Kinetics of Decomposition of Nitramine Propellant by Differential Scanning Calorimetry

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ABSTRACT

The paper describes an experimental procedure for the determination of overall kinetic parameters for the exothermic decomposition reaction of nitramine propellant. The kinetic parameters can be obtained through the use of differential thermal analysis (DTA), differential scanning calorimetry (DSC) or thermogravimetric analysis (TGA) methods. The procedure is applicable to reactions whose behaviour can be described by the Arrhenius equation and the general rate law. In the present work, DSC technique has been used for the evaluation of Arrhenius activation parameters and specific rate constants for thermal decomposition of a typical nitramine propellant. The kinetic parameters were computed by Ozawa and Kissinger methods for comparison. The activation energy value obtained from the Ozawa method is refined by an iteration procedure using Doyle approximation for the Arrhenius temperature integral $p(x)$.

1. INTRODUCTION

The thermal analysis technique has proved to be useful for the qualitative and quantitative study of thermal characteristics of propellants and explosive materials. Although considerable thermoanalytical data have been generated and reported over the last few years, the study of thermochemistry of explosives is still an active area of research. The kinetics of exothermic reactions are important in assessing the hazard potential of materials for their handling, safe processing, storage, and shipping. The kinetic parameters, in many cases, also provide other important information on thermal stability, rate of decomposition and life time prediction of materials and systems under different experimental and environmental conditions. Nitramine propellants belong to the category of potentially hazardous systems which undergo a fast exothermic decomposition reaction.

The thermal analysis methods, particularly DSC and TGA, are the proven methods for the evaluation of kinetic parameters of various reactions[1-6]. The method described in this paper provides a means of determining the specific rate constant k, activation energy E, and pre-exponential factor A for thermal decomposition of nitramine propellants using DSC method.

DSC is one of the accurate, reasonably rapid and straight forward method for the evaluation of kinetics of chemical reactions[2]. The kinetic parameters can be derived from DSC based on (i) the peak temperature program rate relationship[7-10], (ii) the shape of heat flow curve obtained[11], and (iii) the derivative of peak[12] Some of these DSC methods assume either zero or first order kenetics while the others provide a means of calculating the reaction order[8,9,11,13]

One of the most widely used DSC methods is the variable program rate method, which was originally developed by Kissinger for DTA[7]. Later Ozawa[12] developed a simpler method which is popularly used for the calculation of kinetic parameters from TG and DSC. The Kissinger method is based on the plot of log (ϕ/T_m^2) versus reciprocal of peak maximum temperature in absolute, where ϕ is the heating rate and T_m is the peak maximum temperature of the DSC curve. The Ozawa method is basically a plot of log (ϕ) versus

$(1/T_m)$. The Ozawa method is also the basis of an ASTM technique developed by the Committee E 27 on hazard potential of chemicals[10] These two methods allow determination of activation parameters and rate constants.

2. EXPERIMENTAL

2.1 Sample

Nitramine propellant developed by the Vikram Sarabhai Space Centre was used for the present study.

2.2 Instrumental

DSC experiments were carried out in a Mettler TA-3000 thermal analysis system equipped with DSC-20 standard cell and TC 10A TA processor. The DSC curves were recorded on a Swiss matrix printer. The heat flow and temperature calibration of DSC were done using indium metal as per the procedure recommended by the manufacturer. All experiments were carried out in an atmosphere of pure nitrogen gas (IOLAR-3 grade, purity > 99.9 per cent) purged at the rate of 30 cm^{3}min^{-1}. Aluminium sample pans (40 μl) were used for the DSC experiments. Almost constant sample mass of 1.2 ± 0.1 mg was used. The heating rate ranged from 2 to 20 °C/min in six steps.

2.3 DSC Analysis

The sample is placed in a tared aluminium pan, sealed with a pierced lid weighed and placed in the DSC cell. The pan is then brought to equilibrium at the starting temperature of 50 °C. An empty aluminium pan with pierced lid is taken as the reference. The sample is then temperature–programmed through the c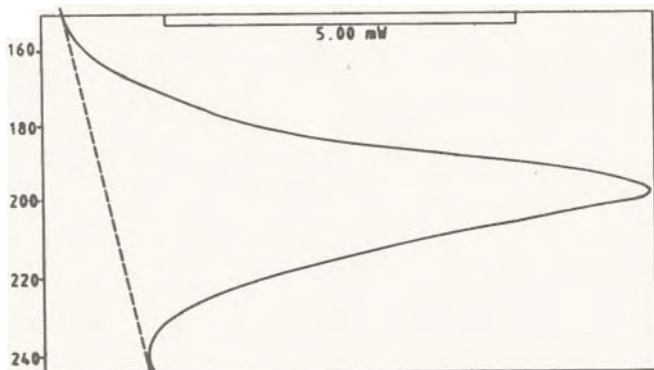ompletion of exothermic transition at the preselected heating rate. This produces a scan similar to that shown in Fig. 1. The experiment is repeated using a new sample and applying a series of heating rates between 2 and 20 °C/min. The variation of peak maximum temperature T_m with heating rate is noted. The variation of peak temperatures corresponding to each program rate is evaluated manually and with the area integration program available in TC 10A TA processor.

2.4 Treatment of Data

2.4.1 Activation Energy

(a) Ozawa method: Log heating rate versus reciprocal of the absolute temperature $(1/T_m)$ is plotted. The slope of the straight line plot, is used for the calculation of approximate value of E. The data used to get the Ozawa plot is given in Table 1 and the

Table 1. DSC experimental data for Ozawa plot

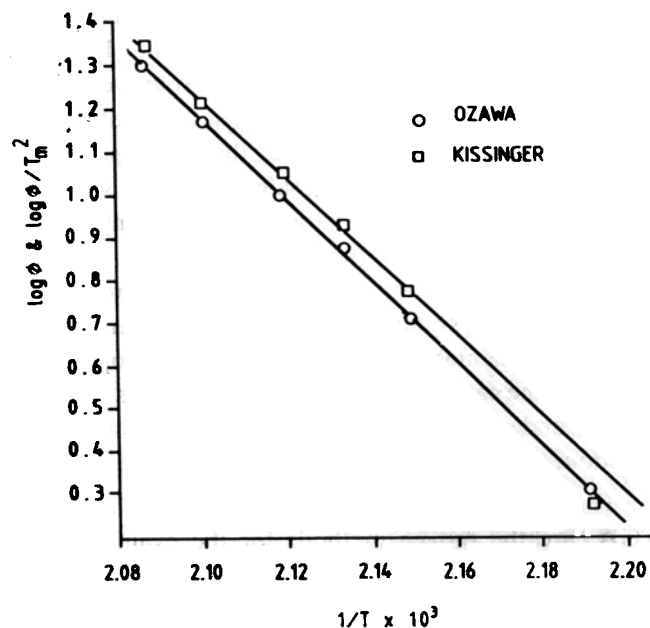| ϕ (°C/min)	T (°K)	$\log \phi$	$(1/T) \times 10^3$
2.0	456.4	0.3010	2.1911
5.0	465.5	0.6990	2.1482
7.5	468.9	0.8751	2.1327
10.0	472.0	1.0000	2.1186
15.0	476.1	1.1761	2.1004
20.0	479.5	1.3010	2.0855

Figure 1. DSC curve of nitramine propellant.

Figure 2. Ozawa and Kissinger kinetioc plots.

corresponding plot is shown in Fig. 2. The equations used for the calculation of k, E and A are given below :

$$k = A \exp (-E/RT) \quad (1)$$

where R is the gas constant (8.314 J/mol/°K)

$$E = 2.19 R \, (d \log \phi/d(1/T_m) \quad (2)$$

$$A = (\phi \, E \exp (E/RT))/RT_m^2 \quad (3)$$

(b) Kissinger method : This is an alternate method for calculating activation energies. Plot of log (ϕ/T_m^2) versus $1/T_m$ is made and E can be calculated from the slope of the curve using the following equations :

$$\text{Slope} = [d \log (\phi/T_m^2)] \, /d(1/T_m) \quad (4)$$

$$E = (R \, d \log (\phi/T_m^2)) \, /d(1/T_m) \quad (5)$$

The data used to calculate E by this method are given in Table 2.

Table 2. DSC experimental data for Kissinger plot

ϕ (°C/min)	T K)	log (ϕ/Tm^2)	$(1/T) \times 10^3$
2.0	456.4	−5.0177	2.1911
5.0	465.5	−4.6369	2.1482
7.5	468.9	−4.4671	2.1327
10.0	472.0	−4.3479	2.1186
15.0	476.1	−4.1793	2.1004
20.0	479.5	−4.0605	2.0855

The Kissinger plot for the decomposition of nitramine propellant is shown in Fig. 2. Both the plots show good linear curves. The correlation constants for the two plots are 0.9996 and 0.9995 respecti..⌐y indicating the goodness of the fits.

2.4.2 Refinement of E from Ozawa Method

The calculated value of E from the Ozawa method is only approximate and therefore requires refinement[14], which is done using a series of iterations based on the relationship[13].

$$g (\alpha) = (AE/\phi R) \, p(x) \quad (6)$$

E and A can be calculated if $g(\alpha)$ and $p(x)$ are known. Here $g(\alpha)$ is the integrated form of $f(\alpha)$, i.e.,

$$g (\alpha) = \int_0^\alpha d\alpha/f(\alpha) \quad (7)$$

where α is the fractional conversion, $p(x)$ is the Arrhenius temperature integral, and x is equal to E/RT.

The temperature integral $p(x)$ can be evaluated from various approximations, viz., simple approximation, numerical and series solutions. The series solution for the $p(x)$ function proposed by Doyle[15] is used for the present work. The approximation is represented as

$$p(x) = (x + 2)^{-1} (x)^{-1} (e)^{-x} \quad (8)$$

The values of x $(=E/RT)$ are calculated, where E is the approximated activation energy in J/mol, T is the peak maximum temperature, and K is obtained using a program rate near the middle of the range (normally 10 °C/min). From these values, $p(x)$ and the derivative $(D) = d \ln p(x)/dx$ are calculated for the refinement of E. By substituting the values of x and D, and slope of the Ozawa plot, E can be calculated as follows:

$$E = [2.303R/D] \, [d \log \phi/d(1/T_m)] \quad (9)$$

The iterative refinements are continued using each calculated value of the activation energy until two successive values are identical. The values of x, D and E on successive iteration are given in Table 3.

Table 3. Values of x, D, and E for iteration by the approximation $P(x) = (x+2)^{-1} (x)^{-1} (e)^{-x}$

E (J/mol)	$x = E/RT$	D
174202.6	44.39204	1.04505
175294.6	44.67006	1.04477
175341.7	44.68205	1.04476
175343.6	44.68257	1.04476
175343.8	44.68259	1.04476

2.4.3 Pre-Exponential Factor

The pre-exponential factor A is calculated from Eqn (3). The logarithmic form of Eqn (3) is represented as

$$\ln A = \ln \phi + \ln E + (E/RT) - \ln R - 2\ln T \quad (10)$$

The pre-exponential factor calculated for all six sets of data using Eqn (10) are given in Table 4. The mean values of A and ln A are 2.38 × 10¹⁹ min⁻¹ and 44.62 respectively, by using the E value (refined) calculated by the Ozawa method. The mean values for A and ln A by using Kissinger E value are 2.435 × 10¹⁹ min⁻¹ and 45.15, respectively. The calculated A values for six sets of experiments along with activation energy from

Table 4. Pre-exponential factor evaluation by Ozawa method

ϕ (°C/min)	log ϕ	(E/RT)	log T	log A	$A \times 10^{19}$ min^{-1}
2.0	0.3010	46.21	2.659	19.375	2.372
5.0	0.6990	45.31	2.668	19.364	2.310
7.5	0.8751	44.98	2.671	19.391	2.459
10.0	1.0000	44.68	2.674	19.382	2.408
15.0	1.1761	44.30	2.678	19.383	2.416
20.0	1.3010	43.98	2.681	19.365	2.320

Table 5. Pre-exponential factor calculation by Kissinger method

ϕ (°C/min)	log ϕ	(E/RT)	log T	log A	$A \times 10^{19}$ min^{-1}
2.0	0.3010	46.23	2.659	19.385	2.428
5.0	0.6990	45.93	2.668	19.374	2.364
7.5	0.8751	45.33	2.671	19.346	2.515
10.0	1.0000	44.70	2.674	19.391	2.642
15.0	1.1761	44.32	2.678	19.393	2.470
20.0	1.3010	44.01	2.681	19.375	2.372

$E = 175430$ J/mol

Table 6. Rate constants using Ozawa values

T (K)	ln k	k
383	−10.450	2.8962×10^{-5}
393	− 9.0484	1.1758×10^{-4}
398	− 8.3742	2.3075×10^{-4}
403	− 7.7167	4.4531×10^{-4}
408	− 7.0754	8.4565×10^{-4}
413	− 6.4496	1.5812×10^{-3}
418	− 5.8388	2.9124×10^{-3}
423	− 5.2424	5.2877×10^{-3}
428	− 4.6599	9.4674×10^{-3}

2.4.4 Rate Constant

The rate constant k is obtained from the Arrhenius equation Eqn (1) for each temperature of interest. The logarithmic form of Eqn (1) is expressed as

$$\ln k = \ln A - E/RT \tag{11}$$

The values of rate constants for temperatures ranging from 383 to 428 K are given in Table 6.

3. CONCLUSION

The activation energy, pre-exponential factor and specific rate constant of the nitramine propellant system are established. The activation parameters calculated using the two methods, viz, Ozawa and Kissinger methods are in good agreement with each other and their values are not considerably influenced by the range of heating rates employed in the present study.

Kissinger method are given in Table 5. Since the deviations of A from the value of the middle of heating rate (10 °C/min) are very small, it can be inferred that the influence of heating rate on the Arrhenius parameters is negligible for the thermal decomposition of nitramine propellant.

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