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A STUDY OF REACTION BETWEEN RDX AND UREA BY A SINGLE NON-ISOTHERMAL DSC CURVE

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ABSTRACT

A method and a relative formula for estimating the critical temperature of thermal explosion for explosives under linear temperature increase conditions are presented. The experimental and calculated results show that the reaction between RDX and the incompatible additive, urea, can be characterized and evaluated with the changes in value of eight criteria. (The apparent activation energy (E), the pre-exponential constant (A), the reaction order (n), the initial point (T_o), at which the DSC curve deviates from the baseline, the maximum peak temperature of the DSC curve (T_m), the heat-temperature quotient (H_o/T_m), the activating entrop ($\Delta S^{\#}$) and the critical temperature of thermal explosion (T_b) obtained by a single non-isothermal DSC curve.

INTRODUCTION

Urea is fairly incompatible with RDX. Mixtures of RDS and urea are typical examples of incompatible systems. The reactivity or compatibility of the mixtures under isothermal DSC conditions has been investigated by Rogers [1]. It is the purpose of this paper to propose eight criteria obtained by a single non-isothermal DSC curve for observing chemical interactions between explosives and other materials.

EXPERIMENTAL

RDX (1, 3, 5-trinitro-1, 2, 4-triazacyclohexane) was prepared by our institute. It contained no detectable HMX. The urea used was of analytical purity. It was purchased. Mixtures of RDX and urea were prepared with 70% RDX.

All measurements were made with a Shanghai Balance Manufactures CDR-1 differential scanning calorimeter. The RDX of 0.70mg or the 70/30-RDX/urea mixture of 0.70mg/0.30mg were sealed in a sealed

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cell of stainless steel used previously [2], working under static ambient conditions at a heating rate of 5°C/min. α-Al_2O_3 was used as reference sample. Sensitivity and paper speed were 41.84 mJ/s and 20 mm/min respectively.

THE DERIVATION OF THE RELATIVE FORMULA OF THE CRITICAL TEMPERATURE OF THERMAL EXPLOSION UNDER LINEAR TEMPERATURE INCREASE CONDITIONS

According to a previous paper [2], the reaction rate equation used to determine non-isothermal kinetic parameters by a single non-isothermal DSC curve is

$$\frac{d\alpha}{dt} = A\left\{f(\alpha)\left[1+\frac{E}{RT}\left(1-\frac{T_0}{T}\right)\right]\right\}\exp\left(-\frac{E}{RT}\right) \qquad (1)$$

where α stands for the conversion degree, T for the temperature(K), $f(\alpha)$ for the differential mechanism functions, T_o for the initial point, at which DSC curve deviates from the baseline, t for the time, R for the gas constant, A for the preexponential factor, and E for the activation energy.

In the general case $f(\alpha)=(1-\alpha)^n$, where n stands for the reaction order. Since the transition from thermal decomposition to thermal explosion starts in the range of low conversion degree, i.e. $f(\alpha)\approx 1$, eqn.(1) can be simplified to the form

$$\frac{d\alpha}{dt} = A\left[1+\frac{E}{RT}\left(1-\frac{T_0}{T}\right)\right]\exp\left(-\frac{E}{RT}\right) \qquad (2)$$

Hence, the corresponding heat q_1 liberated within the reactor in unit time for one mole explosive will be

$$q_1 = AQ\left[1+\frac{E}{RT}\left(1-\frac{T_0}{T}\right)\right]\exp\left(-\frac{E}{RT}\right) \qquad (3)$$

where Q stands for the decomposition heat of the explosive. When the thermal explosion starts, eqn.(3) becomes

$$q_1 = AQ\left[1+\frac{E}{RT_b}\left(1-\frac{T_0}{T_b}\right)\right]\exp\left(-\frac{E}{RT_b}\right) \qquad (4)$$

where T_b stands for the critical temperature of thermal explosion (see Fig.1.).

The amount of heat transferred by the wall of the reactor to the surrounding medium is

$$q_2 = \lambda s(T-T_c) \qquad (5)$$

where λ stands for the overall heat transfer coefficient, s for the external surface of the reactor, T_c for the temperature of the wall of the reactor and the furnace space programmed according to the linear relationship $T_c = T_o + \phi t$. Where ϕ stands for the constant heating rate. When the thermal explosion starts, eqn.(5) becomes

$$q_2 = \lambda s(T_b - T_c') \tag{6}$$

where T_c' stands for the temperature corresponding to $d^3H/dt^3=0$ in the DSC curve or $d^2(\ T)/dt^2=0$ in the DTA curve (see Fig.2.). According to Semenov's theory [3], the sufficient and necessary conditions for a thermal explosion are as follows

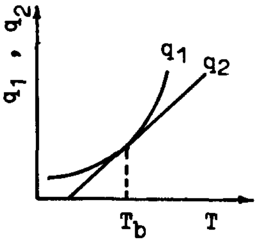

Fig.1 q_1 - q_2 relation

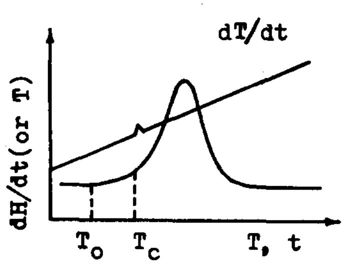

Fig.2 Typical DSC (or DTA) curve of explosive

$$\begin{cases} (q_1)_{T_b} = (q_2)_{T_b} & (7) \\ \left(\frac{dq_1}{dT}\right)_{T_b} = \left(\frac{dq_2}{dT}\right)_{T_b} & (8) \end{cases}$$

From eqn.(3), we have

$$\left.\frac{dq_1}{dt}\right|_{T=T_b} = QAe^{-\frac{E}{RT}} \frac{E}{RT_b^2} \left(\frac{dT}{dt}\right)_b \left[\frac{2T_o}{T_b} + \frac{E}{RT_b}\left(1 - \frac{T_o}{T_b}\right)\right] \tag{9}$$

From eqn.(5), we have

$$\left.\frac{dq_2}{dt}\right|_{T=T_b} = \lambda S\left[\left(\frac{dT}{dt}\right)_b - \phi\right] \tag{10}$$

Combining eqns.(4), (6) and (7), we have

$$QA\left[1+\frac{E}{RT_b}\left(1-\frac{T_o}{T_b}\right)\right]\exp\left(-\frac{E}{RT_b}\right)=\lambda S\,(T_b-T_c') \qquad (11)$$

Combining eqns.(8), (9) and (10), we have

$$\lambda S\left[\left(\frac{dT}{dt}\right)_b-\phi\right]=QA\exp\left(-\frac{E}{RT_b}\right)\frac{E}{RT_b^{2}}\left(\frac{dT}{dt}\right)_b\left[\frac{2T_o}{T_b}+\frac{E}{RT_b}\left(1-\frac{T_o}{T_b}\right)\right] \qquad (12)$$

From eqns.(11) and (12), we have

$$\frac{\left(\frac{dT}{dt}\right)_b-\phi}{\left(\frac{dT}{dt}\right)_b}=\frac{\frac{E}{RT_b^2}\left[\frac{2T_o}{T_b}+\frac{E}{RT_b}\left(1-\frac{T_o}{T_b}\right)\right]\left(T_b-T_c'\right)}{1+\frac{E}{RT_b}\left(1-\frac{T_o}{T_b}\right)} \qquad (13)$$

As the thermal explosion starts, $(dT/dt)_b \gg \phi$, and eqn.(13) will be simplified to the form

$$\frac{E(T_b-T_o)+2RT_bT_o}{RT_b^2+E(T_b-T_o)}\cdot\frac{E}{RT_b^2}\,(T_b-T_c')=1 \qquad (14)$$

Equation (14) is known as the relative formula for estimating the critical temperature of thermal explosion of explosives under non-isothermal DSC conditions. Once the values of T_o, T_c' and E have been calculated from a single non-isothermal DSC curve, the corresponding value of T_b can then be obtained from eqn.(14).

RESULTS AND DISCUSSION

The DSC curves of pure RDX and the 70/30-RDX/urea mixture are shown in the Fig.3. The results obtained by the method used previously [2] are shown in Table 1.

These data indicate that the values of T_o and T_m for the 70/30-RDX/urea mixture drop to a much lower temperature and the value of H_o/T_m increases obviously in comparison with that of pure RDX. These phenomena imply that the decomposition reaction of the mixture is ready to take place and the mixture is scarcely compatible.

In comparison with pure RDX, the values of E and n for the 70/30-RDX/urea mixture increase approximately by a factor of 2 which means a relative change of reaction mechanism due to incompatibility. The value of A for the 70/30-RDX/urea mixture rises to a greater extent than that of pure RDX showing the increase of the rate of the decomposition reaction or reactivity and the poor compatibility of the mixture. In contrast with pure RDX, the value of $\Delta S^{\#}$ for the 70/30-RDX/urea mixture increase enormously. This means an increase in reactive ability and a decrease in the thermal stability of the mixture. In comparison with pure RDX, the lower value of T_b for the 70/30-RDX/urea mixture shows that the transition from thermal decomposition to thermal explosion is ready to take place.

On the basis of experiments and calculated results shown in Fig.3. and Table 1, we believe that the 70/30-RDX/urea mixture is extremely incompatible.

Table 1 Results obtained by a single non-isothermal DSC curve

Explosive		The integral eqn.*		The exothermic rate eqn.*							
	α	E	lgA	E	lgA	n	T_o	T_m	$\frac{H_o}{T_m}$	$\Delta S^{\#}$	T_b
RDX	0~0.6	157.8	12.8	139.7	11.6	0.88	486	514	5.67	-35.7	507
70/30 RDX/urea	0~0.4	273.0	27.8	256.9	27.0	2.10	439	469	5.95	260	456

* Calculated according to the methods of ref. 2 .

α, The fraction of material reacted; E, the apparent activation energy (kJ/mol); A, the pre-exponential constant (1/s); n, the reaction order; T_o, the initial point, at which the DSC curve deviates from the baseline (K); T_m, the maxima peak temperature of the DSC curve (K); H_o, the total exothermicity of the substance corresponding to the global area under the DSC curve (J/g); H_o/T_m, the heat-temperature quotient (J/gK); $\Delta S^{\#}$, the activating entropy at T_m (J/molK); T_b, the critical temperature of thermal explosion of explosive (K).

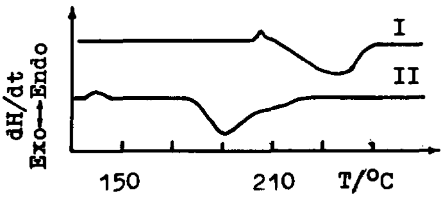

Fig.3 Typical DSC curves of thermal decomposition of explosive I, pure RDX; II, the 70/30-RDX/urea mixture

CONCLUSIONS

The reaction between RDX and urea can quickly be characterized and evaluated with the changes of the values of eight criteria (E, A, n, T_o, H_o/T_m, $\Delta S^{\#}$ and T_b) obtained by a single non-isothermal DSC curve. The results indicate that the 70/30-RDX/urea mixture is extremely incompatible.

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