENCE OF THE ACTIVATION ENERGY OF THE TESTED**  
**1 – HMX; 2 – PETN; 3 – HMX-based composition;**  
**4 – PETN-based composition.**

In [1] Ye.Ya. Yurin supposes that the behavior of a high explosive  $E=f(T)$  can be described if some part of it ( $p_1$ ) is taken to have a lower activation energy ( $E_1$ ) than the main HE mass ( $p_2, E_2$ ). In principle, this means that the conditions are created under which the thermal decomposition reaction is proceeding in the presence of a catalyst.

For the accepted HE thermal decomposition model [4] including chemical kinetics and heat transfer the heat

conduction and kinetics equations look as follows:<sup>1</sup>

conduction and kinetics equations look as follows:<sup>2</sup>

$$\partial T / \partial t - \lambda / \rho c * (\partial^2 T / \partial r^2 + m / r * \partial T / \partial r) -$$

$$-q_0(1-\alpha) / c * \varphi(E_1, E_2, T, p_1, p_2) = 0; \quad (2)$$

$$\partial \alpha / \partial t = (1-\alpha) * q_0 / q_0 * \varphi(E_1, E_2, T, p_1, p_2), \quad (3)$$

$$\text{where : } \varphi = p_1 * \exp(-E_1 / RT) +$$

$$p_2 \exp(-E_2 / RT),$$

$$p_1 + p_2 = 1.$$

In this case it is a priori taken that the constant  $B=q_0/q_0$  remains constant and equal to  $4.71 * 10^{13} \text{ s}^{-1}$  for HMX.

Then the effective activation energy (for the Arrhenius - Franck-Kamenetsky model) is related to the temperature as follows:

$$E(T) = -RT * \ln[p_1 * \exp(-E_1 / RT) +$$

$$p_2 \exp(-E_2 / RT)] \quad (4)$$

Based on the experimental data given in table 2, the factors for HMX and HMX-based composition included in expression (4) were selected. They are as follows:

$$\begin{aligned} \text{-for HMX} \quad E_1 &= 1.7 * 10^4 \text{ cal/mole;} \\ E_2 &= 4.34 * 10^4 \text{ cal/mole,} \\ p_1 &= 0.68 * 10^{-13}; \quad p_2 = 1; \end{aligned}$$

for HMX-based composition

<sup>1</sup> The fact that the catalyst concentration is unaffected with time is taken implicitly here.

<sup>2</sup> The fact that the catalyst concentration is unaffected with time is taken implicitly here.

$$E1 = 1.7 \cdot 10^4 \text{ cal/mole};$$

$$E2 = 4.3 \cdot 10^4 \text{ cal/mole},$$

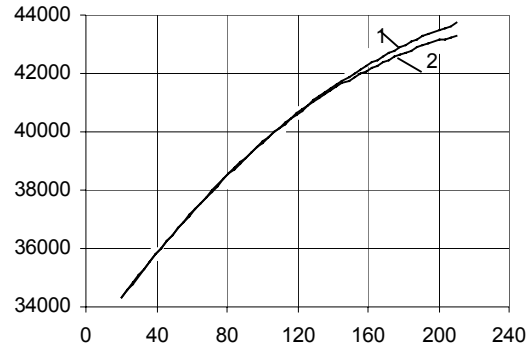
$$p1 = 0.7 \cdot 10^{-13}; p2 = 1.$$

Selection of the similar factors for PETN and PETN-based composition failed.

Figure 4 shows the two curves in 20...200°C temperature range calculated from equation (4) for HMX (the equation factors were obtained in this work) and for HMX plasticized with fluoroplastic (the factors were taken from [1]).

Despite the proximity of the calculation curves the fact of their separation after 120°C should be noted. This may be explained by the catalyzing effect produced by fluoroplastic. We note that this tendency only manifests itself at the temperatures higher than ~ 120°C. At the temperatures below 120°C the curves run together. This allows to conclude that the catalyzing effect produced by fluoroplastic on thermal decomposition of plasticized HMX is almost missing over the operational temperature range and it may be neglected.

From fig. 2 and fig .3 it follows that the same could be said about the influence of polyisobutylene on PETN thermal decomposition at operational temperatures.



**FIGURE 4. TEMPERATURE DEPENDENCE OF THE THERMAL DECOMPOSITION ACTIVATION**  
**1-HMX; 2-plasticized HMX**

#### REFERENCES

1. V.N.German, S.E.Grebennikova, G.A.Kashcheeva, L.Ye.Kornilova, S.P.Lobanova, L.V.Fomicheva, Ye.Ya.Yurin Estimation of HE thermal stability. Decomposition of plasticized HMX at operating temperatures // Proceedings of the 1998 Life Cycles of Energetic Material Conference, 29 March - 1 April 1998, Fullerton, USA, pp 174-173.
2. K.K.Andreev, A.F.Belyaev. Theory of explosives // M., Oborongiz, 1960
3. V.N.German, Ye.S.Kozlova, L.Ye.Kornilova et al. Problems of studies into decomposition kinetics of energetic materials // Energetic Materials Technology Symposium. May 18-25, 1994, Pleasanton, California.