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# THE DETERMINATION OF THE MOST PROBABLE MECHANISM FUNCTION AND THREE KINETIC PARAMETERS OF EXOTHERMIC DECOMPOSITION REACTION OF ENERGETIC MATERIALS BY A SINGLE NON-ISOTHERMAL DSC CURVE *

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## ABSTRACT

The determination of the most probable mechanism function and a numerical method of computing three kinetic parameters (The activation energy ($E$), the pre-exponential constant ($A$) and the reaction order ($n$)) of exothermic decomposition reaction of energetic materials by a single non-isothermal DSC curve obtained with a model CDR-1 instrument with a sealed cell of stainless steel and an open cell of aluminium are reported. The data are fitted to the integral, differential and exothermic rate equations by linear least-squares, iterative, combined dichotomous and least-squares methods, respectively. After establishing the most probable general expression of differential or integral mechanism functions by the logical choice method, the corresponding values of $E$, $A$ and $n$ will be obtained by the exothermic rate equation.

## INTRODUCTION

The apparent activation energy, pre-exponential constant and reaction order are three important parameters from the point of view of the evaluation of stability and compatibility for energetic materials [1–3]. The determination of the most probable mechanism function and three kinetic parameters of exothermic decomposition reaction of energetic materials at the same time by a single non-isothermal DSC curve has never been reported before. In this paper, these kinetic parameters and a mechanism function were obtained from the calculation of a single DSC curve by the integral, differential and exothermic rate equations. This is quite useful for us in the analysis and study of stability and compatibility of energetic materials.

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## EXPERIMENTAL

### *Materials*

The 2,6-dinitrophenol (I) used was of analytical purity. It was a commercial product of the Beijing Chemical Engineering Factory. The purified 1,4,5,8-tetranitro 1,4,5,8-tetrazadelin (II), cast single-base propellant (III, 99% nitrocellulose, 1% methyl centralite) and double-base propellant (IV, 60.3% nitrocellulose, 29.9% nitroglycerine, 8.3% triacetin and 1.5% methyl centralite) were prepared by our Institute.

### *Experimental equipment and conditions*

DSC experiments of above-mentioned materials were carried out on a Shanghai Balance Manufacturers' CDR-1 differential scanning calorimeter, using a Ni/Cr–Ni/Si thermoelement and working under static ambient conditions at a heating rate of 5 or 10°C $\text{min}^{-1}$. DSC curves were obtained for both the sealed cell of stainless steel (Fig. 1) and the open cell of aluminium. Heat-treated $\alpha$-$Al_2O_3$ was used as reference sample: the sample weight varied in the range 1.5–2.5 mg. Sensitivity and paper speed were 41.84 mJ $s^{-1}$ and 20 mm $\text{min}^{-1}$ respectively. Heating rate $\phi$ was calculated according to the actual rising rate of temperature from 50°C to the temperature at the end of reaction.

As four typical examples for energetic materials, the DSC curves of exothermic decomposition reaction of the samples I, II, III and IV are shown in Fig. 2. The DSC curve of I was obtained with the sealed cell; the DSC curves of the others were obtained with the open cell.

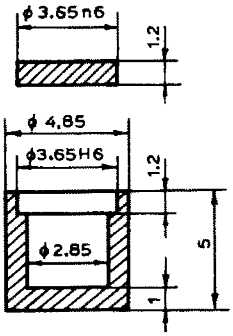

Fig. 1. Sealed cell scheme.

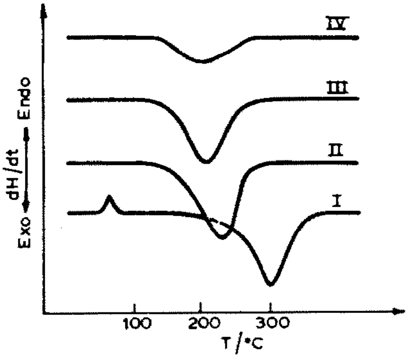

Fig. 2. Typical DSC curves of thermal decomposition of energetic materials I, 2,6-dinitrophenol; II, 1,4,5,8-tetranitro 1,4,5,8-tetrazadelin; III, cast single-base propellant; IV, double-base propellant.

KINETIC EQUATIONS AND ANALYSIS OF KINETIC DATA

In order to analyze kinetic problems, two different equations, i.e., eqns. (1) and (2), are used

$$\mathrm{d}\alpha/\mathrm{d}t = \mathrm{k}f(\alpha) \tag{1}$$

and

$$G(\alpha) = \mathrm{k}t \tag{2}$$

where $\alpha$ is the fraction of the material reacted, $t$ is the time and k is the kinetic constant. $f(\alpha)$ and $G(\alpha)$ are differential and integral mechanism functions, respectively. The relationship between $f(\alpha)$ and $G(\alpha)$ is given by

$$f(\alpha) = \frac{1}{G'(\alpha)} = \frac{1}{\mathrm{d}[G(\alpha)]/\mathrm{d}\alpha} \tag{3}$$

The relationship between the kinetic constant (k) and the absolute temperature ($T$) of reaction is expressed by the well-known Arrhenius equation

$$\mathrm{k} = A\exp(-E/RT) \tag{4}$$

It is believed that eqns. (1)–(4) are also valid for non-isothermal cases (at least empirically) [4]. In this case, $E$ and $A$ are the derived activation energy and pre-exponential constant, respectively. $R$ is the gas constant.

Setting $T_0$ as the initial point of the deviation from the baseline of the DSC curve (see Fig. 3) and $\phi$ as the constant heating rate, we have

$$T = T_0 + \phi t \tag{5}$$

In order to obtain an overall relationship for non-isothermal kinetics, eqns. (2), (4) and (5) are combined to yield

$$G(\alpha) = \frac{A}{\phi}(T - T_0)\,\mathrm{e}^{-E/RT} \tag{6}$$

Taking logarithm on both sides of the eqn. (6), the integral equation (eqn. (7)) may be obtained

$$\ln\left(\frac{G(\alpha)}{T - T_0}\right) = \ln\left(\frac{A}{\phi}\right) - \frac{E}{RT} \tag{7}$$

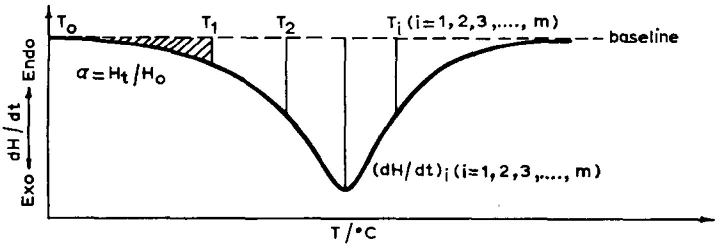

Fig. 3. Schematic diagrams of typical DSC curves of thermal decomposition for energetic materials.

The data are fitted to eqn. (7) by the linear least-squares method on the computer (program IM).

On differentiation, re-arrangement on both sides of the eqn. (6) and recalling eqn. (3), taking logarithms on both sides of the equation, the differential eqn. (8) is obtained

$$\ln\left[\frac{\mathrm{d}\alpha/\mathrm{d}T}{f(\alpha)\left[E(T-T_0)/RT^2+1\right]}\right]=\ln\frac{A}{\phi}-\frac{E}{RT} \tag{8}$$

Equation (8) may be solved by the iterative method (program DM) on the computer. Any arbitrary value may be assumed for $E(E>0)$, and using this

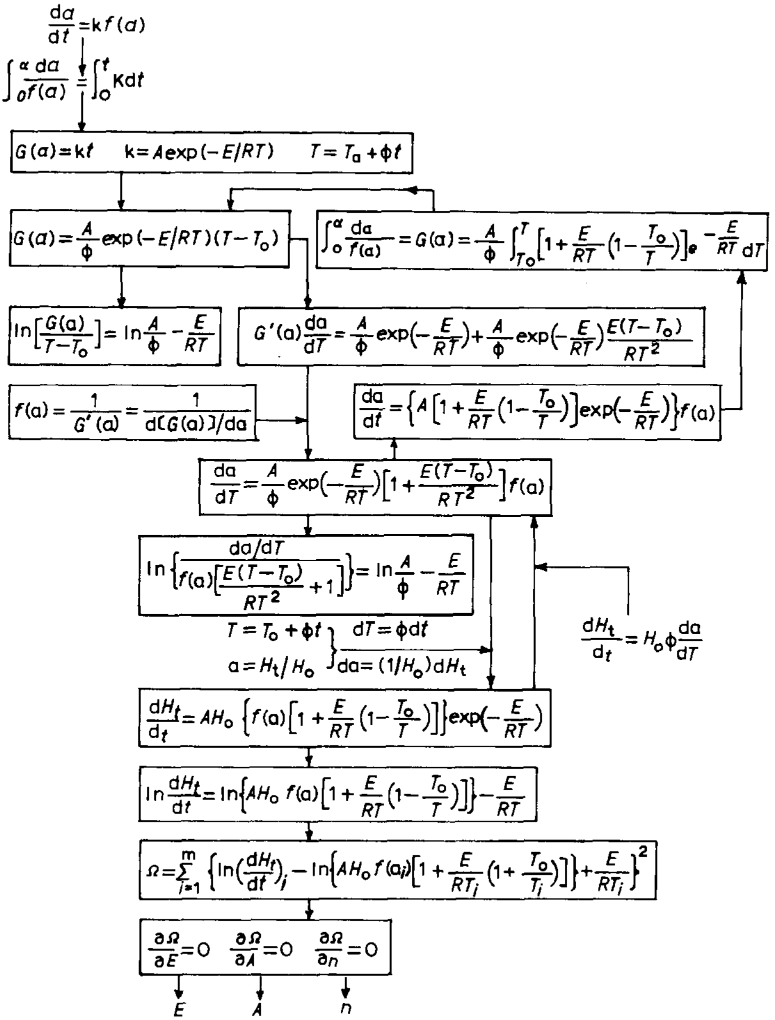

Fig. 4. Different types of kinetic equations for non-isothermal reactions and their derivation process.

value the value of the expression on the left-hand side may be calculated for each data point. This, when plotted against $(1/T)$ by the linear least-squares method, gives new values of $E$ from the slope and $A$ from the intercept. This modified value of $E$ is used as a starting value for the next iteration which yields another modified value of $E$. Thus after a few iterations, consistent values of $E$ and $A$ will be obtained.

Combining eqns. (3), (5) and (8), we have

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \left\{A\left[1 + \frac{E}{RT}\left(1 - \frac{T_0}{T}\right)\right] \exp\left(-\frac{E}{RT}\right)\right\} f(\alpha) \tag{9}$$

Rearranging both sides of eqn. (9) and integrating yields

$$\int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = G(\alpha) = \frac{A}{\phi}\int_{T_0}^{T}\left[1 + \frac{E}{RT}\left(1 - \frac{T_0}{T}\right)\right] \mathrm{e}^{-E/RT}\,\mathrm{d}T \tag{10}$$

Equation (6) may be also obtained from eqn. (10).

Combining eqn. (9) and $\alpha = H_t/H_0$, we have

$$\frac{\mathrm{d}H_t}{\mathrm{d}t} = AH_0\left\{f(\alpha)\left[1 + \frac{E}{RT}\left(1 - \frac{T_0}{T}\right)\right]\right\} \exp\left(-\frac{E}{RT}\right) \tag{11}$$

where $H_0$ is the total exothermicity of the substance (corresponding to the global area under the DSC curve) and $H_t$ is the reaction heat in a certain time (corresponding to the partial area under the DSC curve).

Substituting the probable mechanism function obtained logically from the integral and differential methods, for example $f(\alpha) = (1-\alpha)^n$, into eqn. (11), we have

$$\ln\frac{\mathrm{d}H_t}{\mathrm{d}t} = \ln\left\{AH_0(1-\alpha)^n\left[1 + \frac{E}{RT}\left(1 - \frac{T_0}{T}\right)\right]\right\} - \frac{E}{RT} \tag{12}$$

Equation (12) is known as the exothermic rate equation [5].

Taking minimal values of evaluation functions ($E$, $A$ and $n$)

$$\Omega = \sum_{i=1}^{m}\left\{\ln\left(\frac{\mathrm{d}H_t}{\mathrm{d}t}\right)_i - \ln\left\{AH_0(1-\alpha_i)^n\left[1 + \frac{E}{RT_i}\left(1 - \frac{T_0}{T_i}\right)\right]\right\} + \frac{E}{RT_i}\right\}^2 \tag{13}$$

the following normal equations can be obtained from eqn. (13)

$$\frac{\partial\Omega}{\partial E} = 0 \tag{14}$$

$$\frac{\partial\Omega}{\partial A} = 0 \tag{15}$$

$$\frac{\partial\Omega}{\partial n} = 0 \tag{16}$$

Once the value of $E$ has been calculated from eqn. (14), the corresponding values of $A$ and $n$ can then be obtained from eqns. (15) and (16) by program ETA on the computer. In the iterative computation process of

TABLE 1

Several kinetic functions used for the present analysis

| Function No. | Function form [a] (integral form), $G(\alpha)$ | |
|---|---|---|
| 1 | $\alpha^2$ | |
| 2 | $\alpha+(1-\alpha)\ln(1-\alpha)$ | |
| 3 | $1-(2/3)\alpha-(1-\alpha)^{2/3}$ | |
| 4–5 | $[1-(1-\alpha)^{1/3}]^n$ | $(n=2, 1/2)$ |
| 6 | $[1-(1-\alpha)^{1/2}]^{1/2}$ | |
| 7 | $[(1+\alpha)^{1/3}-1]^2$ | |
| 8 | $[(1/(1-\alpha))^{1/3}-1]^2$ | |
| 9 | $-\ln(1-\alpha)$ | |
| 10–16 | $[-\ln(1-\alpha)]^n$ | $(n=2/3, 1/2, 1/3, 4, 1/4, 2, 3)$ |
| 17–22 | $1-(1-\alpha)^n$ | $(n=1/2, 3, 2, 4, 1/3, 1/4)$ |
| 23–27 | $\alpha^n$ | $(n=1, 3/2, 1/2, 1/3, 1/4)$ |
| 28 | $(1-\alpha)^{-1}$ | |
| 29 | $(1-\alpha)^{-1}-1$ | |
| 30 | $(1-\alpha)^{-1/2}$ | |

[a] Differential form, $f(\alpha)=1/G'(\alpha)$.

combined dichotomous and least-squares methods, we take $AA=10^{-1}$, $BB=10^{10}$, $H=50.0$, $E_1=10^{-10}$ and $E_2=10^{-5}$, where $E$ is the root of eqn. (14). $[AA, BB]$ is the root interval of eqn. (14). $H$ is the step size and $E_1$ and $E_2$ are two constants of the control precision. When the value of a certain point on the left side of the eqn. (14) is less than $E_1$ or a half of the little interval length is less than $E_2$, this point or the intermediate point of the little interval is the solution of eqn. (14). Figure 4 shows a block diagram of

TABLE 2

Data of cast single-base propellant determined by DSC

| Data point | $T_i$ (K) | $\alpha_i$ | $(\mathrm{d}H_t/\mathrm{d}t)_i$ (mJ $\mathrm{s}^{-1}$) | $(\mathrm{d}\alpha/\mathrm{d}T)_i\times10^3$ ($\mathrm{K}^{-1}$) |
|---|---|---|---|---|
| 1 | 456.2 | 0.0190 | 0.9791 | 5.360 |
| 2 | 458.2 | 0.0380 | 1.674 | 9.163 |
| 3 | 461.2 | 0.0640 | 2.427 | 13.29 |
| 4 | 464.2 | 0.1070 | 3.205 | 17.54 |
| 5 | 465.2 | 0.1300 | 3.757 | 20.57 |
| 6 | 467.2 | 0.1590 | 4.435 | 24.28 |
| 7 | 468.2 | 0.1920 | 5.322 | 29.14 |
| 8 | 470.2 | 0.2350 | 6.636 | 36.33 |
| 9 | 472.2 | 0.2840 | 8.301 | 45.45 |
| 10 | 473.2 | 0.3530 | 9.849 | 53.92 |
| 11 | 474.2 | 0.4240 | 10.74 | 58.82 |
| 12 | 477.2 | 0.5070 | 11.08 | 60.66 |

$T_0=448.2$ K; $H_0=2119$ mJ; $\phi=0.0862$ °C $\mathrm{s}^{-1}$.

TABLE 3

Results of analysis of the thermal decomposition data of cast single-base propellant by integral (eqn. (7)) and differential (eqn. (8)) methods

| Function No. | Integral method | | | | Differential method | | | |
|---|---|---|---|---|---|---|---|---|
| | $E$ (kJ mol$^{-1}$) | log $A$ (s$^{-1}$) | $r$ | $Q$ | $E$ (kJ mol$^{-1}$) | log $A$ (s$^{-1}$) | $r$ | $Q$ |
| 1 | 437.44 | 44.9 | 0.988 | 0.687458 | 406.13 | 41.5 | 0.989 | 0.534294 |
| 2 | 453.95 | 46.5 | 0.990 | 0.615434 | 431.25 | 44.0 | 0.992 | 0.433544 |
| 3 | 459.84 | 46.5 | 0.990 | 0.591121 | 440.24 | 44.4 | 0.993 | 0.403690 |
| 4 | 471.65 | 47.8 | 0.992 | 0.547196 | 457.95 | 46.4 | 0.994 | 0.359185 |
| 5 | 36.79 | 1.15 | 0.968 | 0.012904 | 65.96 | 4.41 | 0.951 | 0.066142 |
| 6 | 34.59 | 1.00 | 0.967 | 0.011801 | 60.82 | 3.92 | 0.950 | 0.057707 |
| 7 | 414.00 | 41.2 | 0.985 | 0.772153 | 373.42 | 36.8 | 0.984 | 0.644560 |
| 8 | 508.35 | 52.0 | 0.994 | 0.450655 | 511.29 | 52.4 | 0.996 | 0.330448 |
| 9 | 190.76 | 18.2 | 0.993 | 0.078635 | 202.38 | 19.5 | 0.992 | 0.099703 |
| 10 | 91.12 | 7.35 | 0.989 | 0.026169 | 116.04 | 10.1 | 0.978 | 0.088000 |
| 11 | 41.29 | 1.91 | 0.969 | 0.015934 | 76.38 | 5.81 | 0.950 | 0.091266 |
| 12 | −ve | −ve | 0.624 | 0.016364 | 40.38 | 1.84 | 0.837 | 0.100849 |
| 13 | 1087.5 | 116 | 0.993 | 2.470571 | 1072.7 | 114 | 0.994 | 1.837605 |
| 14 | −ve | −ve | 0.942 | 0.020578 | 24.06 | 0.05 | 0.662 | 0.108899 |
| 15 | 489.68 | 50.8 | 0.993 | 0.491999 | 484.43 | 50.3 | 0.995 | 0.325442 |
| 16 | 788.61 | 83.5 | 0.993 | 1.289312 | 777.04 | 82.3 | 0.995 | 0.896243 |
| 17 | 177.35 | 16.4 | 0.990 | 0.087633 | 177.84 | 16.5 | 0.991 | 0.081851 |
| 18 | 120.49 | 10.7 | 0.957 | 0.191892 | 64.60 | 4.59 | 0.697 | 0.635448 |
| 19 | 141.26 | 12.8 | 0.976 | 0.145320 | 107.47 | 9.21 | 0.924 | 0.282975 |
| 20 | 102.10 | 8.72 | 0.930 | 0.234640 | 26.60 | 0.47 | 0.286 | 1.161563 |
| 21 | 181.74 | 16.7 | 0.991 | 0.083795 | 185.97 | 17.2 | 0.992 | 0.083168 |
| 22 | 183.96 | 16.8 | 0.992 | 0.082174 | 190.06 | 17.5 | 0.992 | 0.085569 |
| 23 | 164.63 | 15.2 | 0.987 | 0.103134 | 153.77 | 14.1 | 0.985 | 0.105989 |
| 24 | 301.03 | 30.0 | 0.988 | 0.328995 | 276.94 | 27.4 | 0.988 | 0.262071 |
| 25 | 28.24 | 0.42 | 0.960 | 0.009876 | 45.75 | 2.39 | 0.926 | 0.049928 |
| 26 | −ve | −ve | 0.915 | 0.008257 | 16.18 | −ve | 0.662 | 0.051478 |
| 27 | −ve | −ve | 0.973 | 0.012972 | 3.89 | −ve | 0.166 | 0.056700 |
| 28 | −ve | −ve | 0.789 | 0.231331 | 252.56 | 25.2 | 0.986 | 0.258986 |
| 29 | 219.68 | 21.5 | 0.994 | 0.090291 | 252.56 | 25.2 | 0.986 | 0.258986 |
| 30 | −ve | −ve | 0.941 | 0.121445 | 227.31 | 22.1 | 0.989 | 0.158928 |

TABLE 4

Data of double-base propellant determined by DSC

| Data point | $T_i$ (K) | $\alpha_i$ | $(\mathrm{d}H_t/\mathrm{d}t)_i$ (mJ s$^{-1}$) | $(\mathrm{d}\alpha/\mathrm{d}T)_i \times 10^3$ (K$^{-1}$) |
|---|---|---|---|---|
| 1 | 448.2 | 0.0176 | 0.4100 | 4.108 |
| 2 | 454.2 | 0.0441 | 0.9205 | 9.222 |
| 3 | 458.2 | 0.0969 | 1.799 | 18.02 |
| 4 | 461.2 | 0.1322 | 2.159 | 21.63 |
| 5 | 463.2 | 0.1806 | 2.611 | 26.16 |
| 6 | 466.2 | 0.2555 | 3.347 | 33.53 |
| 7 | 467.2 | 0.2996 | 3.582 | 35.88 |
| 8 | 468.2 | 0.3480 | 4.008 | 40.16 |
| 9 | 470.2 | 0.3921 | 4.100 | 41.08 |
| 10 | 471.2 | 0.4405 | 4.276 | 42.84 |

$T_0 = 441.2$ K; $H_0 = 1140$ mJ; $\phi = 0.0876$ °C s$^{-1}$.

TABLE 5

Data of 1,4,5,8-tetranitro 1,4,5,8-tetrazadecalin determined by DSC

| Data point | $T_i$ (K) | $\alpha_i$ | $(\mathrm{d}H_t/\mathrm{d}t)_i$ (mJ s$^{-1}$) | $(\mathrm{d}\alpha/\mathrm{d}T)_i \times 10^3$ (K$^{-1}$) |
|---|---|---|---|---|
| 1 | 477.2 | 0.0145 | 0.3314 | 2.429 |
| 2 | 485.2 | 0.0253 | 0.5556 | 4.073 |
| 3 | 487.2 | 0.0393 | 0.9037 | 6.624 |
| 4 | 490.2 | 0.0556 | 1.228 | 9.004 |
| 5 | 493.2 | 0.0857 | 1.918 | 14.6 |
| 6 | 495.2 | 0.1190 | 2.634 | 19.31 |
| 7 | 497.2 | 0.1654 | 3.769 | 27.63 |
| 8 | 499.2 | 0.2332 | 5.295 | 38.81 |
| 9 | 500.2 | 0.3064 | 6.823 | 50.05 |
| 10 | 502.2 | 0.3904 | 8.485 | 62.19 |
| 11 | 503.2 | 0.5164 | 9.864 | 72.30 |
| 12 | 504.2 | 0.6133 | 10.73 | 78.68 |
| 13 | 505.2 | 0.6942 | 11.20 | 82.09 |
| 14 | 506.2 | 0.7868 | 11.34 | 83.12 |
| 15 | 507.2 | 0.8740 | 10.50 | 76.99 |

$T_0 = 471.2$ K; $H_0 = 1554$ mJ; $\phi = 0.0878$ °C s$^{-1}$.

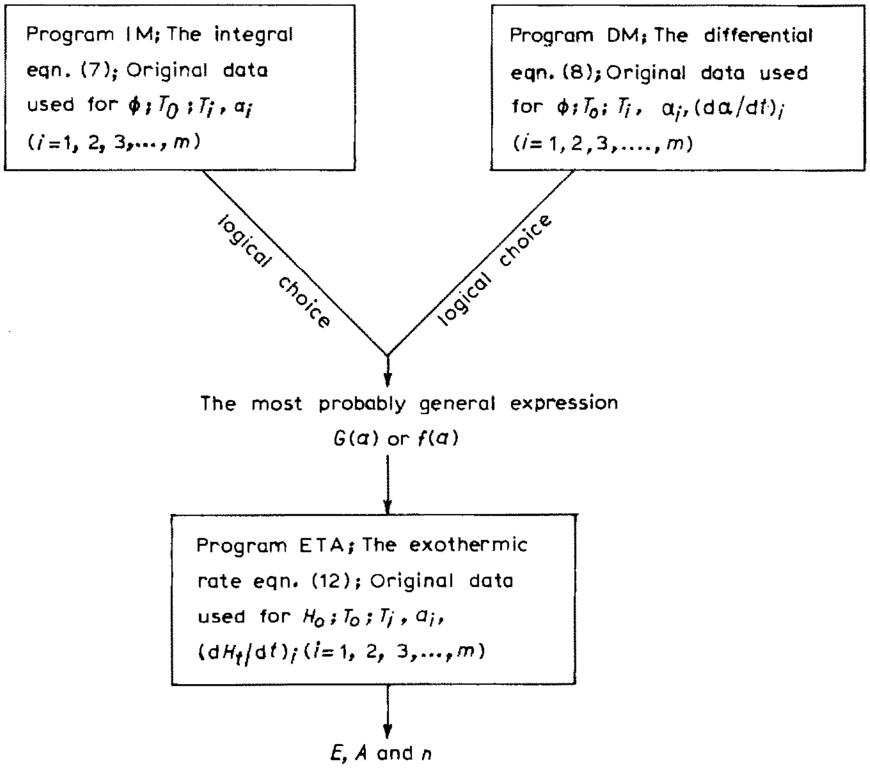

Fig. 5. Block diagram of the process of computing three kinetic parameters.

above-mentioned different types of kinetic equations for non-isothermal reactions and their derived process. For example, using all the forms of $G(\alpha)$ and $f(\alpha)$ as tabulated in Table 1, the data of cast single-base propellant tabulated in Table 2, are analyzed by eqns. (7) and (8). The results obtained from Table 3 clearly show that when all conditions (viz. the values of $E$ and $A$ are in the ordinary range of the thermal decomposition kinetic parameters for energetic materials ($E = 80$–$250$ kJ mol$^{-1}$; $\log A = 7$–$30$ s$^{-1}$, linear correlation coefficient $r > 0.99$ and variance $Q < 0.1$) are satisfied at the same time the probable mechanism function is logically function No. 9, 17, 21 and 22. Their general expression is $f(\alpha) = (1 - \alpha)^n$. By substituting the most probable mechanism function into the exothermic rate eqn. (12), the proper values of $E$, $A$ and $n$ are determined thereafter by eqns. (14)–(16). The value of $E$ for sample III is in good agreement with the

TABLE 6

Data of 2,6-dinitrophenol determined by DSC with the sealed cell of stainless steel. Traces 1 and 2

| Data point | $T_i$ (K) | $\alpha_i$ | $(dH_t/dt)_i$ (mJ s$^{-1}$) | $(d\alpha/dT)_i \times 10^3$ (K$^{-1}$) |
|---|---|---|---|---|
| 1 | 522.2 | 0.0073 | 0.9774 | 0.8484 |
| 2 | 534.2 | 0.0249 | 2.721 | 2.362 |
| 3 | 542.2 | 0.0484 | 4.398 | 3.818 |
| 4 | 549.2 | 0.0822 | 7.223 | 6.270 |
| 5 | 554.2 | 0.1174 | 9.921 | 8.612 |
| 6 | 560.2 | 0.1809 | 13.87 | 12.04 |
| 7 | 564.2 | 0.2315 | 18.02 | 15.65 |
| 8 | 569.2 | 0.3098 | 24.33 | 21.12 |
| 9 | 574.2 | 0.4095 | 32.43 | 28.16 |
| 10 | 577.2 | 0.5014 | 38.26 | 33.21 |
| 11 | 580.2 | 0.5869 | 42.14 | 36.58 |
| 12 | 582.2 | 0.6596 | 43.10 | 37.41 |

$T_0 = 503.2$ K; $H_0 = 6843$ mJ; $\phi = 0.1683$ °C s$^{-1}$

| | | | | |
|---|---|---|---|---|
| 1 | 521.2 | 0.0061 | 0.9774 | 0.8632 |
| 2 | 534.2 | 0.0223 | 2.721 | 2.403 |
| 3 | 542.2 | 0.0452 | 4.398 | 3.885 |
| 4 | 549.2 | 0.0783 | 7.223 | 6.380 |
| 5 | 555.2 | 0.1135 | 9.921 | 8.762 |
| 6 | 560.2 | 0.1608 | 13.87 | 12.25 |
| 7 | 564.2 | 0.2131 | 18.02 | 15.92 |
| 8 | 568.2 | 0.2920 | 24.33 | 21.49 |
| 9 | 572.2 | 0.3915 | 32.43 | 28.65 |
| 10 | 575.2 | 0.4361 | 38.26 | 33.79 |
| 11 | 577.2 | 0.5760 | 42.14 | 37.22 |
| 12 | 580.2 | 0.6454 | 43.10 | 38.06 |

$T_0 = 503.2$ K; $H_0 = 6726$ mJ; $\phi = 0.1683$ °C s$^{-1}$

TABLE 7

Data of 2,6-dinitrophenol determined by DSC with the sealed cell of stainless steel. Traces 3 and 4

| Data point | $T_i$ (K) | $\alpha_i$ | $(\mathrm{d}H_t/\mathrm{d}t)_i$ (mJ $\mathrm{s}^{-1}$) | $(\mathrm{d}\alpha/\mathrm{d}T)_i \times 10^3$ ($\mathrm{K}^{-1}$) |
|---|---|---|---|---|
| 1 | 545.90 | 0.0166 | 2.182 | 1.822 |
| 2 | 554.15 | 0.0480 | 4.107 | 3.430 |
| 3 | 559.65 | 0.0578 | 6.042 | 5.045 |
| 4 | 563.90 | 0.0816 | 8.211 | 6.857 |
| 5 | 567.95 | 0.1134 | 10.93 | 9.126 |
| 6 | 572.15 | 0.1573 | 14.60 | 15.87 |
| 7 | 576.15 | 0.2134 | 19.00 | 19.85 |
| 8 | 579.65 | 0.2738 | 23.77 | 24.54 |
| 9 | 582.90 | 0.3457 | 29.39 | 29.66 |
| 10 | 585.55 | 0.4233 | 35.52 | 34.28 |
| 11 | 588.15 | 0.5102 | 41.05 | 34.28 |
| 12 | 590.75 | 0.6099 | 43.66 | 36.46 |
| $T_0 = 524.65$ K; $H_0 = 6668$ mJ; $\phi = 0.1796$ °C $\mathrm{s}^{-1}$ | | | | |
| 1 | 540.15 | 0.0188 | 2.035 | 1.694 |
| 2 | 548.65 | 0.0372 | 2.996 | 2.494 |
| 3 | 556.40 | 0.0656 | 5.118 | 4.260 |
| 4 | 563.40 | 0.0993 | 7.849 | 6.534 |
| 5 | 568.40 | 0.1449 | 11.37 | 9.467 |
| 6 | 573.40 | 0.1992 | 15.63 | 13.01 |
| 7 | 577.55 | 0.2576 | 19.54 | 16.27 |
| 8 | 580.40 | 0.3101 | 23.12 | 19.24 |
| 9 | 583.65 | 0.3816 | 28.44 | 23.67 |
| 10 | 586.40 | 0.4513 | 33.13 | 27.58 |
| 11 | 589.40 | 0.5327 | 37.74 | 31.41 |
| 12 | 591.65 | 0.6141 | 39.76 | 33.10 |
| $T_0 = 514.40$ K; $H_0 = 6596$ mJ; $\phi = 0.1821$ °C $\mathrm{s}^{-1}$ | | | | |

calculated value ($E = 169.5$ kJ $\mathrm{mol}^{-1}$, $r = 0.9975$) obtained by Ozawa's method [5]. Similar computational results (see Tables 8–13) for samples IV (original data see Table 4), II (original data see Table 5) and I (original data see Tables 6 and 7), are not illustrated here one by one. The results of kinetic parameters of the above-mentioned energetic materials are all listed in Table 14.

Figure 5 shows a block diagram of the process of computing three kinetic parameters.

## CONCLUSIONS

If kinetic data of a single non-isothermal DSC curve are analyzed by differential (eqn. (8)) and integral (eqn. (7)) methods, all the forms of $f(\alpha)$

TABLE 8

Results of analysis of the thermal decomposition data of double-base propellant by integral (eqn. (7)) and differential (eqn. (8)) methods

| Function No. | Integral method | | | | Differential method | | | |
|---|---|---|---|---|---|---|---|---|
| | $E$ (kJ mol$^{-1}$) | log $A$ (s$^{-1}$) | $r$ | $Q$ | $E$ (kJ mol$^{-1}$) | log $A$ (s$^{-1}$) | $r$ | $Q$ |
| 1 | 389.57 | 40.0 | 0.997 | 0.153859 | 352.07 | 35.8 | 0.992 | 0.320362 |
| 2 | 402.64 | 41.2 | 0.997 | 0.134292 | 371.65 | 37.8 | 0.992 | 0.235232 |
| 3 | 407.26 | 41.0 | 0.998 | 0.128888 | 378.59 | 37.9 | 0.995 | 0.209472 |
| 4 | 416.52 | 42.1 | 0.998 | 0.121353 | 392.30 | 39.4 | 0.997 | 0.168187 |
| 5 | 25.44 | −ve | 0.836 | 0.044804 | 46.99 | 2.33 | 0.962 | 0.028431 |
| 6 | 23.72 | −ve | 0.826 | 0.041974 | 43.20 | 1.98 | 0.943 | 0.037429 |
| 7 | 370.31 | 36.8 | 0.996 | 0.182561 | 325.35 | 31.8 | 0.988 | 0.438096 |
| 8 | 445.14 | 45.4 | 0.998 | 0.125970 | 433.59 | 44.2 | 0.998 | 0.114736 |
| 9 | 162.85 | 15.2 | 0.994 | 0.052932 | 163.51 | 15.4 | 0.996 | 0.035584 |
| 10 | 73.59 | 5.44 | 0.973 | 0.049450 | 88.57 | 7.17 | 0.992 | 0.020832 |
| 11 | 28.96 | 0.53 | 0.851 | 0.051138 | 54.68 | 3.44 | 0.983 | 0.016273 |
| 12 | −ve | −ve | 0.645 | 0.055111 | 24.31 | 0.07 | 0.939 | 0.013019 |
| 13 | 966.17 | 103 | 0.998 | 0.495714 | 937.83 | 100 | 0.998 | 0.544559 |
| 14 | −ve | −ve | 0.894 | 0.057955 | 10.66 | −ve | 0.799 | 0.011981 |
| 15 | 430.62 | 44.7 | 0.998 | 0.118238 | 412.82 | 42.8 | 0.998 | 0.128565 |
| 16 | 698.4 | 74.2 | 0.998 | 0.265832 | 673.63 | 71.4 | 0.998 | 0.297161 |
| 17 | 152.35 | 13.7 | 0.994 | 0.042087 | 144.84 | 12.9 | 0.990 | 0.065788 |
| 18 | 106.75 | 9.26 | 0.986 | 0.051128 | 58.40 | 3.90 | 0.674 | 0.657929 |
| 19 | 123.65 | 11.0 | 0.990 | 0.038996 | 91.28 | 7.47 | 0.895 | 0.331628 |
| 20 | 91.54 | 7.62 | 0.976 | 0.067514 | 28.69 | 0.66 | 0.328 | 1.101179 |
| 21 | 155.80 | 13.9 | 0.994 | 0.045007 | 151.03 | 13.5 | 0.993 | 0.052527 |
| 22 | 157.54 | 14.0 | 0.994 | 0.046718 | 154.13 | 13.7 | 0.994 | 0.047096 |
| 23 | 142.32 | 12.8 | 0.994 | 0.036929 | 126.53 | 11.1 | 0.977 | 0.124922 |
| 24 | 265.95 | 26.4 | 0.997 | 0.076655 | 236.16 | 23.1 | 0.989 | 0.204336 |
| 25 | 18.70 | −ve | 0.786 | 0.034683 | 32.07 | 0.87 | 0.827 | 0.076498 |
| 26 | −ve | −ve | 0.811 | 0.042263 | 6.83 | −ve | 0.345 | 0.062247 |
| 27 | −ve | −ve | 0.929 | 0.047614 | 4.90 | −ve | 0.546 | 0.545584 |
| 28 | −ve | −ve | 0.855 | 0.226550 | 201.75 | 19.7 | 0.995 | 0.060280 |
| 29 | 185.25 | 17.8 | 0.991 | 0.097092 | 201.75 | 19.7 | 0.995 | 0.060280 |
| 30 | −ve | −ve | 0.944 | 0.135792 | 182.5 | 17.2 | 0.997 | 0.033882 |

or $G(\alpha)$ should be used so as to single out the most probable general expression of $f(\alpha)$ or $G(\alpha)$ by the method of logical choice. By substituting this expression of $f(\alpha)$ into the exothermic rate equation (eqn. (12)), the corresponding values of $E$, $A$ and $n$ may be determined.

Equations (7), (8) and (12) are suitable for computer programming for fast computations.

TABLE 9

Results of analysis of the thermal decomposition data of 1,4,5,8-tetranitro 1,4,5,8-tetrazadecalin by integral (eqn. (7)) and differential (eqn. (8)) methods

| Function No. | Integral method | | | | Differential method | | | |
|---|---|---|---|---|---|---|---|---|
| | $E$ (kJ mol$^{-1}$) | log $A$ (s$^{-1}$) | $r$ | $Q$ | $E$ (kJ mol$^{-1}$) | log $A$ (s$^{-1}$) | $r$ | $Q$ |
| 1 | 499.28 | 48.6 | 0.975 | 3.408301 | 496.71 | 48.3 | 0.983 | 2.246143 |
| 2 | 527.64 | 51.3 | 0.971 | 4.361546 | 544.07 | 53.0 | 0.979 | 3.314534 |
| 3 | 538.75 | 51.8 | 0.970 | 4.815237 | 562.84 | 54.4 | 0.976 | 3.980052 |
| 4 | 561.25 | 54.2 | 0.966 | 5.867469 | 598.96 | 58.2 | 0.971 | 5.658812 |
| 5 | 60.49 | 3.35 | 0.726 | 0.863867 | 128.21 | 10.3 | 0.945 | 0.508820 |
| 6 | 56.34 | 2.99 | 0.717 | 0.789531 | 116.17 | 9.21 | 0.958 | 0.310885 |
| 7 | 467.94 | 44.2 | 0.977 | 2.657792 | 452.95 | 42.6 | 0.984 | 1.680247 |
| 8 | 653.22 | 62.2 | 0.952 | 10.760357 | 707.75 | 69.8 | 0.951 | 13.881100 |
| 9 | 245.13 | 22.7 | 0.926 | 2.618090 | 312.75 | 29.8 | 0.945 | 3.041259 |
| 10 | 127.94 | 10.5 | 0.862 | 1.490356 | 204.31 | 18.5 | 0.931 | 0.168649 |
| 11 | 69.35 | 4.54 | 0.740 | 1.046374 | 152.33 | 13.1 | 0.917 | 1.143375 |
| 12 | 10.75 | − ve | 0.206 | 0.682314 | 102.88 | 8.01 | 0.894 | 0.698126 |
| 13 | 1299.84 | 131 | 0.970 | 27.153831 | 1348.28 | 136 | 0.970 | 29.890557 |
| 14 | − ve | − ve | 0.381 | 0.530256 | 79.53 | 5.54 | 0.873 | 0.515419 |
| 15 | 596.70 | 59.0 | 0.960 | 7.919443 | 652.53 | 64.9 | 0.961 | 9.097446 |
| 16 | 948.27 | 95.3 | 0.967 | 16.098023 | 999.30 | 100 | 0.967 | 18.053791 |
| 17 | 219.11 | 19.6 | 0.935 | 1.802018 | 260.86 | 23.9 | 0.967 | 1.207520 |
| 18 | 131.58 | 10.9 | 0.942 | 0.576677 | 29.66 | 0.35 | 0.145 | 10.758566 |
| 19 | 159.64 | 13.8 | 0.946 | 0.787591 | 113.13 | 8.94 | 0.720 | 3.122452 |
| 20 | 109.51 | 8.72 | 0.932 | 0.474659 | − ve | − ve | – | – |
| 21 | 227.41 | 20.3 | 0.932 | 2.032752 | 278.06 | 25.6 | 0.961 | 1.683292 |
| 22 | 231.69 | 20.6 | 0.931 | 2.162539 | 286.70 | 26.4 | 0.957 | 1.972058 |
| 23 | 196.42 | 17.4 | 0.941 | 1.295677 | 209.95 | 18.8 | 0.975 | 0.598644 |
| 24 | 347.85 | 33.0 | 0.966 | 2.225625 | 351.08 | 33.3 | 0.980 | 1.279116 |
| 25 | 44.99 | 1.92 | 0.680 | 0.618457 | 80.53 | 5.60 | 0.931 | 0.259863 |
| 26 | − ve | − ve | 0.131 | 0.448879 | 43.18 | 1.73 | 0.819 | 0.240324 |
| 27 | − ve | − ve | 0.631 | 0.374620 | 26.26 | − ve | 0.651 | 0.248628 |
| 28 | 4.52 | − ve | 0.039 | 3.473650 | 418.50 | 41.0 | 0.903 | 10.342634 |
| 29 | 307.37 | 29.3 | 0.900 | 0.580763 | 418.50 | 41.0 | 0.903 | 10.342634 |
| 30 | − ve | − ve | 0.595 | 1.242520 | 365.36 | 35.1 | 0.923 | 6.088878 |

TABLE 10

Results of analysis of the thermal decomposition data of 2,6-dinitrophenol by integral (eqn. (7)) and differential (eqn. (8)) methods. Trace 1

| Function No. | Integral method | | | | Differential method | | | |
|---|---|---|---|---|---|---|---|---|
| | $E$ (kJ mol$^{-1}$) | log $A$ (s$^{-1}$) | $r$ | $Q$ | $E$ (kJ mol$^{-1}$) | log $A$ (s$^{-1}$) | $r$ | $Q$ |
| 1 | 312.40 | 25.0 | 0.998 | 0.201199 | 305.14 | 24.3 | 0.998 | 0.150481 |
| 2 | 324.11 | 25.8 | 0.999 | 0.105319 | 323.74 | 25.8 | 0.999 | 0.036428 |
| 3 | 328.40 | 25.6 | 0.999 | 0.083051 | 330.58 | 25.8 | 0.999 | 0.034356 |
| 4 | 337.04 | 26.5 | 0.999 | 0.062642 | 343.96 | 27.1 | 0.999 | 0.096269 |
| 5 | 42.27 | 0.83 | 0.989 | 0.024762 | 64.54 | 2.88 | 0.976 | 0.127193 |
| 6 | 40.67 | 0.76 | 0.991 | 0.018353 | 60.14 | 2.55 | 0.983 | 0.079217 |
| 7 | 297.22 | 22.6 | 0.997 | 0.355075 | 283.59 | 21.3 | 0.996 | 0.364377 |
| 8 | 364.28 | 29.1 | 0.998 | 0.223438 | 384.19 | 31.0 | 0.996 | 0.803482 |
| 9 | 147.17 | 10.5 | 0.998 | 0.040923 | 166.48 | 12.3 | 0.992 | 0.296809 |
| 10 | 79.45 | 4.43 | 0.995 | 0.039488 | 103.46 | 6.67 | 0.980 | 0.276464 |
| 11 | 45.59 | 1.39 | 0.984 | 0.041970 | 73.38 | 3.95 | 0.963 | 0.261968 |
| 12 | 11.73 | −ve | 0.805 | 0.046588 | 45.06 | 1.37 | 0.916 | 0.243589 |
| 13 | 756.65 | 65.2 | 0.999 | 0.437916 | 766.98 | 66.2 | 0.999 | 0.599376 |
| 14 | −ve | −ve | 0.503 | 0.049696 | 31.88 | 0.14 | 0.855 | 0.233346 |
| 15 | 350.33 | 28.7 | 0.999 | 0.096446 | 363.90 | 30.0 | 0.998 | 0.347604 |
| 16 | 553.49 | 46.9 | 0.999 | 0.228765 | 564.92 | 48.0 | 0.998 | 0.440956 |
| 17 | 137.32 | 9.25 | 0.999 | 0.005817 | 147.19 | 10.1 | 0.997 | 0.059245 |
| 18 | 98.42 | 6.23 | 0.983 | 0.207287 | 55.54 | 2.28 | 0.705 | 1.944926 |
| 19 | 112.06 | 7.38 | 0.994 | 0.090923 | 90.86 | 5.43 | 0.949 | 0.564652 |
| 20 | 86.90 | 5.22 | 0.967 | 0.321524 | 23.74 | −ve | 0.278 | 4.189039 |
| 21 | 140.52 | 9.38 | 0.999 | 0.012344 | 153.60 | 10.6 | 0.996 | 0.116133 |
| 22 | 142.15 | 9.42 | 0.999 | 0.017442 | 156.81 | 10.8 | 0.995 | 0.152951 |
| 23 | 128.20 | 8.66 | 0.999 | 0.010777 | 128.11 | 8.67 | 0.998 | 0.023192 |
| 24 | 220.30 | 16.8 | 0.998 | 0.075754 | 215.54 | 16.4 | 0.998 | 0.062387 |
| 25 | 36.1 | 0.47 | 0.996 | 0.006268 | 47.05 | 1.47 | 0.992 | 0.019754 |
| 26 | 5.41 | −ve | 0.708 | 0.018202 | 23.59 | −ve | 0.968 | 0.023002 |
| 27 | −ve | −ve | 0.835 | 0.026687 | 13.06 | −ve | 0.898 | 0.025397 |
| 28 | −ve | −ve | 0.412 | 0.697572 | 205.54 | 16.0 | 0.975 | 1.370212 |
| 29 | 169.07 | 12.6 | 0.991 | 0.295176 | 205.54 | 16.0 | 0.975 | 1.370212 |
| 30 | −ve | −ve | 0.857 | 0.283497 | 185.95 | 13.8 | 0.983 | 0.734228 |

TABLE 11

Results of analysis of the thermal decomposition data of 2,6-dinitrophenol by integral (eqn. (7)) and differential (eqn. (8)) methods. Trace 2

| Function No. | Integral method | | | | Differential method | | | |
|---|---|---|---|---|---|---|---|---|
| | $E$ (kJ mol$^{-1}$) | log $A$ (s$^{-1}$) | $r$ | $Q$ | $E$ (kJ mol$^{-1}$) | log $A$ (s$^{-1}$) | $r$ | $Q$ |
| 1 | 333.23 | 26.9 | 0.999 | 0.086250 | 319.99 | 25.7 | 0.999 | 0.080455 |
| 2 | 344.61 | 27.8 | 0.999 | 0.113440 | 337.99 | 27.2 | 0.998 | 0.167229 |
| 3 | 348.76 | 27.5 | 0.999 | 0.139907 | 344.59 | 27.2 | 0.998 | 0.245366 |
| 4 | 357.11 | 28.3 | 0.998 | 0.220098 | 357.50 | 28.4 | 0.996 | 0.469051 |
| 5 | 45.82 | 1.15 | 0.974 | 0.066509 | 62.94 | 2.76 | 0.958 | 0.203967 |
| 6 | 44.28 | 1.09 | 0.976 | 0.055092 | 58.74 | 2.45 | 0.967 | 0.140130 |
| 7 | 318.24 | 24.5 | 0.998 | 0.124732 | 298.67 | 22.7 | 0.998 | 0.136093 |
| 8 | 383.40 | 30.9 | 0.995 | 0.725478 | 396.31 | 32.2 | 0.990 | 1.710100 |
| 9 | 156.00 | 11.3 | 0.994 | 0.162876 | 168.97 | 12.5 | 0.983 | 0.559457 |
| 10 | 84.69 | 4.91 | 0.986 | 0.112984 | 102.82 | 6.63 | 0.966 | 0.435650 |
| 11 | 49.03 | 1.70 | 0.968 | 0.094563 | 71.37 | 3.80 | 0.942 | 0.373565 |
| 12 | 13.38 | −ve | 0.752 | 0.080494 | 41.97 | 1.12 | 0.876 | 0.311503 |
| 13 | 797.85 | 69.0 | 0.998 | 1.395091 | 801.22 | 69.4 | 0.997 | 2.197955 |
| 14 | −ve | −ve | 0.366 | 0.075091 | 28.42 | −ve | 0.792 | 0.281555 |
| 15 | 369.95 | 30.5 | 0.997 | 0.416982 | 376.74 | 31.2 | 0.994 | 0.975792 |
| 16 | 583.90 | 49.8 | 0.997 | 0.827709 | 588.43 | 50.2 | 0.996 | 1.514520 |
| 17 | 146.49 | 10.1 | 0.997 | 0.067004 | 150.39 | 10.5 | 0.992 | 0.191404 |
| 18 | 108.47 | 7.16 | 0.992 | 0.099099 | 61.79 | 2.87 | 0.755 | 1.687010 |
| 19 | 121.89 | 8.30 | 0.998 | 0.026874 | 96.05 | 5.94 | 0.964 | 0.411737 |
| 20 | 97.05 | 6.17 | 0.983 | 0.191209 | 30.45 | 0.06 | 0.350 | 3.892779 |
| 21 | 149.58 | 10.2 | 0.996 | 0.092660 | 156.56 | 10.9 | 0.990 | 0.289788 |
| 22 | 151.16 | 10.2 | 0.996 | 0.107741 | 159.66 | 11.0 | 0.988 | 0.348103 |
| 23 | 137.64 | 9.54 | 0.999 | 0.021127 | 132.00 | 9.06 | 0.997 | 0.042778 |
| 24 | 235.44 | 18.2 | 0.999 | 0.040015 | 224.83 | 17.3 | 0.999 | 0.053285 |
| 25 | 39.85 | 0.81 | 0.984 | 0.029591 | 46.26 | 1.43 | 0.984 | 0.039248 |
| 26 | 7.26 | −ve | 0.667 | 0.038490 | 21.70 | −ve | 0.936 | 0.038580 |
| 27 | −ve | −ve | 0.722 | 0.044080 | 10.79 | −ve | 0.798 | 0.039051 |
| 28 | −ve | −ve | 0.460 | 0.747822 | 206.58 | 16.1 | 0.963 | 1.948244 |
| 29 | 177.07 | 13.3 | 0.984 | 0.569559 | 206.58 | 16.1 | 0.963 | 1.948244 |
| 30 | −ve | −ve | 0.860 | 0.300999 | 187.71 | 14.0 | 0.973 | 1.145461 |

TABLE 12

Results of analysis of the thermal decomposition data of 2,6-dinitrophenol by integral (eqn. (7)) and differential (eqn. (8)) methods. Trace 3

| Function No. | Integral method | | | | Differential method | | | |
|---|---|---|---|---|---|---|---|---|
| | $E$ (kJ $mol^{-1}$) | log $A$ ($s^{-1}$) | $r$ | $Q$ | $E$ (kJ $mol^{-1}$) | log $A$ ($s^{-1}$) | $r$ | $Q$ |
| 1 | 349.22 | 27.8 | 0.996 | 0.266415 | 343.63 | 27.3 | 0.998 | 0.076285 |
| 2 | 363.41 | 28.9 | 0.996 | 0.300691 | 365.93 | 29.1 | 0.998 | 0.113442 |
| 3 | 368.56 | 28.7 | 0.996 | 0.322688 | 374.05 | 29.2 | 0.998 | 0.152831 |
| 4 | 378.89 | 29.7 | 0.995 | 0.381928 | 389.96 | 30.7 | 0.997 | 0.269269 |
| 5 | 46.21 | 1.19 | 0.964 | 0.049480 | 75.08 | 3.76 | 0.979 | 0.074336 |
| 6 | 44.29 | 1.10 | 0.966 | 0.042902 | 69.88 | 3.37 | 0.983 | 0.049384 |
| 7 | 330.20 | 25.1 | 0.996 | 0.265044 | 316.61 | 23.8 | 0.998 | 0.115718 |
| 8 | 411.30 | 32.7 | 0.993 | 0.709770 | 437.80 | 35.1 | 0.992 | 0.935352 |
| 9 | 165.03 | 11.9 | 0.990 | 0.160013 | 190.63 | 14.2 | 0.989 | 0.231114 |
| 10 | 88.47 | 5.17 | 0.981 | 0.090925 | 119.49 | 7.96 | 0.981 | 0.170785 |
| 11 | 50.18 | 1.80 | 0.960 | 0.065559 | 85.56 | 4.95 | 0.968 | 0.147789 |
| 12 | 11.89 | – ve | 0.695 | 0.046310 | 53.60 | 2.09 | 0.933 | 0.129821 |
| 13 | 854.19 | 72.6 | 0.995 | 1.883074 | 869.36 | 74.0 | 0.996 | 1.787744 |
| 14 | – ve | – ve | 0.541 | 0.038980 | 38.71 | 0.73 | 0.888 | 0.123116 |
| 15 | 394.75 | 32.1 | 0.994 | 0.514127 | 413.69 | 33.8 | 0.994 | 0.539201 |
| 16 | 624.47 | 52.3 | 0.995 | 1.088476 | 640.92 | 53.9 | 0.995 | 1.055483 |
| 17 | 123.27 | 10.5 | 0.993 | 0.100165 | 167.72 | 11.8 | 0.996 | 0.058595 |
| 18 | 105.44 | 6.78 | 0.986 | 0.094354 | 59.50 | 2.66 | 0.712 | 1.053708 |
| 19 | 122.49 | 8.21 | 0.993 | 0.062119 | 101.00 | 6.28 | 0.958 | 0.277830 |
| 20 | 90.77 | 5.52 | 0.973 | 0.138462 | 22.73 | – ve | 0.251 | 2.347839 |
| 21 | 157.10 | 10.7 | 0.992 | 0.116542 | 175.33 | 12.3 | 0.994 | 0.102600 |
| 22 | 159.05 | 10.7 | 0.991 | 0.126010 | 179.15 | 12.5 | 0.993 | 0.129672 |
| 23 | 142.27 | 9.78 | 0.994 | 0.068772 | 145.08 | 10.0 | 0.999 | 0.008036 |
| 24 | 245.75 | 18.8 | 0.996 | 0.148217 | 243.08 | 18.5 | 0.999 | 0.024326 |
| 25 | 38.79 | 0.74 | 0.970 | 0.028089 | 54.45 | 2.11 | 0.986 | 0.025387 |
| 26 | 4.30 | – ve | 0.444 | 0.023142 | 28.23 | – ve | 0.929 | 0.038651 |
| 27 | – ve | – ve | 0.835 | 0.022283 | 16.43 | – ve | 0.799 | 0.046826 |
| 28 | – ve | – ve | 0.410 | 0.389954 | 237.06 | 18.5 | 0.973 | 0.938601 |
| 29 | 190.88 | 14.3 | 0.982 | 0.400918 | 237.06 | 18.5 | 0.973 | 0.938601 |
| 30 | – ve | – ve | 0.877 | 0.149367 | 213.76 | 16.0 | 0.981 | 0.524683 |

TABLE 13

Results of analysis of the thermal decomposition data of 2,6-dinitrophenol by integral (eqn. (7)) and differential (eqn. (8)) methods. Trace 4

| Function No. | Integral method | | | | Differential method | | | |
|---|---|---|---|---|---|---|---|---|
| | $E$ (kJ mol$^{-1}$) | log $A$ (s$^{-1}$) | $r$ | $Q$ | $E$ (kJ mol$^{-1}$) | log $A$ (s$^{-1}$) | $r$ | $Q$ |
| 1 | 301.99 | 23.6 | 0.999 | 0.013256 | 302.13 | 23.6 | 0.999 | 0.037150 |
| 2 | 314.37 | 24.4 | 0.999 | 0.041378 | 321.65 | 25.1 | 0.998 | 0.094766 |
| 3 | 318.87 | 24.2 | 0.999 | 0.061344 | 328.76 | 25.1 | 0.998 | 0.142722 |
| 4 | 327.90 | 25.1 | 0.998 | 0.117143 | 342.70 | 26.4 | 0.997 | 0.277651 |
| 5 | 41.14 | 0.69 | 0.977 | 0.033880 | 69.63 | 3.20 | 0.970 | 0.125593 |
| 6 | 39.46 | 0.61 | 0.979 | 0.027719 | 64.98 | 2.86 | 0.975 | 0.091701 |
| 7 | 285.47 | 21.0 | 0.999 | 0.018380 | 278.61 | 20.4 | 0.999 | 0.053532 |
| 8 | 365.24 | 27.8 | 0.995 | 0.440462 | 384.60 | 30.3 | 0.992 | 1.013378 |
| 9 | 143.65 | 9.96 | 0.994 | 0.096167 | 170.51 | 12.3 | 0.987 | 0.327403 |
| 10 | 77.62 | 4.15 | 0.987 | 0.062794 | 108.64 | 6.93 | 0.975 | 0.253536 |
| 11 | 44.60 | 1.25 | 0.972 | 0.049203 | 78.96 | 4.30 | 0.961 | 0.217559 |
| 12 | 11.58 | −ve | 0.775 | 0.037677 | 50.80 | 1.77 | 0.925 | 0.182225 |
| 13 | 737.99 | 62.2 | 0.998 | 0.768161 | 756.78 | 63.9 | 0.997 | 0.127974 |
| 14 | −ve | −ve | 0.489 | 0.032687 | 37.58 | 0.56 | 0.885 | 0.165088 |
| 15 | 341.77 | 27.3 | 0.997 | 0.245839 | 363.48 | 29.3 | 0.994 | 0.579342 |
| 16 | 539.88 | 44.8 | 0.998 | 0.469828 | 559.66 | 46.6 | 0.996 | 0.894347 |
| 17 | 133.37 | 8.68 | 0.997 | 0.038879 | 150.35 | 10.2 | 0.993 | 0.121408 |
| 18 | 91.70 | 5.49 | 0.993 | 0.048899 | 54.56 | 2.14 | 0.743 | 1.020442 |
| 19 | 106.52 | 6.73 | 0.998 | 0.011094 | 91.43 | 5.36 | 0.964 | 0.269013 |
| 20 | 78.98 | 4.40 | 0.982 | 0.096307 | 21.61 | −ve | 0.281 | 2.311504 |
| 21 | 136.72 | 8.82 | 0.996 | 0.054292 | 157.05 | 10.6 | 0.991 | 0.176025 |
| 22 | 138.43 | 8.86 | 0.996 | 0.063313 | 160.41 | 10.8 | 0.990 | 0.208607 |
| 23 | 123.77 | 8.07 | 0.999 | 0.010781 | 130.39 | 8.66 | 0.997 | 0.042246 |
| 24 | 212.88 | 15.8 | 0.999 | 0.010451 | 215.28 | 16.0 | 0.998 | 0.039709 |
| 25 | 34.65 | 0.31 | 0.986 | 0.014236 | 51.18 | 1.75 | 0.981 | 0.042389 |
| 26 | 4.95 | −ve | 0.627 | 0.016082 | 27.91 | −ve | 0.942 | 0.041924 |
| 27 | −ve | −ve | 0.841 | 0.017135 | 17.34 | −ve | 0.867 | 0.041873 |
| 28 | −ve | −ve | 0.368 | 0.386909 | 211.32 | 16.1 | 0.971 | 1.116862 |
| 29 | 166.27 | 12.1 | 0.985 | 0.336725 | 211.32 | 16.1 | 0.971 | 1.116862 |
| 30 | −ve | −ve | 0.875 | 0.142409 | 190.85 | 13.9 | 0.979 | 0.659426 |

TABLE 14

Calculated values of kinetic parameters of thermal decomposition for some energetic materials

| Energetic material | $\alpha$ | $G(\alpha)$ | Eqn. (7) | | Eqn. (8) | | Eqn. (12) | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | $E$ | $\log A$ | $E$ | $\log A$ | $E$ | $\log A$ | $n$ |
| I [6] | 0.007–0.66 | $\alpha$ | 133<br>$\pm 8$ | 9.01<br>$\pm 0.79$ | 134<br>$\pm 8$ | 9.10<br>$\pm 0.63$ | 134<br>$\pm 9$ | 9.17<br>$\pm 0.77$ | 0 |
| II | 0.015–0.087 | $\alpha$ | 196 | 17.5 | 210 | 18.9 | 209 | 18.8 | 0 |
| III | 0.019–0.51 | $1-(1-\alpha)^{1/2}$ | 177 | 16.4 | 178 | 16.5 | 180 | 17.0 | 0.54 |
| IV | 0.018–0.44 | $-\ln(1-\alpha)$ | 163 | 15.3 | 164 | 15.4 | 174 | 16.6 | 1.2 |

$\alpha$, The fraction of material reacted; $G(\alpha)$, the integral mechanism function; $E$, the activation energy (kJ $\text{mol}^{-1}$); $A$, the pre-exponential constant ($1/s$); $n$, the reaction order.

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