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ESTIMATION OF ACTIVATION ENERGIES FROM DIFFERENTIAL THERMAL ANALYSIS CURVES

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ABSTRACT

An average activation energy $\Delta E^{\neq}$ of 31.7 $\pm$10.0 kcal/mole was calculated from exothermic peaks of urea nitrate differential thermal analysis (DTA) curves using the Murray and White equation and various other reaction rate equations developed by the authors. An average enthalpy of activation, $\Delta H^{\neq}$ of 30.8 $\pm$9.7 kcal/mole was calculated from the same results. The values of $\Delta E^{\neq}$ and $\Delta H^{\neq}$ differed by a fraction of a kcal/mole indicating that $\Delta E^{\neq} < \Delta H^{\neq}$ cannot be differentiated experimentally in our study. Application of the Kissinger method of calculating $\Delta E^{\neq}$ and $\Delta H^{\neq}$ produced respectively 21.6 $\pm$7.9 and 20.7 $\pm$8.0 kcal/mole, which are quite low. The values of $\Delta E^{\neq}$ and $\Delta H^{\neq}$ calculated thermogravimetrically were 28.1 $\pm$1.1 kcal/mole and 27.6 $\pm$1.2 kcal/mole which are close to those obtained from the Murray and White approach and the authors' approach to treatment of the DTA data. These results illustrate the pronounced effect of self heating on calculation of activation energies.

The Kissinger method of calculating the reaction order developed for endothermic DTA peaks produced good results when applied to the present DTA study.

INTRODUCTION

The activation energy ($\Delta E^{\neq}$) and the order of the reaction (n) may be estimated from differential thermal analysis (DTA) curves using three general procedures: (1) trial and error[1-3], (2) a direct method[4,5] and (3) a semidirect method[6-9] in which $\Delta E^{\neq}$ may be estimated after assuming a value for n. The authors adopted a semidirect procedure to determine $\Delta E^{\neq}$ from the induction period data and also used the Murray and White equation[10] and Kissinger plot[11]. The Kissinger semidirect method[12] of determining the reaction order n from the endothermic DTA peaks of several minerals was used in this paper to determine the reaction order from the exothermic DTA peak of urea nitrate heated at a rate of 1 °C/min in open air.

EXPERIMENTAL

A Fisher differential thermoanalyzer, Model 360, was used for the DTA measurements. All samples were tested in open air in a quartz tube 3 mm in diameter and 6 cm long. Heating rates of 1, 2, 5 and 10°C/min were used to determine the temperature gradient, ΔT, between the sample and the alumina reference. The temperature was measured by a chromel–alumel thermocouple. The sample was loosely placed in the sample holder and only gentle tapping was applied for packing.

RESULTS AND DISCUSSION

The experimental results for the decomposition are summarized in Table 1 and an experimental exothermic DTA peak with points of interest using a heating rate of 1 °C/min is shown in Fig. 1. The reaction order n was calculated from this peak using the Kissinger method[12] as will be shown later. The shift in the position of the DTA peak due to the change in heating rate is clearly indicated in Table 1 by the values of τ and T_i. The gases, N_2O, CO_2, and water vapor, evolved[13] at a higher rate with higher heating rates diffused away slowly enough to retard the reaction sufficiently that the DTA peak appears at a higher temperature[14], comparing higher heating

TABLE 1

SUMMARY OF RESULTS

Φ (°C/min)	W_0 (mg)	τ (min)	T_i (°K)	T_f (°K)	ΔT (°C)	T_s (°K)	t_p (min)
1	5.40	131.7	413.0	416.0	3.6	419.60	133.4
2	5.75	65.0	419.0	420.0	6.0	426.50	66.3
5	5.45	32.8	429.75	431.55	11.0	442.55	33.2
10	6.35	14.5	437.25	439.75	16.6	456.35	14.9

Φ, Heating rate; W_0, sample weight in mg; τ, induction time in minutes, or time elapsed until the start of the DTA curve. T_i, temperature of furnace at the end of the induction period; T_f, temperature of the furnace at the time of maximum deflection on the DTA curve; ΔT, the maximum increase in the temperature of the sample due to self-heating; T_s, temperature of the sample at the time of the maximum deflection on the DTA curve, *i.e.*, $T_s = T_f + \Delta T$; t_p, time in minutes taken to reach maximum deflection on DTA curve.

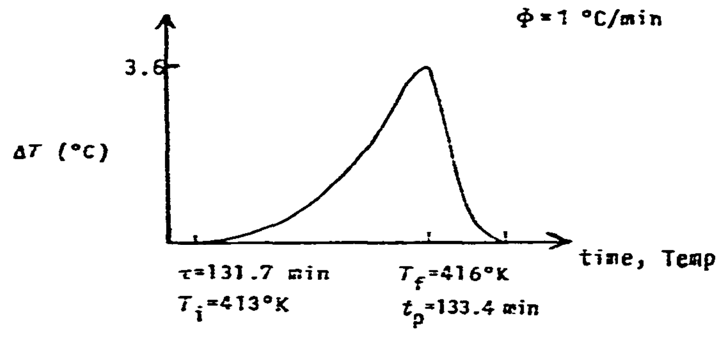

Fig. 1. Actual exothermic DTA curve for urea nitrate in open air (see Table 1 for definition of notations).

rates with lower rates. The peak height is also affected by the heating rate[14]. The peak shift and height might also have been affected slightly by the slight variation in sample size[4].

In considering the results of Table 1 a few kinetic equations helpful in calculating the values of the activation energy $\Delta E^{\ddagger}$ and the activation enthalpy $\Delta H^{\ddagger}$ will be derived.

The reaction rate constant K is directly proportional to the specific rate constant[13] K' and inversely proportional to the induction period τ. Therefore

$$K = aK' = \frac{b}{\tau}$$

or

$$K' = \frac{c}{\tau} \tag{1}$$

where a, b, and their ratio c are proportionality constants. The value of K', is given by the Arrhenius equation as

$$K' = A \exp\left(\frac{-\Delta E^{\ddagger}}{RT}\right) \tag{2}$$

where A, $\Delta E^{\ddagger}$, R and T are respectively frequency factor, activation energy, universal gas constant and absolute temperature. Relating eqn (2) with eqn (1), followed by rearrangement yields in the logarithmic form

$$\log\left(\frac{1}{\tau}\right) = \lambda - \frac{\Delta E^{\ddagger}}{2.3\,RT} \tag{3}$$

where λ is a constant equal to log (A/c). The value of K' is also given by the Eyring absolute reaction rate theory[15] as

$$K' = \frac{\kappa k T}{h} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right) \exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right) \tag{4}$$

where κ, k, T, h, $S^{\ddagger}$, R, and $\Delta H^{\ddagger}$ are respectively transmission coefficient (normally assumed as 1), Boltzman constant, absolute temperature, Planck's constant, activation entropy, molar gas constant, and activation enthalpy. Equating eqns (4) and (1), rearranging, and taking the logarithm we obtain

$$\log\left(\frac{1}{\tau T}\right) = \left[\log\left(\frac{\kappa k}{ch}\right) + \frac{\Delta S^{\ddagger}}{2.3\,R}\right] - \frac{\Delta H^{\ddagger}}{2.3\,RT}. \tag{5}$$

Similar equations can be derived for $\Delta E^{\ddagger}$ and $\Delta H^{\ddagger}$ by using the time, t_p, at which the DTA temperature peak appears instead of τ.

The activation energy ($\Delta E^{\ddagger}$) can also be calculated from the Murray and White equation[10]

$$\log\left(\frac{\Phi}{T_s^2}\right) = I - \frac{\Delta E^{\ddagger}}{2.3\,RT_s} \tag{6}$$

where Φ, T_s, and I are respectively heating rate, absolute temperature of the sample at maximum deflection on the DTA curve, and a constant which also contains the conversion factor. The term T_s is defined by $T_s = T_f + \Delta T$, where T_f is the furnace temperature at the time of the maximum increase in the temperature of the sample due to self heating and ΔT is the sample temperature rise due to self heating; T_s and T_f occur at time t_p as can be seen in Table 1.

Equation (6) indicates that the reaction rate constant K is proportional to Φ/T_s^2, *i.e.*

$$K = \beta\frac{\Phi}{T_s^2} \tag{7}$$

where β is the proportionality constant, and contains conversion factors.

But the reaction rate constant K was given by eqn (1) namely

$$K = aK' \tag{1}$$

where the specific rate constant, K' is either given by eqn (2) or eqn (4) depending on whether we want to calculate $\Delta E^{\ddagger}$ or $\Delta H^{\ddagger}$. If we substitute eqns (2) and (7) into eqn (1), rearrange and take the logarithm provided that $T_s = T$, we obtain an equation exactly similar to eqn (6) with $I = \log(aA/\beta)$: while if we insert eqn (4) and (7) into eqn (1), rearrange and take the logarithm we obtain

$$\log\frac{\Phi}{T_s^3} = I' - \frac{\Delta H^{\ddagger}}{2.3\,RT_s} \tag{8}$$

where the constant I' is given by

$$I' = \log\left[\frac{a}{\beta}\frac{\kappa k}{h}\,e^{\Delta S^{\ddagger}/R}\right]$$

Table 2 summarizes the various ways of calculating $\Delta E^{\ddagger}$ and $\Delta H^{\ddagger}$ using the method of least squares at 95% confidence range[16]. All the calculations are based on the data presented in Table 1. The values of $\Delta E^{\ddagger}$ and $\Delta H^{\ddagger}$ based on thermogravimetric measurements[13] were calculated and included for the sake of comparison.

The following conclusions may be drawn from the results presented in Table 2.

(*1*) Plots (1) and (2) produced slightly higher values for $\Delta E^{\ddagger}$ and $\Delta H^{\ddagger}$ than those obtained from the thermogravimetric (TG) results[13] shown at the bottom of Table 2. This slight difference could be attributed to experimental error, method of calculation, and sample weight. The average sample weight used in the DTA measurements was about ten times heavier than that used in the TG measurements.

TABLE 2

ESTIMATIONS OF $\Delta E^{\ddagger}$ AND $\Delta H^{\ddagger}$

Number	*Form of plot used to find* $\Delta E^{\ddagger}$	$\Delta E^{\ddagger}$ *(kcal/mole)*	*Form of plot used to find* $\Delta H^{\ddagger}$	$\Delta H^{\ddagger}$ *(kcal/mole)*
1	Induction period; $\log \frac{1}{\tau}$ vs. $\frac{1}{T_i}$	31.0 ± 11.0	$\log \frac{1}{\tau T_i}$ vs. $\frac{1}{T_i}$	30.2 ± 11.2
2	Induction period; $\log \frac{\Phi}{T_i^2}$ vs. $\frac{1}{T_i}$	31.8 ± 4.8	$\log \frac{\Phi}{T_i^3}$ vs. $\frac{1}{T_i}$	30.9 ± 4.8
3	Considering ΔT; $\log \frac{1}{t_p}$ vs. $\frac{1}{T_s}$	21.6 ± 8.3	$\log \frac{1}{t_p T_s}$ vs. $\frac{1}{T_s}$	20.7 ± 8.3
4	Considering ΔT; $\log \frac{\Phi}{T_s^2}$ vs. $\frac{1}{T_s}$	21.5 ± 7.6	$\log \frac{\Phi}{T_s^3}$ vs. $\frac{1}{T_s}$	20.6 ± 7.7
5	Neglecting ΔT; $\log \frac{1}{t_p}$ vs. $\frac{1}{T_f}$	31.6 ± 13.2	$\log \frac{1}{t_p T_f}$ vs. $\frac{1}{T_f}$	30.7 ± 13.2
6	Neglecting ΔT; $\log \frac{\Phi}{T_f^2}$ vs. $\frac{1}{T_f}$	32.3 ± 10.9	$\log \frac{\Phi}{T_f^3}$ vs. $\frac{1}{T_f}$	31.5 ± 10.9
Average based on plots (1), (2), (5) and (6)		31.7 ± 10		30.8 ± 9.7
Thermogravimetric results		28.3 ± 1.1		27.6 ± 1.2

(*2*) Plots (3) and (4) produced lower values for $\Delta E^{\ddagger}$ and $\Delta H^{\ddagger}$ than those obtained from the TG results. This is due to the variation of the peak height (ΔT) with the heating rate Φ, *i.e.*, there is a thermal lag which is not comprehended using the Kissinger method[11] of calculating $\Delta E^{\ddagger}$ or $\Delta H^{\ddagger}$. This illustrates the incorrectness of Kissinger's assumption[11] of maximum reaction rate at the time of the DTA peak.

(*3*) Plots (5) and (6) produce results similar to those obtained for plots (1) and (2). These results might be explained by the fact that the great thermal lag introduced is compensated for by neglecting the peak height, ΔT, and this results in obtaining values for $\Delta E^{\ddagger}$ and $\Delta H^{\ddagger}$ close to those obtained thermogravimetrically.

(*4*) The various ways of calculating $\Delta E^{\ddagger}$ and $\Delta H^{\ddagger}$ lead to the fact that plots (1) and (2) are equivalent. The same is true for plots (3) and (4); and (5) and (6).

(*5*) The values of $\Delta E^{\ddagger}$ and $\Delta H^{\ddagger}$ differ by an average of 0.754 kcal/mole. This small difference could not be differentiated experimentally and in our present study we could safely say that $\Delta E^{\ddagger}$ and $\Delta H^{\ddagger}$ are equivalent.

(*6*) The calculated values of the correlation factor "r" ranged from 0.990 to 0.999 indicating quite good correlation between the log variable and the inverse of the absolute temperature variable for plots (1) through (6).

(*7*) Since the values of $\Delta E^{\ddagger}$ and $\Delta H^{\ddagger}$ obtained from plots (3) and (4) are incorrect, the values of $\Delta E^{\ddagger}$ and $\Delta H^{\ddagger}$ based on plots (1), (2), (5) and (6) were averaged and found to be close to those obtained thermogravimetrically; thus, the TG values seem substiantiated.

(*8*) The lower value of the calculated precision for the DTA results compared to the thermogravimetric results is mainly due to the lesser number of degrees of freedom used for the DTA results. Four degrees of freedom were used for calculating the precision at 95% confidence range for the TG results, while only two were used in calculating the precision for the DTA results.

The reaction order, n, can be related to the shape of the DTA peaks. Kissinger[12] defined a shape index S for endothermic DTA peaks of various minerals, as the ratio of the slope of the tangent at the inflection point on the left side of the peak to that at the inflection point on the right side. The shape index, S, and the reaction order, n, are related by[12]

$$n = 1.26\, S^{1/2} \tag{9}$$

when the general rate equation[11]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A(1-\alpha)^n\, \mathrm{e}^{-\Delta E^{\ddagger}/RT} \tag{10}$$

was used, where α, A, and $\Delta E^{\ddagger}$ respectively are fraction reacted at time t, frequency factor, and activation energy.

To relate n to TG data consider a growing nuclei model[17] of decomposition as given by

$$\alpha^{1/m} = K(t-t_0) \tag{11}$$

in which α = fraction reacted at time t, K = reaction rate constant, t_0 = induction period based on TG measurements, and $1/m$ = constant of value 0.33.

Equation (11) may be differentiated with respect to time, t, and arranged to

$$\mathrm{d}\alpha/\mathrm{d}t = K_1\alpha^{(1-1/m)} \tag{12}$$

where $K_1 = mK$ is a new reaction rate constant. The value of α in eqn (12) may be replaced by $(1-w)$, where w is the fraction unreacted at time t. Then

$$-\mathrm{d}w/\mathrm{d}t = K_1(1-w)^{(1-1/m)}$$

where $K_1 = A_1\,\mathrm{e}^{-\Delta E^{\ddagger}/RT}$, with $A_1 = mA$

or

$$-\mathrm{d}w/\mathrm{d}t = K_1(1-w)^n = A_1(1-w)^n\,\mathrm{e}^{-\Delta E^{\ddagger}/RT} \tag{13}$$

where the reaction order n is given by

$$n = 1 - 1/m \tag{14}$$

The form of eqn (13) is similar to that of eqn (10).

The shape index S of the exothermic peak presented in Fig. 1 was calculated to be 0.265. According to eqn (9), a value of $n = 0.649$ was calculated. Then a value of $1/m$ of 0.35 was obtained from eqn (14).

This value of $1/m$ of 0.35 calculated from eqn (14) was in good agreement with that of eqn (11) namely 0.33. This indicates the validity of applying Kissinger's procedure[12] for calculating reaction order, *n*, originally developed for application to endothermic DTA peaks of minerals to exothermic DTA peaks of organic materials, *i.e.*, urea nitrate.

Reich's direct procedure[5], which was developed and applied to determine *n* from endothermic DTA peaks of inorganic materials, was not applicable to the present DTA data. This is because Reich developed a model for DTA peaks of which the majority of the area of two peaks obtained at different heating rates must be located within a limited temperature region. This was not the case in the present study.

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