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Obtaining kinetic data of energetic material decomposition by differential thermal analysis

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Abstract

A study was made by differential thermal analysis (DTA) to obtain the kinetic parameters of decomposition of energetic materials. The calculation utilized direct experimental results as well as the model described earlier by the authors. The energetic materials investigated were TNT, Tetryl, PETN, RDX, and HMX. The kinetic data obtained were in very good agreement with literature data. The characteristics of thermal decomposition of these explosives were determined. The effect of heating rate on the decomposition of the explosives was also studied.

INTRODUCTION

In view of its advantages of rapidity and convenient operation, differential thermal analysis (DTA) has been widely applied to determine reaction kinetics and thermal properties of energetic materials. There are several methods proposed to calculate the kinetic parameters. Kissinger [1] proposed a semidirect procedure to determine the activation energy (E). In applying Kissinger's method, however, several DTA curves with different heating rates are required. The method proposed by Borchardt and Daniels [2] involved an analysis of the area under the DTA curve. They assumed that the rate of reaction is very small at the lowest temperature practically attainable and that the heat capacity, heat transfer coefficient and heat of reaction do not vary over the temperature interval where the reaction occurs. Unfortunately, those assumptions do not apply to the decomposition reaction of energetic materials.

Yang and Steinberg [3] pointed out that the shape of DTA curve changes in line with the reaction order. They proposed therefore, a model that employed the characteristic temperatures, such as the peak tempera-

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ture (T_m), the two inflection temperatures (T_{i1} and T_{i2}) and the end temperature (T_e), to estimate kinetic parameters. Liu et al. [4] modified Yang and Steinberg's model and obtained a somewhat more convenient one. However, the methods of both Yang and Steinberg and Liu et al. are still complicated and have to be solved by a trial and error approach. Huang et al. [5] recently presented a more convenient and simple method for rapidly determining the kinetic parameters from a single DTA curve. Verification of the theorem was achieved in the same paper with the DTA curves reported in literature. The purpose of this paper is to evaluate the model proposed by the authors with use of DTA measurements on five energetic materials. The tests cover five organic explosives: trinitrotoluene (TNT), Tetryl, pentaerythritol tetranitrate (PETN), cyclotrimethylene trinitramine (RDX) and cyclotetramethylene tetranitramine (HMX). The characteristics of thermal decomposition of these explosives were determined, and the effect of heating rate on their decomposition was also studied.

THEORETICAL MODELING

Most decomposition reactions of a solid can be described by a general rate equation

$$\frac{\mathrm{d}x}{\mathrm{d}t} = A(1-x)^n \, \mathrm{e}^{-E/RT} \tag{1}$$

Huang et al. [5] employed the approximate equation of the thermogram derived by Doyle [6], and produced the following equations

$$\Delta T = \beta A \, \mathrm{e}^{-E/RT} \left[\frac{ART^2}{\phi E} \mathrm{e}^{-E/RT} (n-1) + 1 \right]^{n/(1-n)} \tag{2}$$

For $n < 1$

$$\ln(1-n) \frac{T_e^2}{T_m^2} = -\frac{E}{R} \left(\frac{T_e - T_m}{T_e T_m} \right) \tag{3}$$

For $n = 1$

$$\frac{E}{RT_i^2} \left(\frac{E}{RT_i^2} - \frac{3A}{\phi} \mathrm{e}^{-E/RT_i} - \frac{2}{T_i} \right) = -\frac{A^2}{\phi^2} \mathrm{e}^{-2E/RT_i} \tag{4}$$

For $n > 1$

$$\left(\frac{E}{RT_i^2} \right)^2 - \frac{3nAE}{\phi RT_i^2} \mathrm{e}^{-E/RT_i} \alpha_i + \frac{n(2n-1)}{\phi} A^2 \, \mathrm{e}^{-2E/RT_i} \alpha_i^2 = 0 \tag{5}$$

where

$$\alpha_i = \left[\frac{ART_i^2}{\phi E} e^{-E/RT_i}(n-1) + 1 \right]^{-1} \tag{6}$$

Equation (4) is the same as one which Yang and Steinberg [3] derived. The derivation of the above equations was described in detail in our earlier paper [5].

To estimate the reaction order (n), Kissinger [1] reported a convenient semi-empirical equation

$$n = 1.26\ S^{1/2} \tag{7}$$

Krug [7] pointed out that, if S is between 0 and 0.63, eqn. (7) could give a good result for determining the reaction order. He presented eqn. (8) for the case when S is larger than 0.63 and less than 1.17

$$n = \sqrt{\frac{S - 0.45}{0.18}} \tag{8}$$

According to the DTA curve, one can easily obtain the reaction order from eqn. (7) or (8). Then the activation energy (E) of a decomposition reaction can be obtained by a simple calculation with the appropriate one of eqns. (3), (4) and (5).

No matter what the reaction order is, the frequency factor (A) can be calculated by using the equation

$$A = \frac{\phi E}{RT_m^2} e^{E/RT_m} \tag{9}$$

Equation (9) implies that the frequency factor is affected by the heating rate and is independent of the reaction order. Substituting eqn. (9) into eqn. (2), the relationship between the peak temperature and the heating rate is obtained if the activation energy is held constant.

$$\Delta T_m T_m^2 \propto \phi \tag{10}$$

Equation (10) implies that the peak temperature of the DTA curve as well as the height of the peak should increase as the heating rate increases.

EXPERIMENTAL

This work was performed with a DuPont 910 thermal analysis system type 1600 differential thermal analyzer. As a standard material, pure silver, was used to calibrate temperature measurements. The heating rates applied were 6, 10 and 15°C min^{-1}. A nitrogen purge flow of 50 ml min^{-1} was employed. The energetic materials investigated were TNT, Tetryl, PETN, RDX, and HMX. Since these five explosives decompose exothermi-

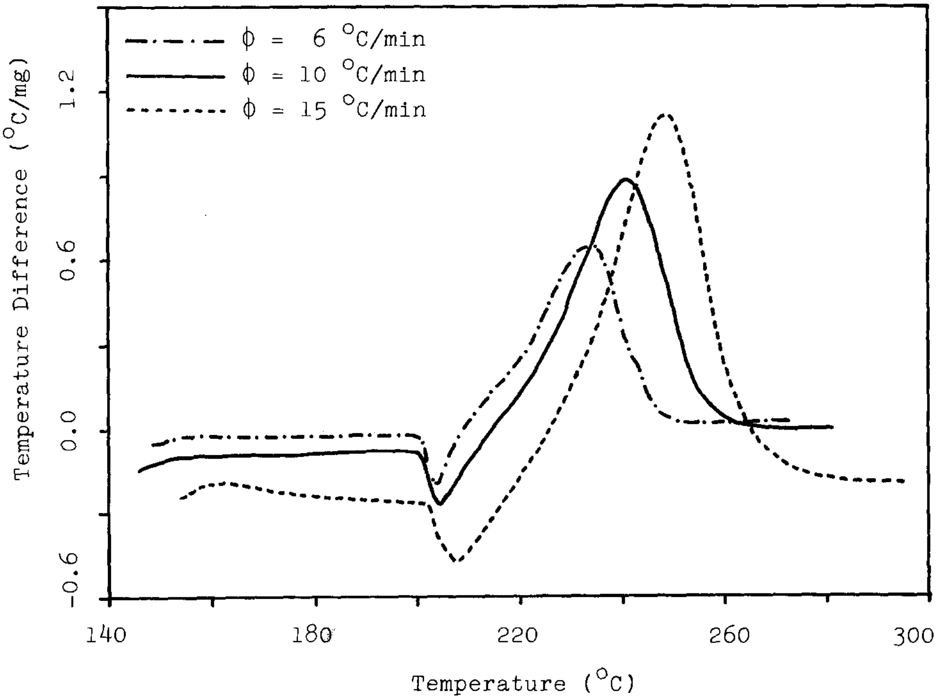

Fig. 1. DTA thermograms of RDX at various heating rates with N_2 flow rate of 50 ml min^{-1}.

cally in the condensed state with a high heat of reaction, sample sizes were kept as small as a few milligrams. In all DTA measurements the samples, except TNT, were placed in an open aluminum cell. The TNT samples were put in a hermetically sealed aluminum cell to limit the escape of TNT vapor.

RESULTS AND DISCUSSION

Decomposition kinetics studies

RDX

The DTA thermograms of RDX at heating rates of 6, 10 and 15°C min^{-1} are shown in Fig. 1. The melting point of RDX is around 205°C, which is very close to the literature value [15]. The exothermic and endothermic peaks of the DTA curves are not clearly separated. This implies that RDX might decompose at a temperature as low as its melting point. It is also found that the peak temperature (T_m) of the exothermic curve shifts to a high value as the heating rate increases. The shape indexes, S, of the DTA curves at heating rates of 6, 10 and 15°C min^{-1} are 0.455, 0.545 and 0.58, respectively. Therefore the reaction order of RDX decomposition is less than one. The characteristic temperatures of the DTA curves of RDX are

TABLE 1

Characteristic temperatures of DTA curves at various heating rates

Compound	Sample weight (mg)	ϕ (°C min^{-1})	T_m (°C)	T_{i1} (°C)	T_e (°C)
RDX	2.8	6	233.4	225.4	254.9
	2.7	10	240.9	238.9	272.4
	2.8	15	248.3	241.7	286.5
HMX	1.6	6	283.2	278.1	296.1
	1.6	10	287.2	281.9	308.4
	1.6	15	290.4	286.0	323.8
Tetryl	3.4	6	202.2	196.8	219.8
	3.5	10	211.1	203.5	232.5
	3.4	15	218.3	212.9	243.5
PETN	3.6	6	197.7	188.5	229.4
	3.6	10	206.1	196.2	247.2
	3.6	15	213.2	203.5	249.8
TNT	4.8	6	304.2	302.7	320.2
	4.8	10	318.4	315.7	338.5
	4.8	15	328.5	325.1	362.9

listed in Table 1. By using eqns. (7), (3) and (9), the reaction order, the activation energy and the frequency factor of RDX decomposition were determined. The activation energy was also calculated by the Kissinger method with three DTA curves. The kinetic parameters obtained, as well as literature data, are listed in Table 2. The activation energy obtained by the authors' model is around 45 kcal mol^{-1}. However, it is as low as 32.6 kcal mol^{-1} when the Kissinger method is applied. Kishore [8] pointed out that the decomposition mechanisms of RDX are different in an open and in a closed system, and reported an activation energy of 42.0 kcal mol^{-1} under a nitrogen purge. Oyumi [9] studied the thermal decomposition of RDX under argon flow and found that the activation energy is between 43.1 and 47.9 kcal mol^{-1}. As shown in Table 2, the activation energies obtained by this study are similar to those reported by other researchers [11,12].

HMX

Figure 2 shows the DTA results for HMX at various heating rates. A sample weight of 1.6 mg was used in this investigation. However, the exothermic peak is so sharp and so high that the endothermic peak seems to be trivial. It is also evident from Fig. 2 that the exothermic peak and the endothermic peak are not clearly separated. That is, a rapid decomposition reaction of HMX took place at slightly above its melting point and a lot of

TABLE 2

Kinetic parameters of the thermal decomposition of explosives

Compound	Calculated by this method				Calculated by the Kissinger method	Values in literature		
	ϕ (°C min^{-1})	n	E (kcal mol^{-1})	A (s^{-1})	E (kcal mol^{-1})	n	E (kcal mol^{-1})	Ref.
RDX	6	0.85	44.9	2.0×10^{17}	32.6	0.6	42.0	8
	10	0.93	44.8	1.8×10^{17}		1.0	43.1–47.9	9
	15	0.96	46.8	8.9×10^{17}			45.2	11
							47.5	12
						0	67.5	18
HMX	6	0.67	51.7	1.8×10^{19}	82.0	1.0	52.7	13
	10	0.82	50.0	4.2×10^{17}		0.86	54.0	4
	15	0.95	57.8	5.9×10^{20}			177.0	14
							228.0 ± 24	18
						1.0	52.7 (liq.)	16
						1.0	52.9 (vap.)	16
Tetryl	6	0.73	32.7	7.9×10^{12}	25.3	1.0	34.9	13
	10	0.79	33.6	1.7×10^{13}		0.0	54.9	18
	15	0.81	31.2	1.2×10^{12}		1.0	38.4	15
PETN	6	1.1	47.0	7.0×10^{19}	25.79	1.0	33.0	10
	10	1.24	46.6	3.1×10^{19}		1.0	47.0	13
	15	1.29	47.3	4.5×10^{19}		1.0	47.0	15
TNT	6	1.65	22.0	7.1×10^{5}	19.3	1.0	24.2	10
	10	1.75	21.0	2.9×10^{5}			14.0	16
	15	(2.66)				0	29.4	17

heat was released. From the DTA thermograms, all three shape indexes are less than 0.63; in other words, the reaction order of HMX decomposition is less than one. By applying eqns. (3) and (9) with the characteristic temperatures listed in Table 1, the kinetic parameters of HMX decomposition were obtained, and are listed in Table 2. The activation energies obtained by this study are around 55 kcal mol^{-1}, which are in agreement with some literature data. Kimura and Kubota [14] employed thermogravimetry (TG) and differential scanning calorimetry (DSC) to study the thermal decomposition process of HMX. They reported an activation energy of 177 kcal mol^{-1}, which is compatible with the values obtained by Rogers and Morris [18]. Kimura and Kubota explained the large difference in the activation energies of HMX by the existence of a run-away reaction by self heating and of an autocatalytic reaction. From Table 2, it is clear that the reaction order and the activation energy of HMX decomposition are affected by the heating rate. It may be noted that the Kissinger method

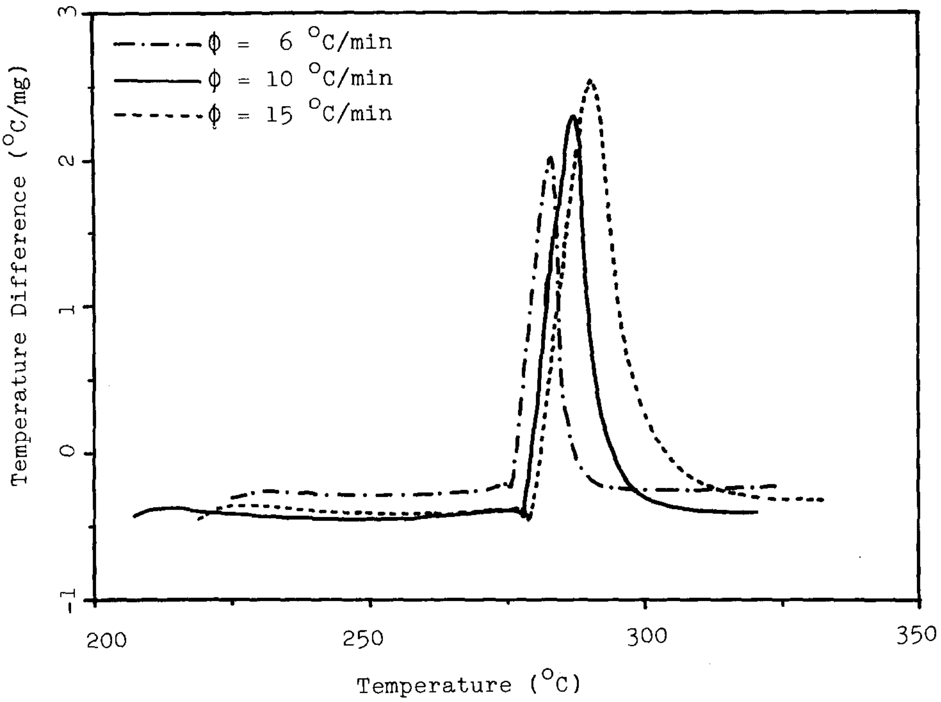

Fig. 2. DTA thermograms of HMX at various heating rates with N_2 flow rate of 50 ml min^{-1}.

is not suitable to calculate the activation energy of HMX decomposition. Harris [10] reported similar results.

Tetryl

The DTA curves of Tetryl at heating rates of 6, 10 and 15°C min^{-1} are shown in Fig. 3. The melting point of Tetryl is around 130°C, which is very close to the literature data [15]. From the DTA thermograms, all three shape indexes are less than 0.63. The reaction order of Tetryl decomposition was considered to be around 0.8. By applying eqns. (3) and (9) with the characteristic temperatures listed in Table 1, the activation energy and the frequency factor of the Tetryl decomposition reaction were obtained, and are listed in Table 2. The activation energies obtained by this study agree with literature data [13,15]. The activation energy was also calculated by the Kissinger method and was found to be lower than reported values.

PETN

Figure 4 presents the DTA measurements on PETN at heating rates of 6, 10 and 15°C min^{-1}. The melting point of PETN is around 142°C, which is very close to that reported by Gibbs and Popolato [15]. From the DTA thermograms, all three shape indexes are larger than 0.63. In other words,

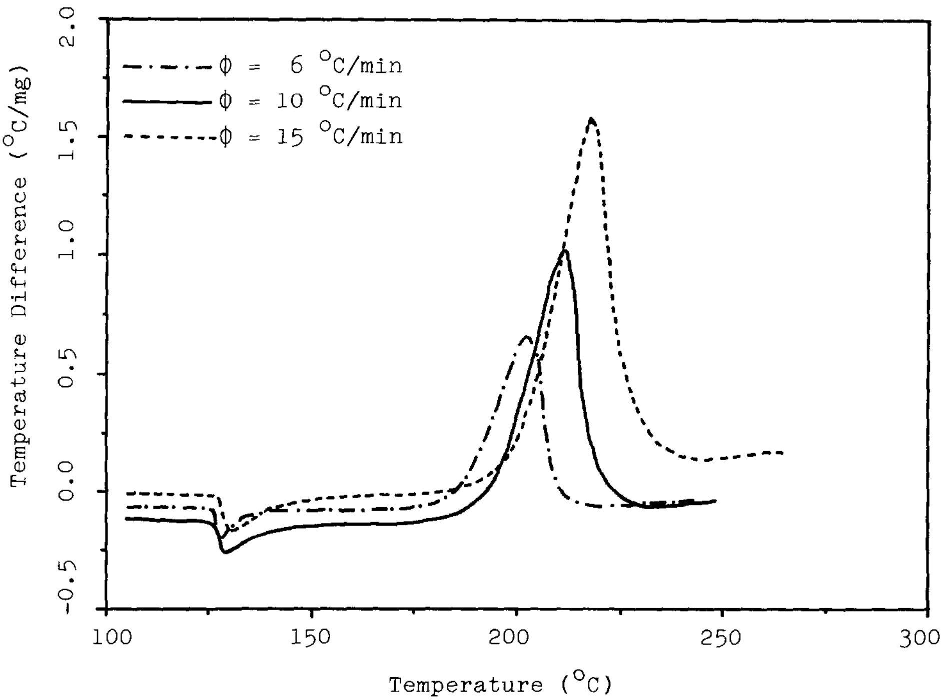

Fig. 3. DTA thermograms of Tetryl at various heating rates with N_2 flow rate of 50 ml min^{-1}.

the reaction order of PETN decomposition is greater than one. By applying eqns. (5) and (9) with the characteristic temperatures listed in Table 1, the activation energy and the frequency factor of the PETN decomposition reaction were determined, and are listed in Table 2. The activation energies obtained by this study are in good agreement with literature data [13,15]. However, when Kissinger's method was used, the activation energy was lower than that obtained by this study.

TNT

The DTA measurements on TNT at different heating rates are given in Fig. 5. The melting point of TNT is around 80°C, which is very close to the value reported by Gibbs and Popolato [15]. All three shape indexes of the DTA curves are larger than 0.63. That is, the reaction order of TNT decomposition is greater than one. For the run with a heating rate of 15°C min^{-1} the shape index is larger than 1.17 and it was out of the range of our model to calculate the reaction order. The value listed in Table 2 was obtained by eqn. (8). It seems that the decomposition mechanism of TNT alters as the heating rate increases to 15°C min^{-1}. By applying eqns. (5) and (9) with the characteristic temperatures listed in Table 1, the activation energy and the frequency factor of the TNT decomposition reaction were

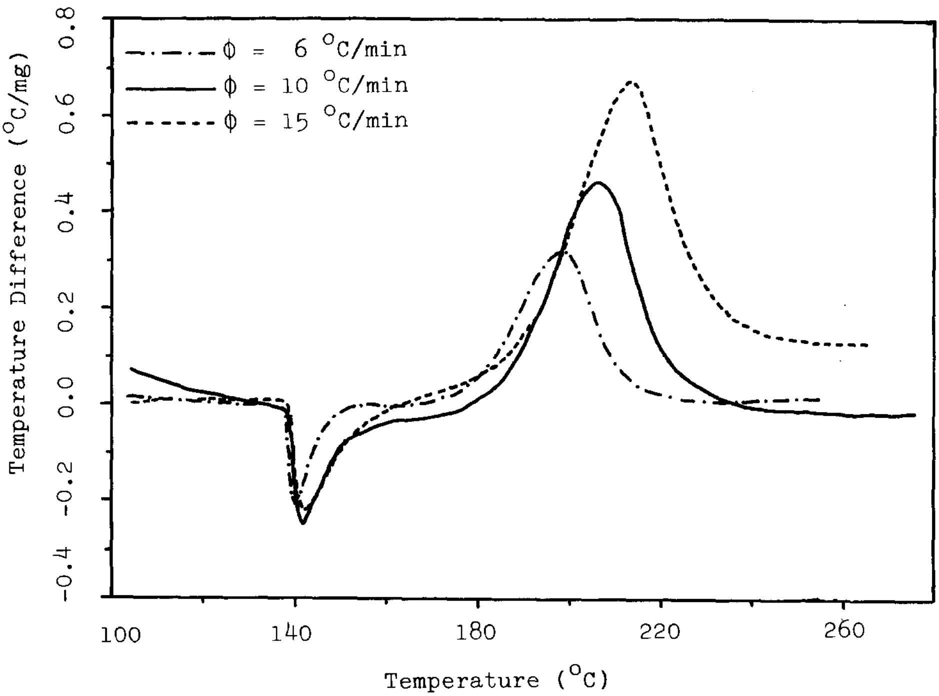

Fig. 4. DTA thermograms of PETN at various heating rates with N_2 flow rate of 50 ml min^{-1}.

determined except for the run with heating rate 15°C min^{-1}. The data obtained are listed in Table 2. The activation energies obtained by this study are in agreement with literature data [10]. The activation energy calculated by the Kissinger method is also listed in Table 2 for comparison.

Effect of heating rate on decomposition of explosives

As shown in Figs. 1–5, the peak temperatures of the exothermic curves shift to higher values as the heating rate increases. In general, the kinetic parameters of a reaction are independent of heating rate if the reaction mechanism is the same. As listed in Table 2, the kinetic data obtained are almost independent of heating rate except for HMX and TNT. This finding implies that the decomposition mechanisms of HMX and TNT are different at the various heating rates. Kimura and Kubota [14] studied the thermal decomposition of HMX and reported that the heating rate is a decisive parameter in determining the kind of elementary process that appears and in what phase the decomposition occurs. From eqn. (10), the product of ΔT_m and T_m^2 is proportional to the heating rate under the same reaction mechanism. Figure 6 illustrates the relationship between $(\Delta T_m T_m^2)$

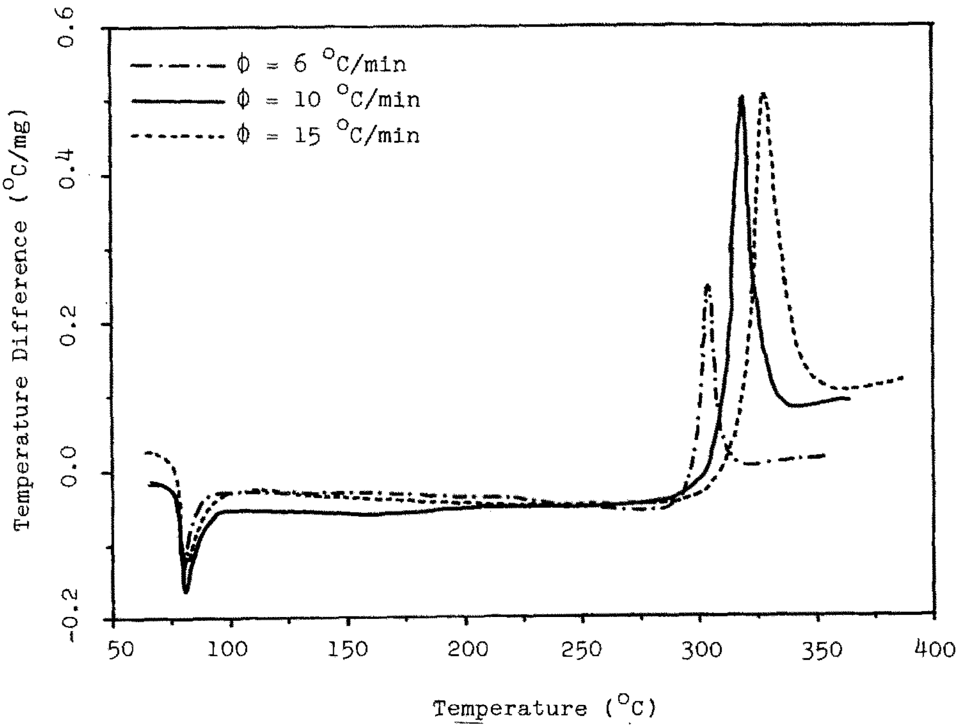

Fig. 5. DTA thermograms of TNT at various heating rates with N_2 flow rate of 50 ml min^{-1}.

and ϕ. It is found that the plots are straight lines except for HMX and TNT. The decomposition mechanisms of RDX, Tetryl and PETN remain the same over the heating rate range between 6 and 15°C min^{-1}.

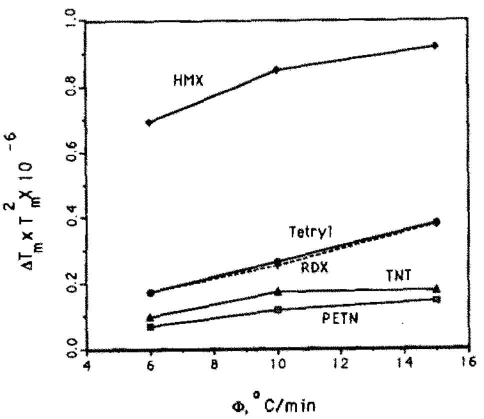

Fig. 6. Relationship between $\Delta T_m T_m^2$ and heating rate ϕ.

CONCLUSIONS

The decomposition reactions of five energetic materials were measured by a differential thermal analyzer with three heating rates. The kinetic parameters of the decomposition reactions were determined by a simple method proposed earlier by the authors. The activation energies obtained are in good agreement with literature data. The decomposition reaction peak temperatures of the DTA curves shift to higher values with increasing heating rate of the DTA operations. The reaction order as well as the decomposition mechanism of HMX and TNT are found to vary according to the heating rate.

NOTATION

A	frequency factor of the Arrhenius equation
E	activation energy of decomposition reaction
n	reaction order
R	gas constant
S	shape index of DTA curve
T	absolute temperature
T_{i1}, T_{i2}	inflection temperature of DTA curve
T_m	peak temperature of DTA curve
T_0	starting decomposition temperature of DTA curve
t	time
x	fraction of material reacted

Greek letters

α	factor as in eqn. (6)
β	proportionality constant
Δ	difference
ϕ	constant heating rate

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