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Note

The relationship between induction temperature and time in the exothermic decomposition reaction of energetic materials

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According to our previous paper [1], the non-isothermal differential kinetic equation describing the fraction of material reacted with time is

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

where α, T, $f(\alpha)$, T_0, t, R, A and E have the usual meanings [1,2].

Combining eqn. (1) and $T = T_0 + \varphi t$

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

where φ is the constant heating rate.

Integrating eqn. (2) between the initial temperature T_0 and the induction temperature T_{ind}, and the fraction of the material reacted between 0 and α_{ind}, yields

$$\frac{1}{A}\int_0^{\alpha_{\mathrm{ind}}}\frac{\mathrm{d}\alpha}{f(\alpha)}=\frac{1}{\varphi}\int_{T_0}^{T_{\mathrm{ind}}}\left[1+\frac{E}{RT}\left(1-\frac{T_0}{T}\right)\right]\exp\left(-\frac{E}{RT}\right)\mathrm{d}T$$

$$=\frac{1}{\varphi}(T_{\mathrm{ind}}-T_0)\exp\left(-\frac{E}{RT_{\mathrm{ind}}}\right) \tag{3}$$

For the case of an isothermal experiment at temperature T_{iso}, eqn. (1)

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can be written

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = Af(\alpha)\exp\left(-\frac{E}{RT_{\mathrm{iso}}}\right) \tag{4}$$

and the variables can be separated to give

$$\frac{1}{A}\frac{\mathrm{d}\alpha}{f(\alpha)} = \exp\left(-\frac{E}{RT_{\mathrm{iso}}}\right)\mathrm{d}t \tag{5}$$

Integrating eqn. (5) between 0 and the induction time t_{ind}, and the fraction of the material reacted between 0 and α'_{ind}, gives

$$\frac{1}{A}\int_0^{\alpha'_{\mathrm{ind}}}\frac{\mathrm{d}\alpha}{f(\alpha)} = \exp\left(-\frac{E}{RT_{\mathrm{iso}}}\right)\int_0^{t_{\mathrm{ind}}}\mathrm{d}t$$

$$= t_{\mathrm{ind}}\exp\left(-\frac{E}{RT_{\mathrm{iso}}}\right) \tag{6}$$

Typical DSC curves defining these integration limits T_0, T_{ind}, α_{ind}, t_0, t_{ind} and α'_{ind} for a non-isothermal and an isothermal experiment are shown in Fig. 1.

The left-hand sides of eqns. (3) and (6) are equal if three assumptions are satisfied: (a) during the induction period, the value of α'_{ind} corresponding to the induction time t_{ind} in the isothermal experiment at temperature T_{iso} is equal to the value of α_{ind} corresponding to the induction temperature T_{ind} in the non-isothermal experiment at the constant heating rate φ; (b) the most

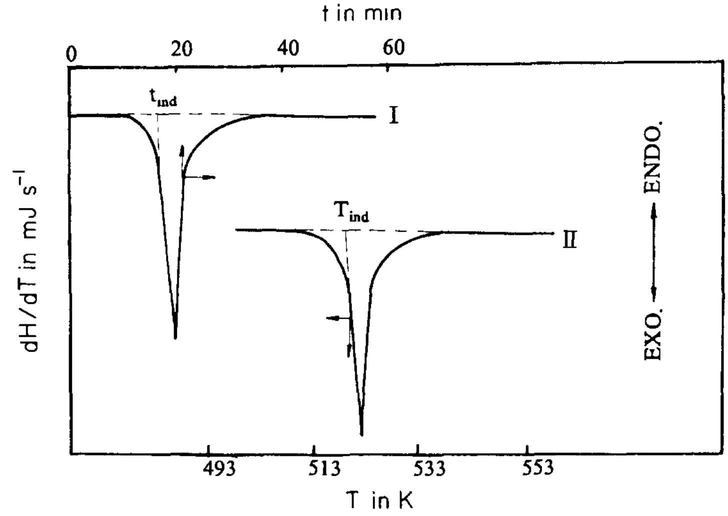

Fig. 1. Typical isothermal and non-isothermal DSC curves of the exothermic decomposition reaction of ethylenediammonium salt of 3-nitro-1,2,4-triazol-5-one. Curve I, held at 490.15 K; curve II, heating rate of 5 K min^{-1}.

probable differential mechanism function, $f(\alpha)$ has the same form in both the isothermal and non-isothermal experiments; and (c) all variables, e.g. sample size and gas pressure, are the same for the isothermal and non-isothermal experiments. Thus the right-hand sides can be equated to give

$$t_{\text{ind}} = \frac{T_{\text{ind}} - T_0}{\varphi} \exp\left[\frac{E}{R}\left(\frac{1}{T_{\text{iso}}} - \frac{1}{T_{\text{ind}}}\right)\right] \tag{7}$$

Taking logarithms on both sides of eqn. (7)

$$\ln(t_{\text{ind}})_i = B + \frac{E}{R}\left(\frac{1}{T_{\text{iso}}}\right)_i \qquad i = 1, 2, \ldots, n \tag{8}$$

where

$$B = \left[\ln\left(\frac{T_{\text{ind}} - T_0}{\varphi}\right) - \frac{E}{RT_{\text{ind}}}\right] \tag{9}$$

When $\ln t_{\text{ind}}$ is plotted versus $1/T_{\text{iso}}$ by the least-squares method, this gives the value of E from the slope.

Equations (7) or (8) relate the induction time t_{ind} of the thermal decomposition for an isothermal run at T_{iso}, to the induction temperature T_{ind} for a non-isothermal run at a heating rate of φ.

Rearranging both sides of eqn. (7) gives

$$E = \frac{RT_{\text{iso}}T_{\text{ind}}}{T_{\text{ind}} - T_{\text{iso}}} \ln\left(\frac{\varphi t_{\text{ind}}}{T_{\text{ind}} - T_0}\right) \tag{10}$$

By substituting the values of t_{ind} and T_{iso} obtained from an isothermal run, and the values of T_0, T_{ind} and φ obtained from a non-isothermal run into eqn. (10), the corresponding value of E may be also determined.

Comparing eqn. (9) with the equation [3]

$$\ln(t_{\text{ind}})_i = C + \frac{E}{R}\left(\frac{1}{T_{\text{iso}}}\right)_i \tag{11}$$

where

$$C = \ln[G(\alpha)] - \ln A \tag{12}$$

derived under isothermal conditions yields

$$\ln A = \ln\left[\frac{\varphi G(\alpha)}{T_{\text{ind}} - T_0}\right] + \frac{E}{RT_{\text{ind}}} \tag{13}$$

Once the value of E has been calculated from eqn. (8) and the values of T_{ind}, T_0 and φ have been obtained from a non-isothermal run, and the value of the integral mechanism function $G(\alpha)$ has been obtained by the method

TABLE 1

Calculated values of the kinetic parameters of the thermal decomposition of the ethylenediammonium salt of 3-nitro-1,2,4-triazol-5-one

Isothermal run					Non-isothermal run						Eqn. (9)	Eqn. (12)
T_{iso}	t_{ind}	α'_{ind}	$E_{ind(iso)}$	r	φ	T_{ind}	α_{ind}	$E_{ind(non\text{-}iso)}$	r_{ind}	T_0	B	C
490.15	960	0.09	207.5	0.994	1.045	502.15	0.08	221.9	0.994	489.15	47.18	46.42
480.65	2940	0.09			2.014	510.55	0.09			507.15	48.36	
474.65	4500	0.08			5.071	519.15	0.08			509.45	47.42	
470.15	9070	0.08			10.95	524.15	0.08			516.65	47.99	
					20.60	533.45	0.09			518.15	47.08	

Key: T_{iso}, temperature of isothermal run (K); t_{ind}, induction time (s); α_{ind} fraction of the material reacted during the inducing period for the non-isothermal run; $E_{ind(iso)}$, apparent energy obtained from eqn. (8) under isothermal conditions (kJ mol^{-1}); r, linear correlation coefficient; φ, heating rate (K min^{-1}); T_{ind}, induction temperature (K); α'_{ind}, fraction of the material reacted during the induction period for the isothermal run; T_0, the initial point of the deviation from the baseline of the DSC curve (K); A, pre-exponential constant (s^{-1}); $E_{ind(non\text{-}iso)}$, apparent energy obtained by Ozawa's method [4] under non-isothermal conditions (kJ mol^{-1}).

of logical choices [1], the corresponding value of pre-exponential constant may be obtained from eqn. (13).

To verify the reliability of eqn. (8), we measured the isothermal and non-isomermal DSC curves of the ethylenediammonium salt of 3-nitro-1,2,4-triazol-5-one, using the same experimental conditions of sample size, gas pressure, etc.; the results are shown in Table 1. Because $\alpha'_{\mathrm{ind}} \approx \alpha_{\mathrm{ind}}$, $E_{\mathrm{ind(iso)}} \approx E_{\mathrm{ind(non\text{-}iso)}}$ and $[\ln(T_{\mathrm{ind}} - T_0/\varphi) - E_{\mathrm{ind(iso)}}/RT_{\mathrm{ind}}] \approx [\ln G(\alpha) - \ln A]$ (i.e. $B \approx C$) (see Table 1), we conclude that our eqn. (7) is tenable.

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