

A simple method for estimating the autoignition temperature of solid energetic materials with a single non-isothermal DSC or DTA curve

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Abstract

A simple method was derived for determining the autoignition temperature of solid energetic materials with high activation energies. The calculation is straightforward. The only parameters employed are the activation energy of the decomposition reaction and the temperature at the beginning of the steepest slope on a single non-isothermal DSC or DTA exotherm. The energetic materials investigated were the conventional explosives RDX, HMX, Tetryl, PETN, TNT and nitrocellulose. Published DSC data for NTO explosive and its salt derivatives were cited to predict their autoignition temperatures. One energetic polymeric binder, GAP, and its mixtures with RDX or HMX were also examined. The autoignition temperatures obtained for the tested materials are in very good agreement with literature data.

LIST OF SYMBOLS

- A Arrhenius frequency or pre-exponential factor/ s^{-1}
 E activation energy/ $J mol^{-1}$
 k overall heat transfer coefficient/ $W m^{-2} K^{-1}$
 n reaction order
 Q heat of reaction/ $J g^{-1}$
 q_1 heat liberated within the reactor during unit time/ J
 q_2 heat transferred by the wall of the reactor to the surrounding medium/ J
 R gas constant/ $J mol^{-1} K^{-1}$
 S external surface of the reactor/ m^2
 T_a autoignition temperature/ K
 T_i temperature at the beginning of the steepest slope on the DTA or DSC exotherm/ K
 T_m temperature at the maximum rate of decomposition on the DTA or DSC exotherm/ K

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- T_s temperature of the surface of the reactor/K
 t time/s
 x fraction of material reacted
 ϕ heating rate/K min⁻¹

INTRODUCTION

Most energetic materials with high activation energies, such as solid explosives, decompose exothermally at temperatures above absolute zero. For safety reasons, it is desirable to be able to predict the response of energetic materials to high temperatures. When chemical decomposition produces heat faster than it can be dissipated to the surroundings, the material mass self-heats to ignition, even to explosion. The lowest temperature at which self-heating occurs followed by ignition is considered to be the autoignition temperature [1]. In some cases, the explosives self-heat to explosion, this temperature being termed the critical temperature [2].

The autoignition temperature of explosives is usually experimentally determined by a slow cook-off method [3]. However, this takes a long time. In steady-state conditions, a simple expression for the critical temperature has been derived by Frank-Kamenetskii (the F-K equation) [4], which includes the kinetic and physical parameters. The kinetic and physical parameters should be given when the F-K equation is applied. Zinn and his co-workers [5, 6] have reported a method for calculating the initial temperature of a thermal explosion system through induction times and bath temperatures. Isler [7, 8] presented a modelization of the process resulting in the autoignition of munitions filled with nitrocellulose-based propellant. Harris [1] developed a method in which several heating rates were utilized in differential thermal analysis (DTA) and the related data extrapolated to a near-zero heating rate to obtain the autoignition temperatures (T_a). A first-order exponential equation derived by Kissinger was employed to calculate the activation energy. Recently, Xie et al. [9] applied a reaction rate equation derived by Hu et al. [10] to derive an equation for estimation of the critical temperature of 3-nitro-1,2,4-triazol-5-one (NTO) and its salt derivatives from a single non-isothermal differential scanning calorimetric (DSC) curve. However, the equation is complicated and has to be solved by a trial-and-error approach. Accordingly, the aim of this paper is to propose a simpler and more convenient method for rapidly calculating the autoignition temperature of solid energetic materials from a single non-isothermal DTA or DSC curve.

THEORETICAL

According to the Arrhenius equation, most decomposition reactions of an energetic material with high activation energy can be described by a general rate equation

$$\frac{dx}{dt} = A \exp\left(\frac{-E}{RT}\right) f(x) \quad (1)$$

where $f(x)$ represents the differential mechanism functions. In a general case, $f(x) = (1 - x)^n$, where n is the reaction order. For energetic materials with high activation energies ($80\text{--}250 \text{ kJ mol}^{-1}$), the transition from thermal decomposition to thermal explosion starts in the range of low conversion degree, i.e. $f(x) \approx 1$. Equation (1) can be simplified to the form

$$\frac{dx}{dt} = A \exp\left(\frac{-E}{RT}\right) \quad (2)$$

If Q is the amount of heat released per unit mole of explosive decomposed, the corresponding heat q_1 liberated within the reactor in unit time will be

$$q_1 = AQ \exp\left(\frac{-E}{RT}\right) \quad (3)$$

In the progress of a dynamic DTA (or DSC) measurement, the temperatures of the sample and reference material increase according to $T = T_0 + \phi t$, before reaching the initial temperature of decomposition. In other words, the baseline is linear before the exothermic reaction occurs. The amount of heat transferred by the wall of the reactor to the surrounding medium is

$$q_2 = kS(T_s - T) \quad (4)$$

As the temperature increases high enough, the sample starts to decompose and to release heat, and the DTA or DSC curve starts to deviate from the baseline. This indicates that the rate of increase of the sample temperature is larger than the programmed value ϕ . The temperature at which the thermal explosion starts is called the autoignition temperature T_a and the temperature of the reference material is designated T_i ($T_i = T_0 + \phi t$). This point would occur on a DTA (or DSC) exotherm at the beginning of the steepest slope [1]. Therefore, eqns. (3) and (4) become

$$q_1 = AQ \exp\left(\frac{-E}{RT_a}\right) \quad (5)$$

and

$$q_2 = kS(T_i - T_a) \quad (6)$$

According to Semenov's theory [11], the sufficient and necessary conditions for a thermal explosion are

$$(q_1)_{T_a} = (q_2)_{T_a} \quad (7)$$

and

$$\left(\frac{dq_1}{dt}\right)_{T_a} = \left(\frac{dq_2}{dt}\right)_{T_a} \quad (8)$$

From eqns. (3) and (4), the differential forms are obtained

$$\left(\frac{dq_1}{dt}\right)_{T_a} = A Q \frac{E}{RT_a^2} \exp\left(\frac{-E}{RT_a}\right) \left(\frac{dT}{dt}\right)_{T_a} \quad (9)$$

and

$$\left(\frac{dq_2}{dt}\right)_{T_a} = k S \left[\left(\frac{dT}{dt}\right)_{T_a} - \phi \right] \quad (10)$$

Substituting eqns. (9) and (10) into eqn. (8), we have

$$k S \left[\left(\frac{dT}{dt}\right)_{T_a} - \phi \right] = A Q \left(\frac{E}{RT_a^2}\right) \exp\left(\frac{-E}{RT_a}\right) \left(\frac{dT}{dt}\right)_{T_a} \quad (11)$$

Substituting eqns. (5) and (6) into eqn. (7), and then combining with eqn. (11), the following is obtained

$$\frac{(dT/dt)_{T_a} - \phi}{T_i - T_a} = \left(\frac{E}{RT_a^2}\right) \left(\frac{dT}{dt}\right)_{T_a} \quad (12)$$

For most explosives, the exothermic peak in DTA or DSC thermoscans is rather steep. Therefore, as the thermal explosion starts, $(dT/dt)_{T_a} \gg \phi$, and eqn. (12) can be simplified to the form

$$T_a^2 = \frac{E}{R} (T_i - T_a) \quad (13)$$

This is a typical quadratic equation. One of the two roots is negative, which is nonsensical and discarded

$$T_a = \frac{-\frac{E}{R} + \sqrt{\left(\frac{E}{R}\right)^2 + 4\left(\frac{E}{R}\right)T_i}}{2} \quad (14)$$

Once the values of T_i and E are given from a DTA or DSC curve, the autoignition temperature of the energetic material is easily obtained by a straightforward calculation using eqn. (14).

EXPERIMENTAL

A Du Pont 9900 thermal analysis system with a 1600 type differential thermal analyzer (DTA) was employed to investigate the thermal decomposition of energetic materials. Linear heating rates of 6, 10 and 15 K min⁻¹ were applied. A nitrogen purge flow of 50 ml min⁻¹ was maintained throughout all experiments. The energetic materials investigated were cyclotrimethylenetrinitramine (RDX), cyclotetramethylene-tetranitramine (HMX), Tetryl, pentaerythritol tetranitrate (PETN), 2,4,6-trinitrotoluene (TNT), nitrocellulose, and glycidyl azide polymer (GAP). Because these materials decompose exothermically and rapidly, sample sizes were kept to a few milligrams.

TABLE 1

Calculated autoignition temperatures of NTO series explosives

Sample	T_i /K	E /kJ mol ⁻¹	T_a^a /K	$T_{a(F-K)}$ /K	$T_{a(Z-M-R)}$ /K	$T_{a[9]}$ /K	T_a^b /K
NTO	544.8	365.8	513	520.8	529.6	528.2	538.2
ENTO	521.8	175.4	497	488.8	517.5	493.3	509.5
KNT0	520.3	180.7	491	495.2	495.6	488.3	508.4
PbNTO	483.4	239.1	472	454.0	476.6	464.3	475.5
CuNTO	485.4	136.2	463	475.2	—	445.3	471.8
Ref.	9	9	9	9	9	9	This method

^a Experimental values measured by Xie et al. [9] using a small-scale time-to-explosion experiment equipment. ^b Values calculated by the present method.

RESULTS AND DISCUSSION

NTO series explosives by DSC measurements

A general theorem has been derived for determining the autoignition temperature of an energetic material from a single non-isothermal DSC or DTA curve, as described above. To demonstrate the applicability of the obtained theorem, published DSC scans of NTO series explosives [9] have been employed in conjunction with the derived equation. The activation energy and T_i values were given by Xie et al. [9]. The calculated autoignition temperatures are compared with literature data in Table 1. The temperatures calculated by the Frank-Kamenetskii (F-K) equation, the Zinn-Mader-Rogers (Z-M-R) method, and the equation proposed by Xie et al. [9] are also listed in Table 1. It can be seen that the autoignition temperatures calculated from the present method are in good agreement with the literature values. In comparison with the experimental values (obtained by Xie et al.) of T_a , the relative error is less than 4.9%.

DTA measurements of six conventional explosives

In the present method for calculating the autoignition temperature, only two parameters (T_i and E) can be obtained from a single DTA or DSC scan. Recently, Huang et al. [12] derived relationships for determining the activation energy of a general n th order decomposition reaction from a single DTA curve. The authors examined the DTA curves of five conventional explosives under three different heating rates (6, 10, 15 K min⁻¹) and reported the activation energies obtained by this method [13]. The autoignition temperatures of these explosives were calculated by substituting the reported T_i and E values in eqn. (14). The calculated autoignition temperatures, together with the literature data, are listed in Table 2. It is clear from Table 2 that the calculated values are fairly close to the literature data. The

TABLE 2

Calculated autoignition temperatures of some explosives using DTA data

Compound	$\phi/\text{K min}^{-1}$	T_i/K	$E/\text{kJ mol}^{-1}$	T_a/K	Literature value/K
RDX	6	479.9	187.9	470.1	488 [9]
	10	483.6	187.4	473.6	470 [1]
	15	489.5	195.8	479.7	487 [14]
HMX	6	549.6	216.3	537.8	529 [9]
	10	550.2	209.2	538.6	534 \pm 10 [1]
	15	553.0	241.8	542.9	531 [14]
Tetryl	6	444.7	136.8	433.3	473 [9]
	10	448.2	140.6	436.9	460 [15]
	15	449.3	130.5	437.1	
PETN	6	439.5	196.6	431.4	478 [9]
	10	442.4	195.0	434.4	439 [1]
	15	453.1	197.9	444.9	459 [3]
TNT	6	554.3	92.0	529.0	548 [1]
	10	560.7	87.9	533.7	561 [15]
NC	10	460.5	180.7	451.1	449 [1]

DTA scan of nitrocellulose with 12.6% nitrogen content was recorded with a heating rate of 10 K min⁻¹. The activation energy and autoignition temperature were determined and are given in Table 2. The autoignition temperature obtained is very close to those reported by Harris [1].

As has been pointed out in the literature [9, 14], the autoignition temperatures vary with the size, shape, previous history, and initial conditions of the sample. Figure 1 shows the effect of the DTA heating rate on the calculated autoignition temperature. The autoignition temperature obtained increases slightly as the heating rate increases. This is expected because of the better heat transfer at the lower heating rate.

Thermal decomposition of GAP, GAP/RDX, and GAP/HMX by DTA measurements

Thermal decompositions of GAP binder and its mixtures with RDX or HMX were determined by DTA at a heating rate of 10 K min⁻¹. DTA scans of GAP, RDX, and their mixtures are shown in Fig. 2. The DTA curve of pure RDX shows an endotherm at 477.2 K and an exotherm at 514.2 K, which are ascribed to melting and decomposition, respectively. These two temperatures agree with the literature data [15]. The maximum exothermic peak temperature (T_m) of GAP is slightly higher than that of RDX. The T_m values of GAP–RDX mixtures are lower than those of pure GAP or pure RDX. Figure 3 illustrates the DTA curves of GAP, HMX, and their mixtures. The T_m values of the mixture samples are lower and are close to

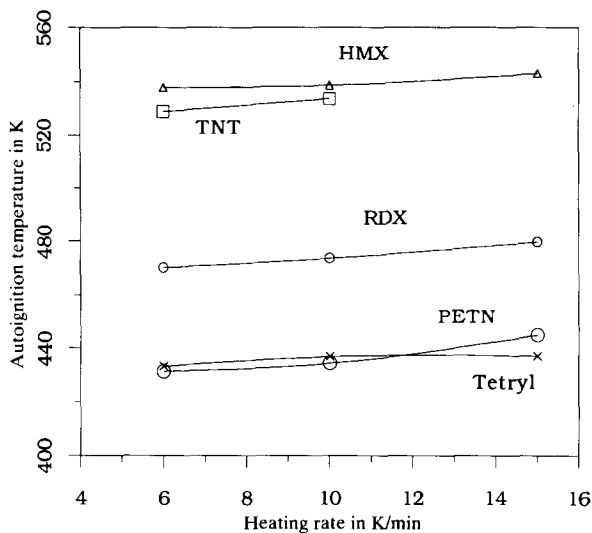


Fig. 1. Heating rate effect on autoignition temperature of explosives, obtained by DTA analysis.

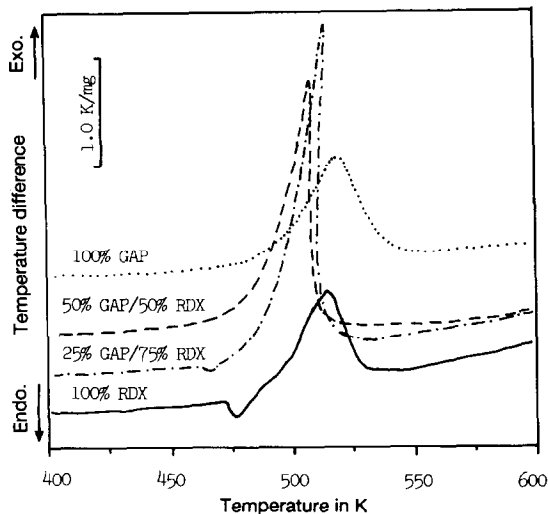


Fig. 2. DTA thermograms of GAP/RDX mixtures at a heating rate of 10 K min^{-1} and 50 ml min^{-1} nitrogen purge.

that of GAP. The T_m of pure HMX is high, 561.4 K, which agrees with data reported in ref. 15. From both Figs. 2 and 3, it is found that the thermal decomposition temperatures of mixtures containing energetic materials fall near the lower decomposition temperature of the pure ingredients. The activation energies were calculated by the method proposed by Huang et al. [12]. The DTA data and calculated activation energies of GAP/RDX and

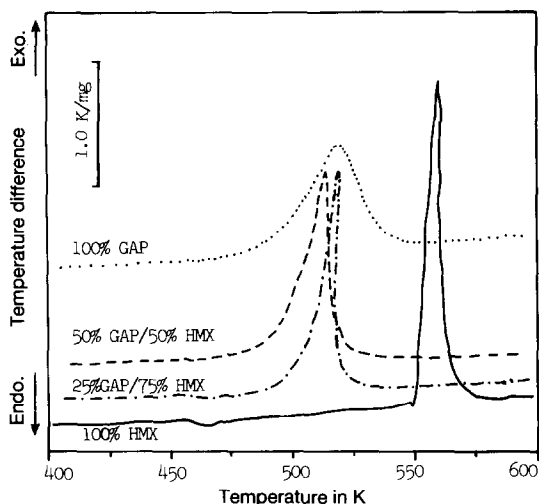


Fig. 3. DTA thermograms of GAP/HMX mixtures at a heating rate of 10 K min^{-1} and 50 ml min^{-1} nitrogen purge.

TABLE 3

DTA data of GAP/RDX and GAP/HMX mixtures with a heating rate of 10 K min^{-1}

Composition/%			Sample weight/mg	T_i /K	T_m /K	E_a /kJ mol ⁻¹	T_a /K
GAP	RDX	HMX					
100			3.70	485.3	519.8	218.1	476.6
50	50		4.40	482.9	508.6	207.9	473.9
25	75		5.60	488.2	516.0	215.0	479.3
	100		3.00	483.6	514.2	187.4	473.6
50		50	4.50	495.3	513.6	224.6	486.5
25		75	5.20	511.6	520.0	190.4	500.6
		100	2.40	550.2	561.2	209.2	538.6

GAP/HMX mixtures are given in Table 3. Estimated autoignition temperatures of GAP mixtures are plotted against GAP content in Fig. 4. The T_a value of GAP is as low as that of RDX. The solid lines, which simply connect the T_a values of the pure constituents, are theoretic T_a values of the ideal solution. From Fig. 4, the T_a values of mixtures containing energetic materials were found to fall in the range between those of its pure ingredients. When the T_a values of the constituents are close to each other, e.g. GAP and RDX, the T_a of the mixture is close to the values of the pure constituents. However, the T_a of the mixture deviates negatively from the line of the ideal solution. In other words, when T_a values of the constituents are very different, e.g. GAP and HMX, the T_a values of their mixtures are lower than those predicted by simple addition of the T_a values of the constituents.

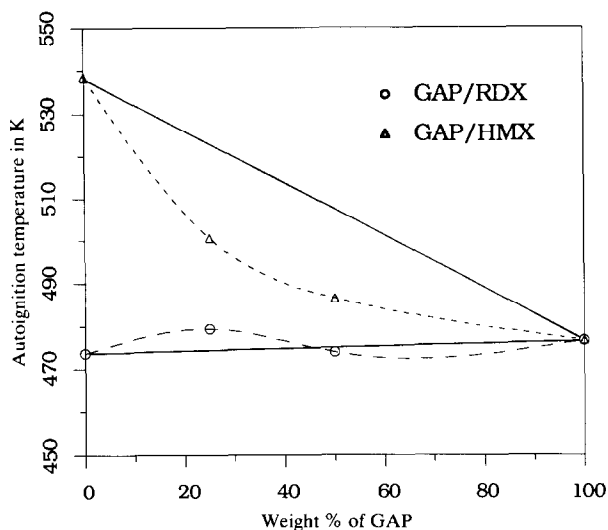


Fig. 4. Autoignition temperatures of GAP/RDX and GAP/HMX mixtures estimated by DTA analysis.

CONCLUSION

A simple method for predicting the autoignition temperature of energetic materials with a single non-isothermal DSC or DTA curve is proposed. Once the temperature T_i at the beginning of the steepest slope on a DTA or DSC exotherm and the activation energy E are known, the autoignition temperature of the energetic material can rapidly be determined using eqn. (14). The calculation is easy and straightforward. The autoignition temperatures of solid energetic materials with high activation energies ($80\text{--}250\text{ kJ mol}^{-1}$) determined by the present method are in fair agreement with literature data.

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