THERMOKINETIC MODELING OF OCTOGEN DECOMPOSITION
USING THE SIMULTANEOUS THERMAL ANALYSIS DATA

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Experimental conditions of synchronous thermal analysis (STA) for gaining the reliable values of kinetic parameters and constructing a thermokinetic model of octogen decomposition were determined. A decrease in the samples' heating rate in the range of 20-0.5 K/min was shown to diminish the values of activation energy (E_a) and preexponential factor (A). E_a measured at low heating rates (2-0.5 K/min) is close to the energy of $N–NO_2$ bond cleavage, which is postulated as the first stage of the decomposition. Results of thermokinetic modeling of the octogen thermal decomposition are presented.

Keywords: differential scanning calorimetry (DSC), thermogravimetry (TG), octogen, thermal decomposition, thermokinetic modeling.

INTRODUCTION

Thermoanalytical methods are indispensable for investigation of the properties of high-energy materials: along with obtaining the physical data (temperature and heat of phase transformations — melting, evaporation, sublimation, etc.), they also provide information on the sequence of physicochemical processes, which is essential for deep insight into decomposition mechanism of high-energy materials. Moreover, thermal analysis makes it possible to describe quantitatively and qualitatively the processes of exothermic decomposition and chemical interaction, and determine the kinetic parameters of these processes.

Octogen (HMX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazole) is among the most widely used and studied high-energy materials. A complicated and multistep mechanism of HMX decomposition leads to the formation of gas phase products: HCN, NO, N_2O, NO_2, CO, CO_2, H_2O, and H_2CO. Thermal decomposition of octogen has been examined in many theoretical and experimental works; nevertheless, the mechanism of this process still remains a difficult problem. Results of thermal analysis are used to develop the global kinetic models for decomposition of octogen and octogen-based condensed high-energy systems [1].

A spread of the octogen decomposition kinetic parameters obtained in experiment is now quite high and provokes a deserved skepticism in researchers. For example, E_a varies from 42 kJ/mol to 1070 kJ/mol [2, 3], and the $E_a(\log(A))$ dependence is linear (the so-called Brill "law of compensation" [3]). This may be caused by self-heating of a sample [3]. Vyazovkin and Wight [4] showed that self-heating of explosives in STA experiment can be prevented by using the samples with a minimum weight and a low heating rate (*ca.* 1 K/min).
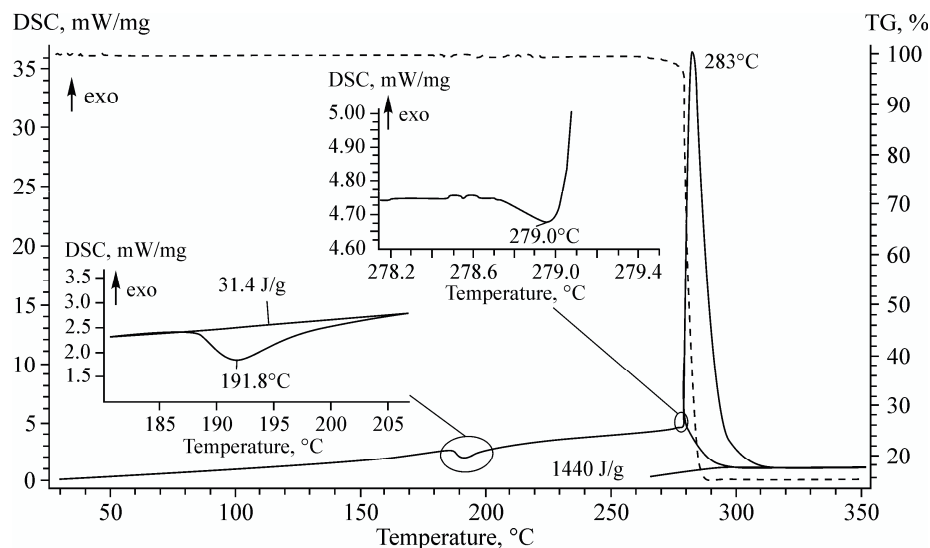
Fig. 1. Changes in the sample weight (TG — dotted line) and heat condition of the sample (DSC — solid line) upon octogen heating at a rate of 10 K/min in a dynamic atmosphere of argon (flow rate 70 ml/min, initial weight of the sample 2 mg).

The goal of this work was to determine the optimal conditions for STA study of octogen decomposition that would allow one to obtain the reliable values of kinetic parameters and develop a thermokinetic decomposition model.

THERMAL DECOMPOSITION OF OCTOGEN — A CHEMICAL ASPECT

A typical form of STA results is shown in Fig. 1; thermal analysis reveals the occurrence of two endothermic processes corresponding to the phase transition β-HMX→δ-HMX at 191°C and melting at 279°C, which is followed by exothermic decomposition process. The obtained value of the octogen phase transition heat $Q_{ph} = 31.4$ J/g is close to the literature data [5], according to which $\Delta H_{ph} = 2350$ cal/mol (33.2 J/g). Upon decomposition, the heat released in condensed phase is 1440 J/g.

A global scheme of the octogen thermal decomposition is usually described by two concurrent reactions:

$$HMX \rightarrow 4\,[N_2O + CH_2O], \text{ and} \tag{1}$$

$$HMX \leftrightarrow 4\,[HONO + HCN] \text{ or } 4\,[N_2O + HCN + H]. \tag{2}$$

Reaction (1) is exothermic ($Q = -209$ kJ/mol), while reaction (2) is endothermic ($Q = 159$ kJ/mol) [6].

According to quantum-chemical calculations, the N–NO$_2$ binding energy in the octogen molecule makes up 200.9 kJ/mol [7]. Researchers generally think that the thermal decomposition starts from homolysis of this most weak bond in the octogen molecule [3, 4, 7].

The modeling results reported in [8] allow estimating the binding energies in octogen molecule in the initial state (Fig. 2*a*) and after the detachment of one NO$_2$ group (Fig. 2*b*). Most likely is the initial cleavage of N–NO$_2$ bond with subsequent cleavage of C–N bond.

Initiation of the first stage of decomposition is followed by a complicated sequence of chemical transformations. The octogen thermal decomposition can be described most correctly by the Tarver model [9], which relies on analysis of the critical time of explosion as a function of inverse temperature in a sealed reactor with the sample. The authors suggest the scheme and main parameters of each decomposition stage (Tables 1 and 2). Stages *1* and *2* are endothermic, whereas the sublimation of solid intermediate decomposition products (stage *3*) is an exothermic process, and main heat release takes place in the gas phase at complete decomposition (stage *4*).
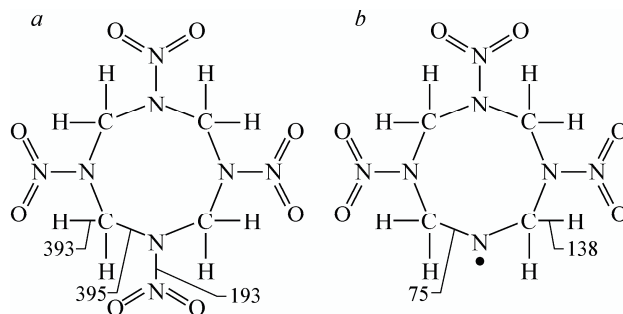
Fig. 2. Results of quantum-chemical modeling [8] — values of the binding energy (kJ/mol) in octogen molecule: *a* — initial HMX molecule, *b* — HMX molecule after detachment of one NO_2 group.

TABLE 1. Stages of Thermal Decomposition of Octogen $C_4H_8N_8O_8$ According to Model [9] with the Corresponding Peaks on DSC Curve (see Fig. 1)

Stage	Reaction	Temperature of the peak, °C
1	β-HMX → δ-HMX	198
2	δ-HMX → solid-phase IP, cleavage of N–NO_2, C–N, C–H, N–O and other bonds	280
3	Solid-phase IP → gas phase IP (CH_2O+N_2O and HCN+HNO_2)	283
4	Gas phase IP → end products (CO_2+H_2O+N_2+CO+C and others)	Not detected by DSC

TABLE 2. Kinetic and Thermal Parameters of Stages in Thermal Decomposition of Octogen According to Model [9]

Stage	ln$A$	E_a, kJ/mol	Reaction order	Reaction heat, J/g
1	48.13	202.6	1	+41.8
2	48.70	220.3	1	+250.8
3	37.80	185.2	1	−556.0
4	28.10	142.5	2	−5588.7

Stage *1* corresponds to the phase transition β-HMX→δ-HMX. At stage *2*, there occurs cleavage of N–NO_2, C–N, C–H and N—O bonds in octogen molecule. The methyl active sites form at the place of methyl bridges destruction. Stage *3* is a combination of processes of the intermediate gas phase products (IP) formation: a weakly endothermic formation of $CH_2O + N_2O$ and a weakly exothermic formation of $HCN + HNO_2$. The total heat effect of this stage is also weakly exothermic (Table 2). Note that this heat effect manifests itself as a distinct exothermic peak on DSC curves and as an abrupt weight loss on TG curves. Stage *4*, corresponding to the formation of the end gas phase products of the reaction, proceeds with a maximum heat release, which exceeds that of stage *3* by an order of magnitude.

It is known that STA records changes in the thermal condition of a sample in condensed phase, but is inapplicable to the gas phase processes. Thus, the exothermic reaction detected in condensed phase is stage *3*. However, the heat effect of decomposition reaction revealed by STA considerably exceeds the value indicated in Table 2 and is equal to 1440 J/g (Fig. 1). This is explained by superposition of the heat flows evolving in condensed phase and coming from the gas phase due to the gas phase reactions accompanied by a very pronounced heat release (stage *4*). As the experiment was performed in a closed crucible, the gas phase decomposition products could not leave the reaction zone immediately.
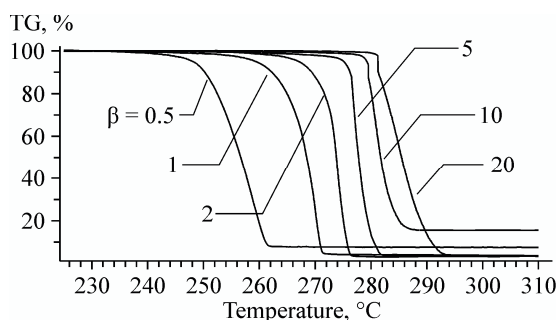
Fig. 3. Weight changes (TG) of octogen samples upon heating at a rate of 0.5-20 K/min.
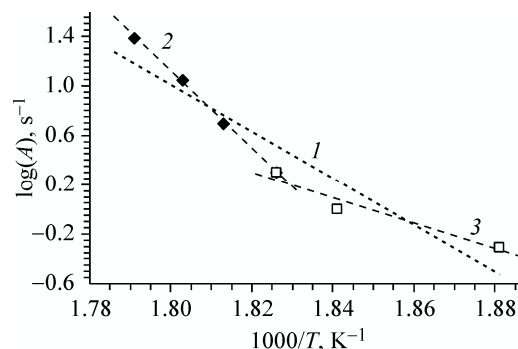

Fig. 4. The logarithm of heating rate β *versus* the inverse temperature T (Kissinger plot) for experimental results obtained upon heating the octogen samples at different rates: *1*) 0.5-20 K/min; *2*) 2-20 K/min; *3*) 0.5-2 K/min.

TABLE 3. Calculation of Kinetic Parameters of the Octogen Thermal Decomposition (model-free Kissinger method)

No.	Heating rate β, K/min	Kinetic parameters	
		E_a, kJ/mol	$\log(A)$, s^{-1}
1	0.5-20	428	39
2	2, 5, 10, 20	588	54
3	0.5, 1, 2	175	14
	[9]	184	16

EXPERIMENTAL

The study was carried out with an STA 449 F3 (Netzsch, Germany) synchronous thermal analysis instrument at heating rates β = 0.5 K/min, 1 K/min, 2 K/min, 5 K/min, 10 K/min, and 20 K/min in the temperature range of 30-400°C in argon flowing at a rate of 70 ml/min. Measurements were performed using standard powder samples of octogen (the average size of crystals was 40 μm). A 2 mg sample was placed in a corundum crucible (D = 5 mm) having a cover with a hole (d = 0.3 mm). For each heating rate, at least three experiments were conducted. The measurement data were processed using the Netzsch Proteus and Thermokinetics software packages.

RESULTS AND DISCUSSION

Figure 3 depicts TG curves obtained upon heating the octogen samples at different rates. As the heating rate (β) increases, the curves shift toward higher temperatures, thus increasing the decomposition rate of a substance.

The values of E_a and $\log(A)$ were determined by the model-free Kissinger method (ASTM E698) [10]. Fig. 4 shows a Kissinger plot, according to which the activation energy of octogen thermal decomposition obtained in experiments for all the studied heating rates is 428 kJ/mol, and $\log(A)$ = 39 s^{-1}. The obtained values are overrated in comparison with the available literature data [9, 11]. We divided the heating rate interval into two ranges with low (0.5 K/min, 1 K/min, and 2 K/min) and high (2 K/min, 5 K/min, 10 K/min, and 20 K/min) heating rates and described each range by a linear dependence; this considerably improved the accuracy and gave the values of E_a and $\log(A)$ for both ranges (Table 3).

It should be noted that the value of activation energy determined at low heating rates is close to the energy of N–NO$_2$ bond cleavage [6].

In the review [3], Brill reports many literature data on the experimentally measured E_a and $\log(A)$ values in various
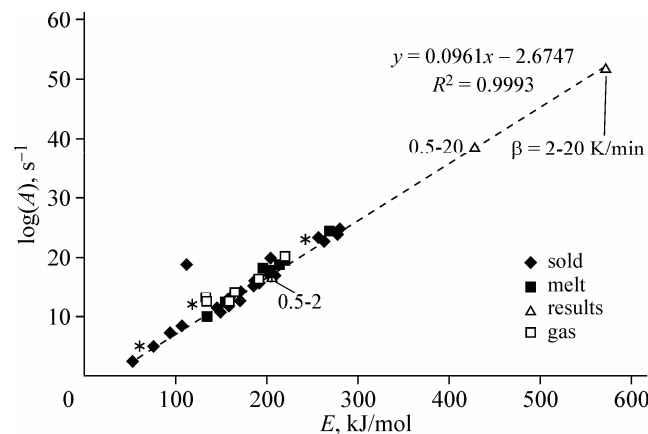
Fig. 5. Graphic representation of the Brill "law of compensation" [4]. The plot shows experimentally measured values of E_a and $\log(A)$ obtained by different authors for solid phase, melt, and gas phase decomposition as well as results of the present work.

TABLE 4. Results of Thermokinetic Modeling: a Single-Stage Model

No.	Reaction type	F_{exp}	$F_{crit}(0.95)$
1	C_1B	1.00	1.05
2	B_na	1.03	1.05
3	C_nB	1.04	1.05
4	A_n	1.06	1.05
5	A_3	1.31	1.05
6	A_2	2.84	1.05
7	B_1	3.20	1.05

phases and under different conditions. Graphic representation of results obtained in [4] and kinetic parameters of decomposition acquired in our study are shown in Fig. 5. A big spread in the $E_a(\log A)$ values is caused by additional physical factors (self-heating of the sample, sample weight, conditions of heat removal, the presence of reactor walls, etc.). Brill indicates the range of activation energy variation as 155-222 kJ/mol (Fig. 5), which corresponds to the chemical process of N–NO$_2$ bond cleavage. The use of low heating rates prevents self-heating of the samples: kinetic parameters obtained in this case are close to numerous literature data and fall in the region of "chemical correctness." Results obtained upon heating at higher rates are far beyond this region.

Thermokinetic modeling of the octogen thermal decomposition (Table 4) performed with TG data for the heating rate of 0.5-2 K/min demonstrated that the process is reliably described by three types of chemical reactions with autocatalysis: C_1B — by the first order reaction, B_na — by an extended Prout–Tompkins equation, and C_nB — by the nth order reaction. For these reaction types, the calculated Fisher's variance ratio (F_{exp}) does not exceed a statistical quantile $F_{crit}(0.95)$ [12]. However, most appropriate is the first order autocatalytic reaction having $F_{exp} = 1$:

$$\frac{d\alpha}{dt} = -A e^{-\frac{E_a}{RT}} \alpha(1 + k_{cat}b),$$

where $\alpha = (m_0 - m)/(m_0 - m_\infty)$ is the conversion of a substance (m_0 — initial sample weight, m — current sample weight, m_∞ — final sample weight); $A = 10^{13}$ s^{-1} is the preexponential factor; $E_a = 178$ kJ/mol is the activation energy; $k_{cat} = 10^{2.23}$ is the catalytic coefficient; and b is the concentration of end products (for single-step processes, $b = 1 - \alpha$).
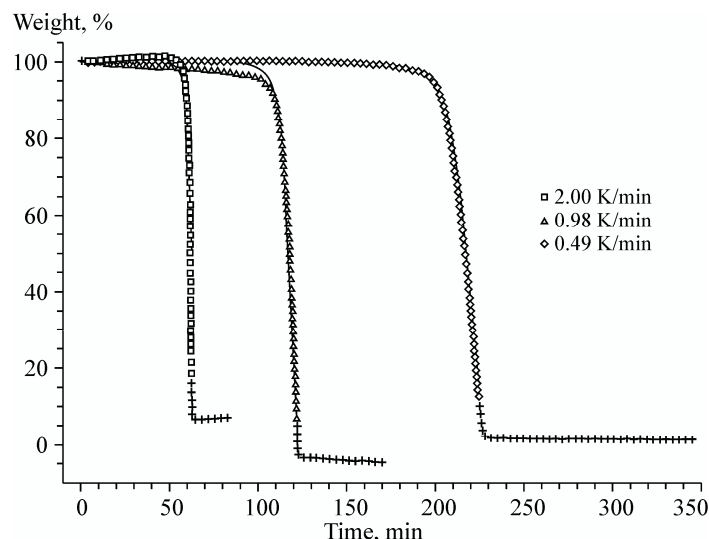
Fig. 6. Results of modeling the octogen thermal decomposition using the first order autocatalytic reaction: solid lines — calculation, dots — experimental data.

Figure 6 presents the experimental data and results of modeling the octogen thermal decomposition using the first order autocatalytic reaction. The correlation coefficient for the obtained dependences and measurement data was 0.986.

CONCLUSIONS

A dependence of the octogen thermal decomposition kinetic parameters on the heating rate was studied using synchronous thermal analysis. The heating rate was shown to strongly affect the decomposition onset temperature and the sample decomposition rate: the lower is the heating rate, the earlier starts the weight loss, and the slower is the sample decomposition. Activation energy and preexponential factor were calculated by the model-free Kissinger method. In the heating rate ranges 0.5-20 K/min and 2-20 K/min, the calculated values of E_a and $\log(A)$ are considerably overrated in comparison with the literature data and quantum-chemical estimates for the octogen decomposition process. All the obtained values of $E_a(\log(A))$ lie on the Brill "law of compensation" line. However, only the values calculated for low heating rates of the samples (0.5-2 K/min) fall in the region of "chemical correctness." Thermokinetic modeling of the decomposition process was made; the best fit with experimental data was provided by describing the decomposition kinetics by the first order autocatalytic model.

It was demonstrated that correct kinetic parameters for decomposition of high-energy components can be obtained if STA study is performed at low heating rates and small sample weight. Results of the study can be used to develop the physicochemical decomposition models of octogen, other explosives, and high-energy condensed systems on their basis.

REFERENCES

1. J. Wang and C. A. Wight, in: *Energetic Materials, Part 2: Detonation, Combustion. Theoretical and Computational Chemistry*, Vol. 13, P. A. Politzer and J. S. Murray (eds.), Elsevier B.V. (2003), pp. 351-371.
2. J. Kimura and N. Kubota, *Propell. Expl. Pyrotech.*, **5**, No. 1, 1 (1980).
3. T. B. Brill, P. E. Gongwer, and G. K. Williams, *J. Phys. Chem.*, **98**, No. 47, 12242 (1994).
4. S. Vyazovkin and C.A. Wight, *Ann. Rev. Phys. Chem.*, **48**, 119 (1997).
5. *NIST, July 2001 Release. Standard Reference Database*, No. 69.

6. T. B. Brill and R. J. Karpowicz, *J. Phys. Chem.*, **86**, No. 21, 4260 (1982).

7. S. F. Melius, in: *Chemistry and Physics of Energetic Materials*, S. Bulusu (ed.), Kluwer Academic, Dordrecht (1990), pp. 21-78.

8. L. Minier and R. Behrens, *Proc. 32nd JANNAF Comb. Subcommittee*, **1**, 13 (1995).

9. C. M. Tarver and T. D. Tran, *Combustion and Flame*, **137**, 50 (2004).

10. H. E. Kissinger, *J. Anal. Chem.*, **29**, No. 11, 1702 (1957).

11. R. Shaw and F. E. Walker, *J. Phys. Chem.*, **81**, 2572 (1977).

12. H-W. Jank and A. Meister, *Kulturpflanze*, **30**, 30 (1982).