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DIFFERENTIAL SCANNING CALORIMETRIC STUDIES ON AMMONIUM PERCHLORATE

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ABSTRACT

Differential scanning calorimetric studies on ammonium perchlorate have been carried out. The enthalpy values for the phase transition endotherm and the two exotherms have been reported in the present communication. A new method has been developed for the estimation of kinetic parameters from DSC thermograms. The values for activation energy as calculated by the above method for low temperature and high temperature exotherms are in close agreement with literature values. The present studies also confirm the presence of small exothermic peaks at the initial stages of high temperature exotherm. Explanation for the same has been given.

INTRODUCTION

Much work has been done on the thermal decomposition of ammonium perchlorate (AP)[1,2] but the quantitative estimation of exothermicity of the two individual exotherms has not yet been reported. TG and DTA studies do show a break around the temperature of the low temperature exotherm (LTE). Differential scanning calorimeter (DSC) being a very sensitive and accurate measuring device, it would be worthwhile to estimate the ratio of the enthalpy of the LTE and that of the high temperature exotherm (HTE) in order to figure out whether the processes leading to LTE and HTE in general are the same or different. Another aspect which the present measurements may clarify is that the DSC studies would either include both solid-state and gas-phase reactions or solid-state processes.

Activation energy (E) values for the thermal decomposition of AP by isothermal techniques are fairly well established[3]. Only few attempts have been made in the past to calculate E from DSC techniques. The actual values reported seem to depend upon the method used to calculate E. It is evident that there is a need for a method which gives a value in agreement with the isothermal values.

All the DTA work shows that following the phase-transformation, AP shows two exotherms, the magnitudes varying with the pre-history of the material. DSC studies have confirmed the above observation. A careful analysis of Sammon's[12] results, however, shows that there are some small little exothermic peaks at the beginning of HTE. These could not be the noise signal of the instrument because they are more pronounced under certain conditions, e.g., purity, grinding, etc. Whereas one can then attribute them to impurities, one cannot reject the supposition that these small exotherms are related to the overall sensitivity of LTE. The present study therefore intends to make careful observations on their authenticity.

EXPERIMENTAL

Powdered AP from Fischer Scientific Co. was used as such without further purification. DSC thermograms were obtained by one of the authors (K.K.) during his stay at the University of Leeds.

Isothermal and scanning thermograms were obtained on a Perkin-Elmer DSC-1B differential scanning calorimeter. Average and differential temperature settings were calibrated before obtaining the thermograms. The performance of the chart recorder was also checked separately. The setting of the calorimeter in the desired temperature range and the calibration of the temperature axis was done according to the Perkin-Elmer instructions[4]. Thermal decomposition studies were carried out at ambient pressure and under dry nitrogen atmosphere.

Weighing of the sample was done on an electrobalance (Research and Industrial Co., EMB-1) which was calibrated against a standard mass.

Weighed samples were kept in aluminium pans and were sealed with a sample sealer. The samples were evenly distributed at the bottom of the sample pan before sealing. AP between 2 to 3.5 mg was used in each run. The bottoms of the pans were pressed hard before sample filling so that they could have good thermal contact with the sample holder. A pin hole was made at the top of the lid so that the product gases could escape during decomposition. The sample and the reference pans were positioned at the center of the holder cells and were covered with aluminium domes.

Scanning operations were carried out at heating rates of 2, 4, 8, 16, 32 and 64 K min^{-1}. In scanning runs the temperature of the assembly was kept at least 25 K below the temperature where the reaction is likely to occur and then the temperature was allowed to increase at a programmed rate. In isothermal runs, the desired temperature, was attained rapidly by manually operating the scanning temperature knob and held constant at the desired temperature. The zero knob was adjusted to get the signal within the chart recorder. The difference in the isothermal signals at the start and end were taken into account while drawing the baseline for isothermal thermograms. Range settings of 2, 4, 8, 16, 32 and 64 mcal sec^{-1} per full scale deflection were used. They were adjusted to a particular value in each run in order to get a proper measureable area under the curve. Thermograms for empty pan, pan containing sample and pan containing products were obtained for each sample.

The total area and the area under the segments at different time intervals were measured for α (fraction decomposed) vs. time plot for each exotherm/endotherm. The area measurement was done by planimeter which was calibrated and constantly checked against known area. The baseline for both isothermal and scanning thermograms were drawn as described earlier[5]. The enthalpy changes under the exotherm/

endotherm were calculated by comparing them with the peak of standard indium of known weight[4].

RESULTS AND DISCUSSION

Typical DSC thermograms for the scanning and the isothermal modes of operation are presented in Figs. 1 and 2, respectively.

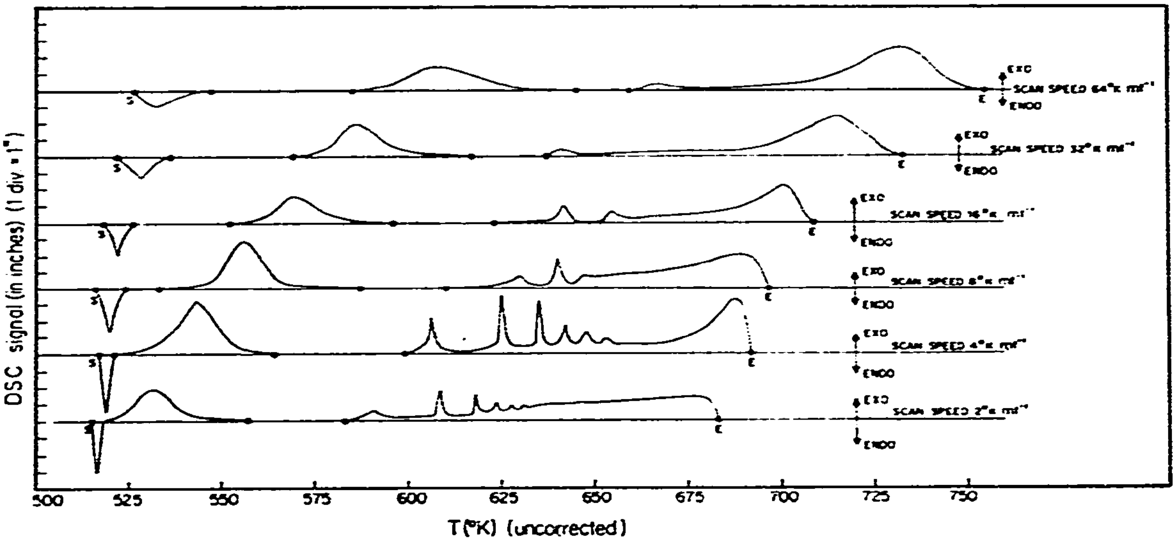

Fig. 1. Thermograms in scanning mode.

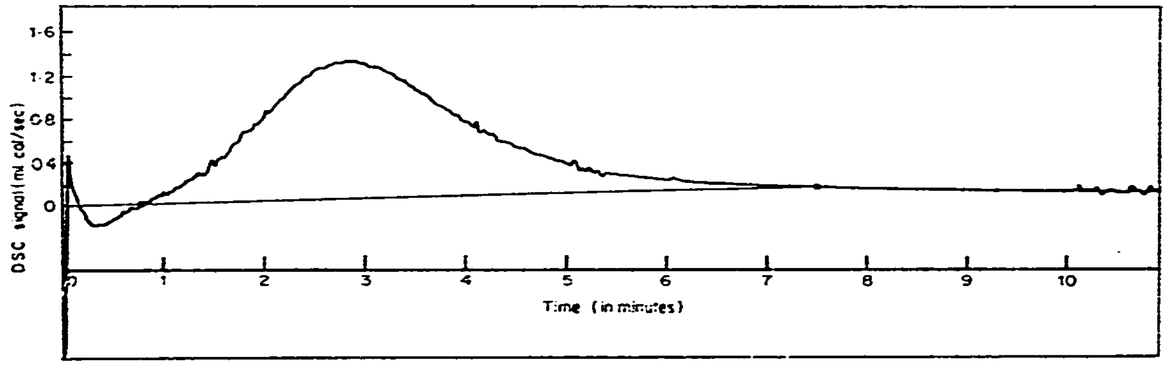

Fig. 2. Typical thermogram in isothermal operation.

The enthalpy data for the endotherm and both exotherms separately and combined are given in Table 1. It is evident that our enthalpy values both for the endotherm and combined exotherms are in good agreement with those reported in the literature[8]. Table 1 shows that the enthalpy for the first exotherm is about 31.6%

TABLE 1

ENTHALPY DATA FOR THE ENDOTHERM AND EXOTHERMS OF AMMONIUM PERCHLORATE

	ΔH			
	cal g^{-1}	*kcal* mol^{-1}	*Literature value*	
			Value *kcal* mol^{-1}	*Ref.*
Phase transformation	20.3 ± 0.6	2.39 ± 0.07	2.30 ± 0.2	6
			2.3	1
			2.7	1
Low temperature exotherm				
Isothermal (268–303 °C)	84.3 ± 4	9.9 ± 0.47		
Scanning	87.5 ± 2.6	10.3 ± 0.30		
High temperature exotherm				
(scanning)	190 ± 7.5	20.3 ± 0.9		
Total heat evolved in LTE and HTE (scanning)	277 ± 10	32.6 ± 1.2	30.6	14
			31.78	8
			38.37	7
% decomposition of LTE				
Scanning	31.6			
Isothermal	27.5			

of the total combined enthalpy of both exotherms. It is interesting to point out that the enthalpy of LTE determined from isothermal runs (268 to 303 K) is also in fairly good agreement with the corresponding scanning value. During the isothermal run, the sample was weighed before the start of the run and after the completion of the run. The weight-loss thus determined was 27.5% (see Table 1), which is not far from the value obtained in TG experiments. The above correspondence also leads to the following findings.

(a) In LTE, enthalpy and weight both show approximately 30% decomposition. This correspondence of the weight-loss to the heat release in LTE further indicates that the basic chemical reactions taking place during the decomposition of AP are likely to be the same in both LTE and HTE. However, it has to be pointed out here that the rate-limiting step may be different in the two regions.

(b) Since TG and DTA record only changes taking place in solid-state, the DSC measurements (under the specified conditions of experiment) relate to the solid-state reactions and preclude the possibility of contribution from any gas-phase reactions. Secondly, the possibility of the gas-phase reactions being recorded are ruled out from the fact that enthalpy values for LTE and HTE at different heating rates (see Table 2) are fairly constant. In the case of gas-phase reaction one would expect the change in enthalpy value with the heating rate.

TABLE 2

ENTHALPY VALUES AT DIFFERENT HEATING RATES

Scan speed ($K\ min^{-1}$)	ΔH (*cal* g^{-1})		
	Endotherm	*LTE*	*HTE*
2	19.0	87.3	189.1
4	19.9	89.3	191.3
8	20.6	93.0	191.7
16	20.9	83.7	182.0
32	20.6	83.8	179.1
64	21.2	88.2	205.6

DSC thermograms represent the net heat released/absorbed as a function of temperature (T) or time in scanning and isothermal operations, respectively. The DSC signal can be represented by the following heat balance equation.

$$\frac{\mathrm{d}Q}{\mathrm{d}t}=\frac{\mathrm{d}m}{\mathrm{d}t}\Delta H-\frac{\mathrm{d}T}{\mathrm{d}t}(C_S-C_R)-(T-T_a)(h_S-h_R) \tag{1}$$

where

$\mathrm{d}Q/\mathrm{d}t$ = DSC signal (S) in cal sec^{-1};

$\mathrm{d}m/\mathrm{d}t$ = rate of decomposition of sample (g sec^{-1});

ΔH = total heat of decomposition (cal g^{-1});

$\mathrm{d}T/\mathrm{d}t$ = heating rate (this quantity is zero in isothermal mode of operation);

C_S = thermal heat capacity of sample, sample pan holder, associated pan, lid and domed cover;

C_R = thermal heat capacity of empty pan holder, empty pan, lid and domed cover;

T = temperature (K) at time t;

T_a = ambient temperature of holder cell assembly;

h_S, h_R = heat transfer coefficient of sample cell and reference cell assembly.

We assume that $T=T_S=T_R$ and $h_S=h_R$. The last term now vanishes. The second term is evaluated in the thermogram itself by proper construction of the baseline. The procedure outlined by Brennan et al.[9] was adopted to construct the baseline. Equation (1) now reduces to

$$\frac{\mathrm{d}Q}{\mathrm{d}t}=S=\frac{\mathrm{d}m}{\mathrm{d}t}\Delta H$$

or

$$\frac{\mathrm{d}m}{\mathrm{d}t}=\frac{S}{\Delta H} \tag{2}$$

We have assumed that the kinetics of thermal decomposition of solids can be expressed by the following equations to represent the extent of decomposition and their dependence on temperature

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{3}$$

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

Combining eqns (2), (3) and (4) we get

$$\frac{d\alpha}{dt} = \frac{dm}{dt} = \frac{S}{\Delta H} = A \exp(-E/RT)(1-\alpha)^n \tag{5}$$

If α and n are maintained constant in equation (5) then

$$\frac{S}{\Delta H} = A' \exp(-E/RT) \tag{6}$$

Equation (6) is equally valid for both scanning and isothermal thermograms provided the necessary conditions are satisfied. The plot of $\log(S/\Delta H)$ vs. $(1/T)$ will directly

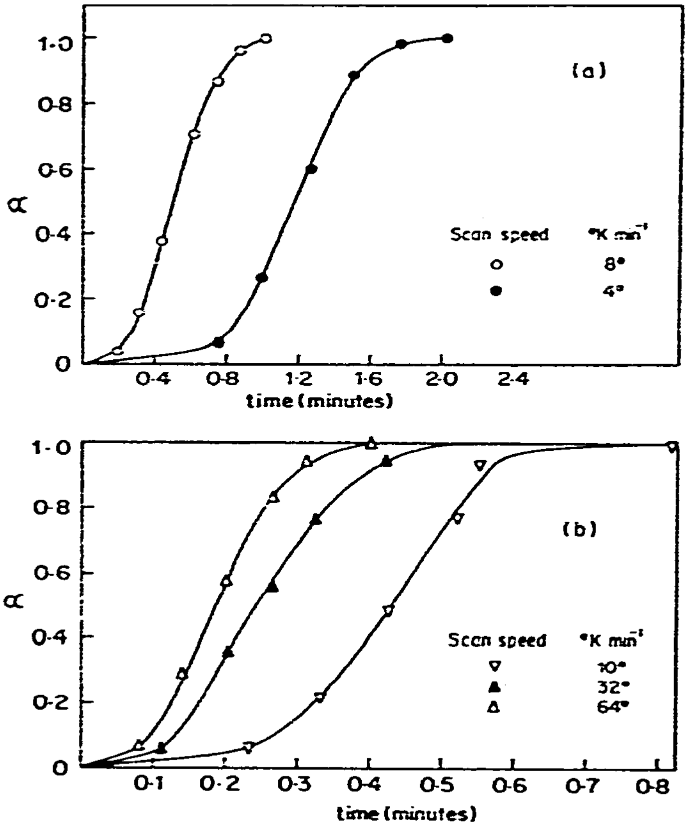

Fig. 3. α vs. t plots for endotherm.

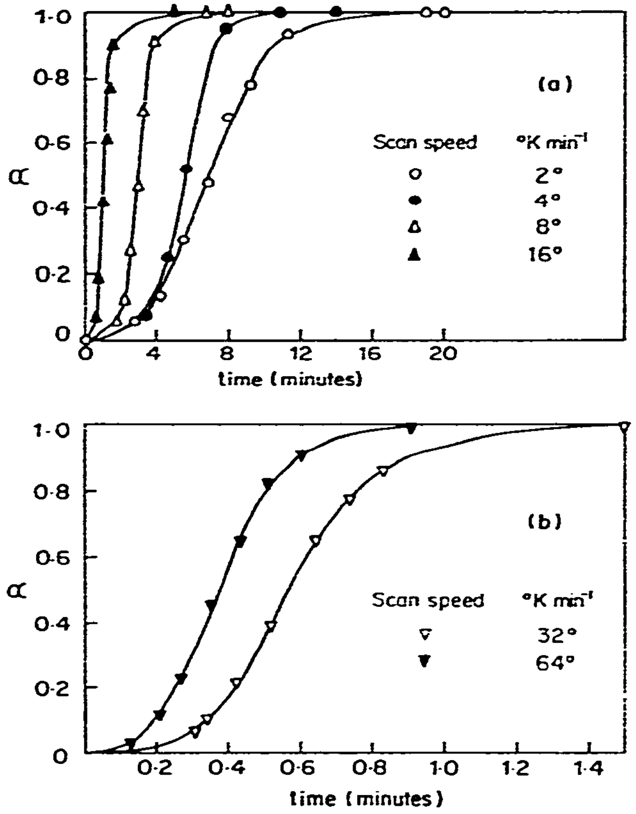

Fig. 4. α vs. t plots for LTE.

yield the value of E. It may be mentioned here that the method of calculation was outlined during one of the authors (K.K.) work with Dr. P. G. Laye of Leeds University, U.K. Detailed mathematical steps and discussion will be published at a later stage.

For scanning runs (at different heating rates) the α vs. time/temperature plot is obtained for different heating rates. From this plot the time at $\alpha = 0.5$ ($t_{\alpha=0.5}$) is calculated. Now α vs. reduced time ($t/t_{\alpha=0.5}$) plot is obtained. If the plot shows that all points corresponding to different heating rates fall on the same curve, it confirms that the kinetic behaviour of decomposition reaction, i.e., the order of reaction is the same at all heating rates. This is one of the desired conditions for the use of eqn (6). α vs. t and α vs. reduced time plots for the endotherm and LTE and HTE are represented in Figs. 3–8, which may clearly indicate that the order of reaction for all thermograms is the same at different heating rates.

In order to comply the second requisite, α is fixed by selecting $\alpha = 0.2$, 0.5 and 0.8 at different scanning runs. Corresponding signals (S) are back calculated from the thermograms in order to evaluate ($S/\Delta H$). A set of data is obtained for $\log(S/\Delta H)$ and ($1/T$) at different α values. Thus E for each value can be calculated to see if the nature of reaction is the same or different at various values in a particular thermo-

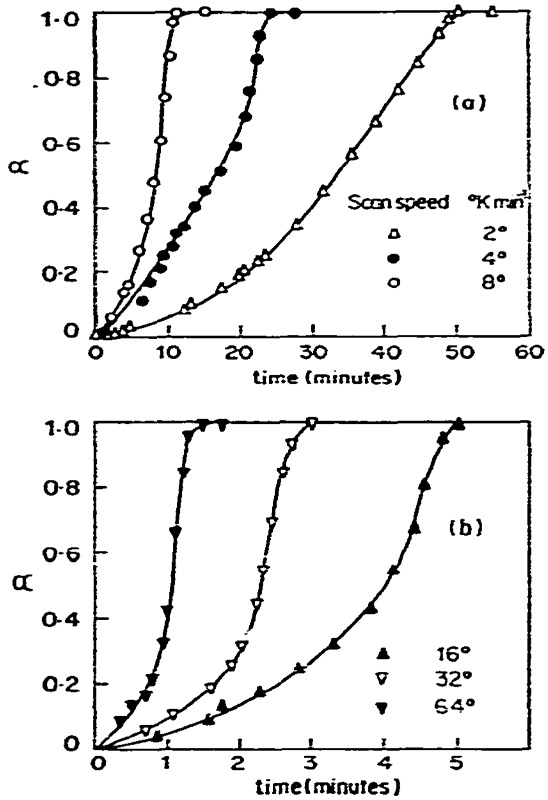

Fig. 5. α vs. t plots for HTE.

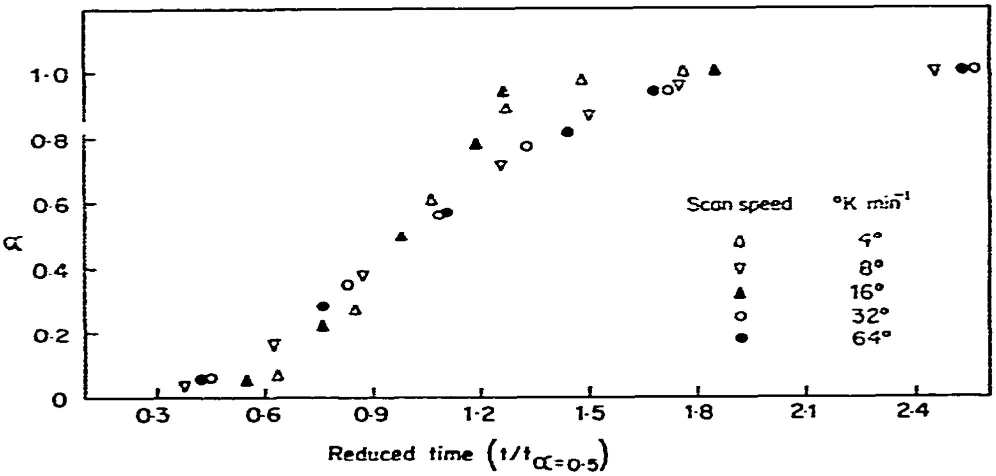

Fig. 6. α vs. reduced time plot for endotherm.

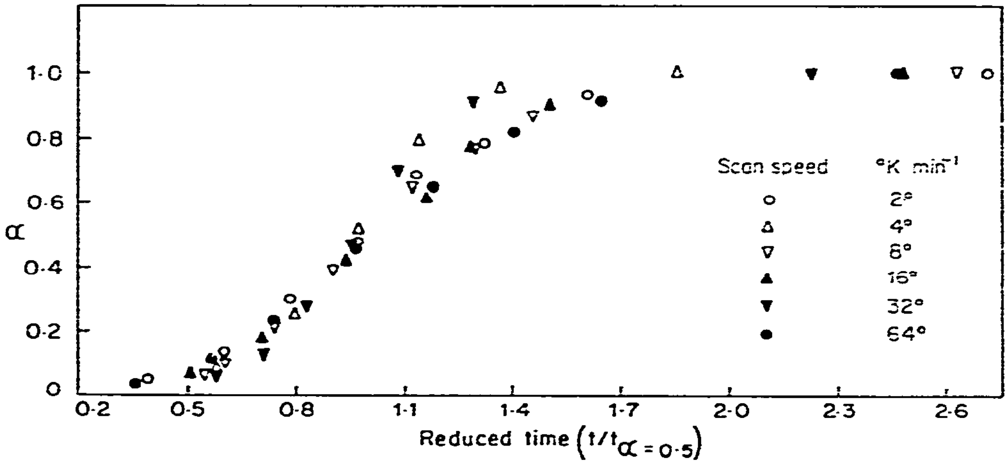

Fig. 7. α vs. reduced time plot for LTE.

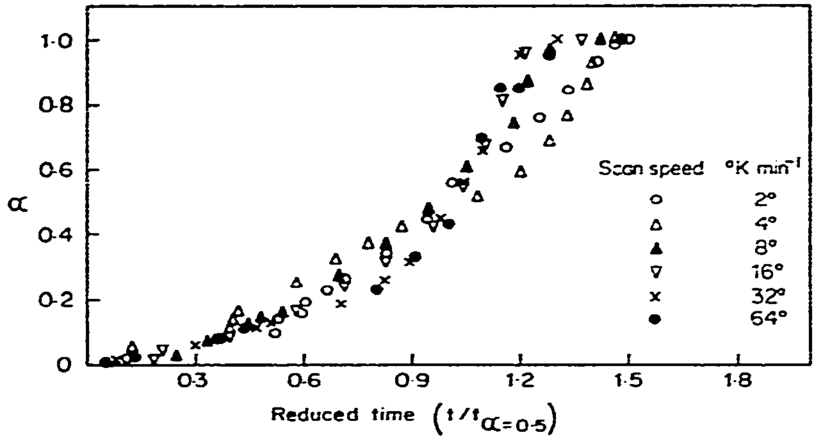

Fig. 8. α vs. reduced time plot for HTE.

gram. Plots of log (*S*/Δ*H*) vs. (1/*T*) for the endotherm and LTE and HTE are represented in Figs. 9–11.

α vs. time and α vs. reduced time plots for LTE isothermal runs are shown in Figs. 12 and 13. Reduced time plot (Fig. 13) indicates that the kinetic behaviour is the same at different temperatures. *E* is evaluated by plotting log (*S*/Δ*H*) vs. (1/*T*) at different α values as described above. The plot is shown in Fig. 14.

Activation energy values computed from the above method for scanning and isothermal operations have been represented in Tables 3 and 4. For LTE the *E* values for both scanning and isothermal operations are in excellent agreement showing the validity of the procedure. The validity of the above computational technique has also been seen from the agreement between the values of the activation energies for the thermal decomposition of HMX and RDX determined by other isothermal techniques

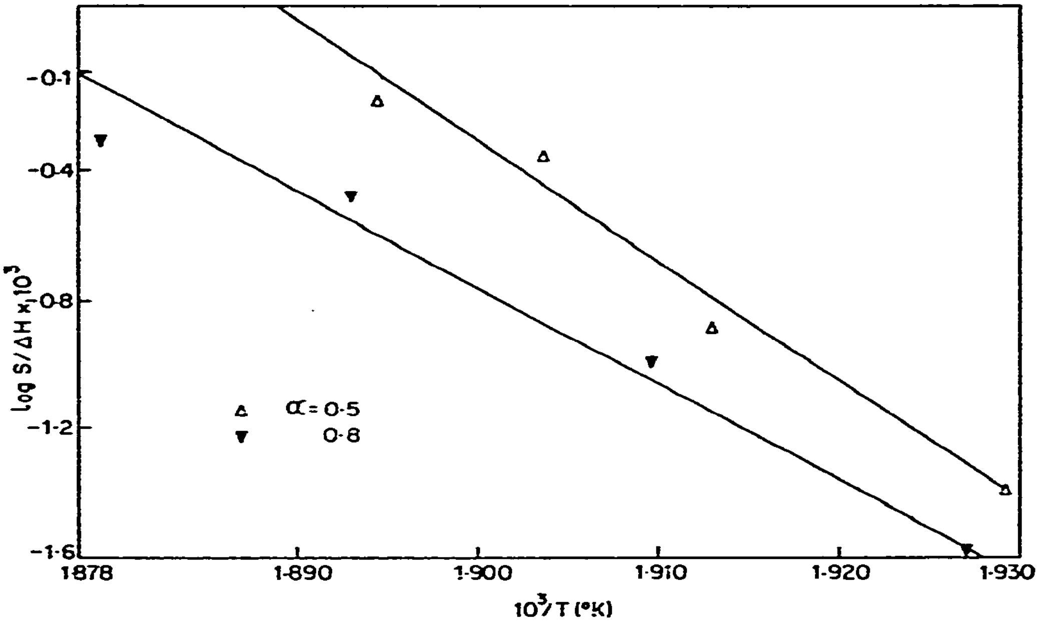

Fig. 9. Plot of log ($S/\Delta H$) vs. $1/T$(K) for endotherm.

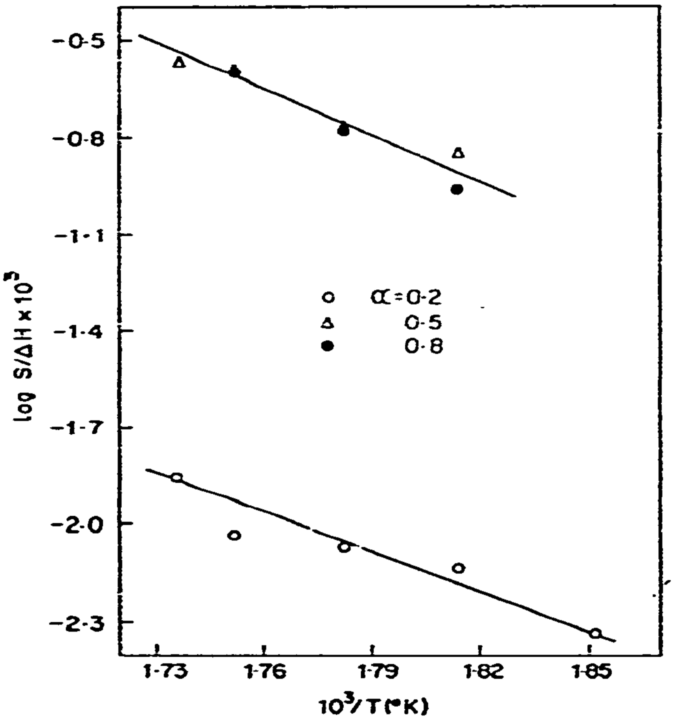

Fig. 10. Plot of log ($S/\Delta H$) vs. $1/T$(K) for LTE.

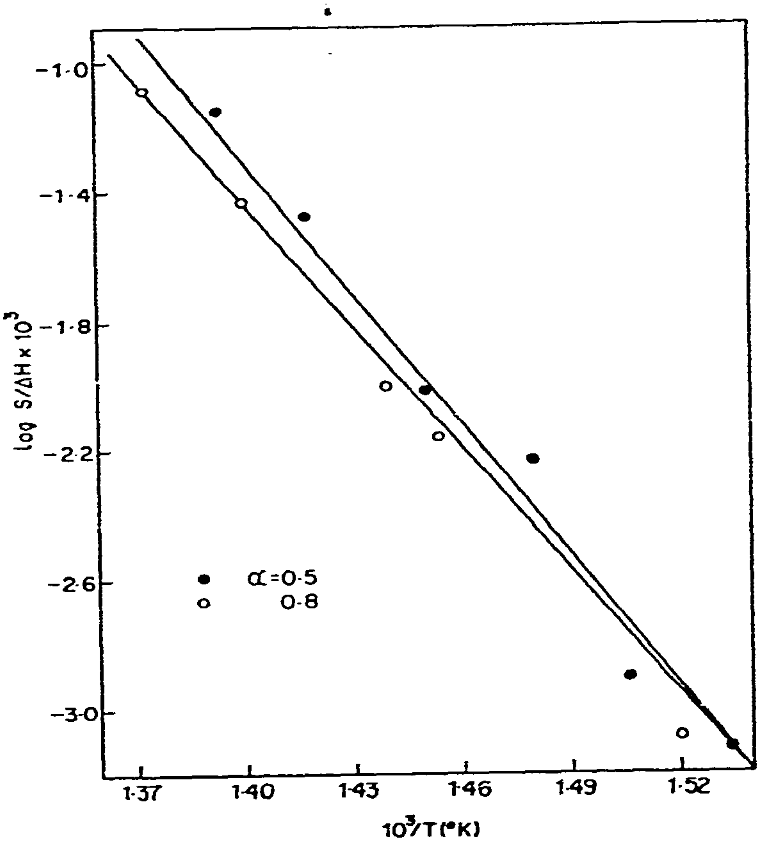

Fig. 11. Plot of log ($S/\Delta H$) vs. $1/T$(K) for HTE.

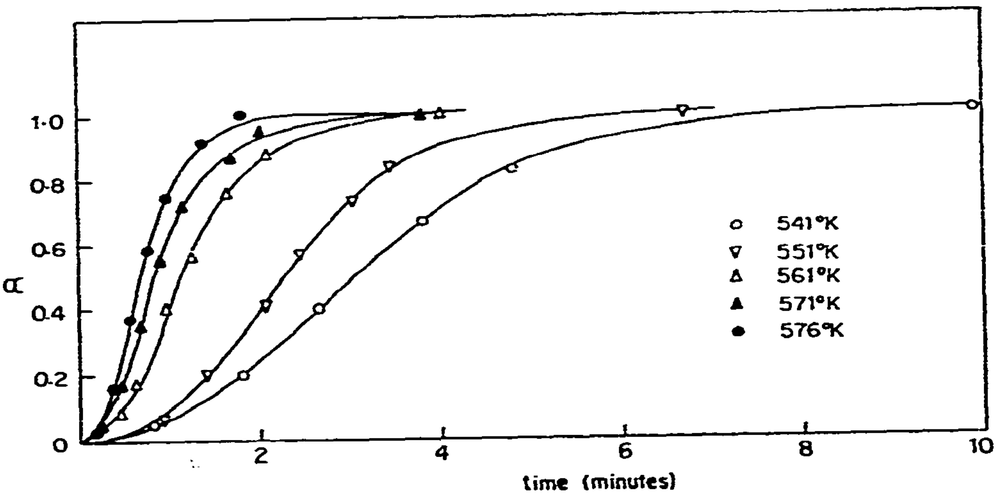

Fig. 12. α vs. t plot for LTE in isothermal operation.

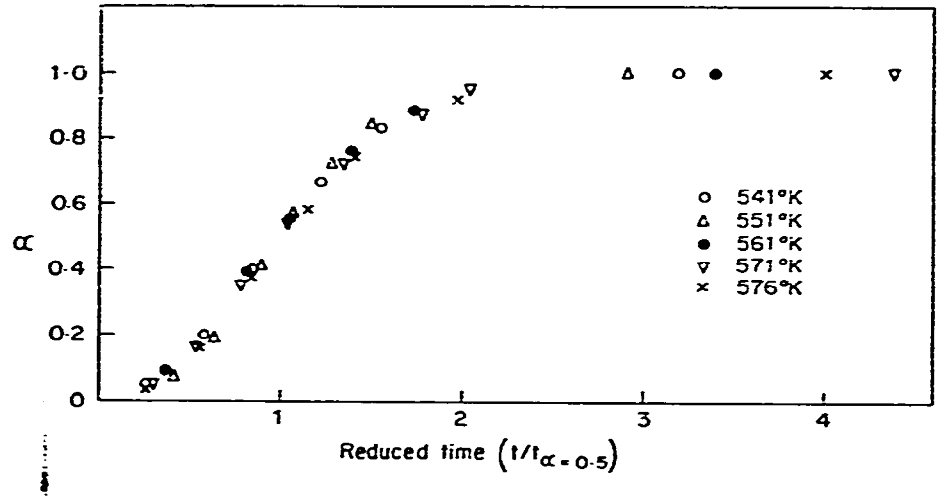

Fig. 13. α vs. reduced time plot for LTE in isothermal operation.

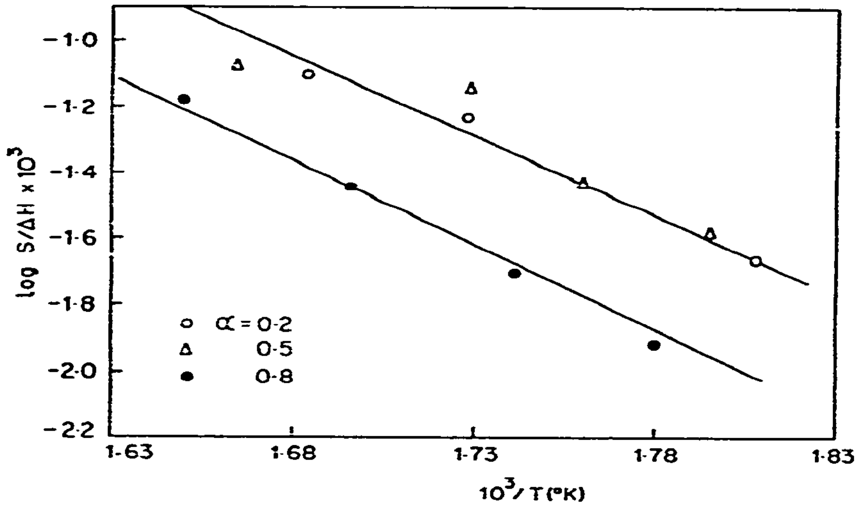

Fig. 14. Plot of log ($S/\Delta H$) vs. $1/T$(K) for LTE in isothermal operation.

and the present technique. E (scanning mode) for HTE is given in Table 3. The E values for LTE and HTE are also in good agreement with the other literature values (see Tables 3 and 4) giving further credit to the method of calculation. In addition to this, the isothermal E values calculated by other methods (i.e., by fitting α–time curve to Avrami–Erofeev equation and then plotting log k vs. $1/T$ (see Figs. 15 and 16) and by the Jacobs–Kurieshy method) agree very well with the value obtained by using our method showing further soundness of the procedure.

We have attempted to calculate E for decomposition of AP from a single dynamic run. Several equations, applicable under dynamic conditions, have been used by us to calculate E. However, most of the equations have given a very high

TABLE 3

DYNAMIC ACTIVATION ENERGY VALUES FOR THE PHASE TRANSFORMATION AND THE THERMAL DECOMPOSITION OF AP

Equation used	*Activation energy (kcal mol⁻¹) for*			*Literature values for*		
	Exotherm I	*Exotherm II*	*Endotherm*	*Exotherm I*	*Exotherm II*	*Endotherm*
(1) log $S/\Delta H$ vs. $1/T$(K)	22.6 ($\alpha = 0.2$ 22.1 $\alpha = 0.5$ 22.1 $\alpha = 0.8$ 23.6)	60.5 ($\alpha = 0.5$ 62.5 $\alpha = 0.8$ 58.5)	159.5 ($\alpha = 0.5$ 180.8 $\alpha = 0.8$ 138.0)			
(2) log $\varnothing$ vs. $1/T_m$(K)	35.2	55.0	335.8			
(3) log $(\mathrm{d}H/\mathrm{d}t)/(A-a)$ vs. $1/T$(K)	156.4					
(4) log $\varnothing/T_m^2$ vs. $1/T_m$(K)	36.9	55.0	299.0	18.9[16]	73.4[15]	110[6]
(5) log $Q/\dot{m}_p$ vs. $1/T$(K)	115.0	179.1[a]			60.0[6]	
(6) log $\dfrac{\mathrm{d}\alpha/\mathrm{d}T}{(1-\alpha)}$ vs. $\dfrac{1}{T(\mathrm{K})}$	154.5			24.8[17]	60.0[3] (theoretical)	
(7) log $\dfrac{\mathrm{d}\alpha/\mathrm{d}T}{(1-\alpha)^{n/m}}$ vs. $\dfrac{1}{T(\mathrm{K})}$	104.4			20.0[3]		
(For $n<1$, $m = 1-n$)	(for $n = 0.5$ and $n = 0.2$)			20±2[6]		
(8) log $\mathrm{d}T/\mathrm{d}t$ vs. $1/T$(K)			187.6			

[a] Waesche and Wenograd[14] report a value of 60 kcal mol⁻¹.

TABLE 4

ISOTHERMAL ACTIVATION ENERGY VALUES FOR THE THERMAL DECOMPOSITION OF AP

Equation used	*Activation energy* (*kcal mol*$^{-1}$)	*Literature value*
(1) log $S/\Delta H$ vs. $1/T$(K)	21.2 ($\alpha = 0.2$ 17.6 $\alpha = 0.5$ 23.0 $\alpha = 0.8$ 23.0)	19.8[16]
(2) log k(mt^{-1}) vs. $1/T$(K) (k obtained from a fit of the α–t curve to Avrami–Erofeev's equation)	24.4	24.8[17]
(3) Jacobs–Kureishy technique (time taken for α to go from $\alpha = 0.2$ to $\alpha = 0.8$)	26.2	

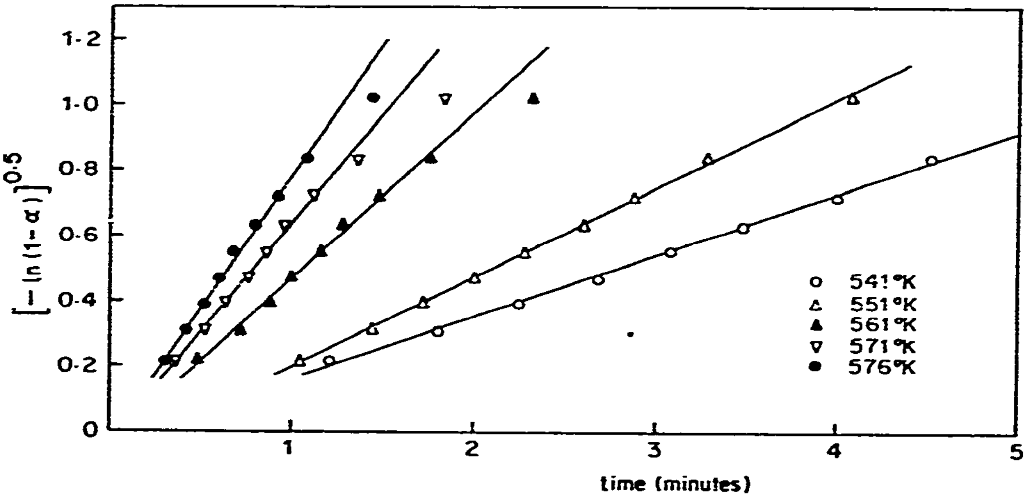

Fig. 15. Avrami–Erofeev plots of LTE in isothermal operation.

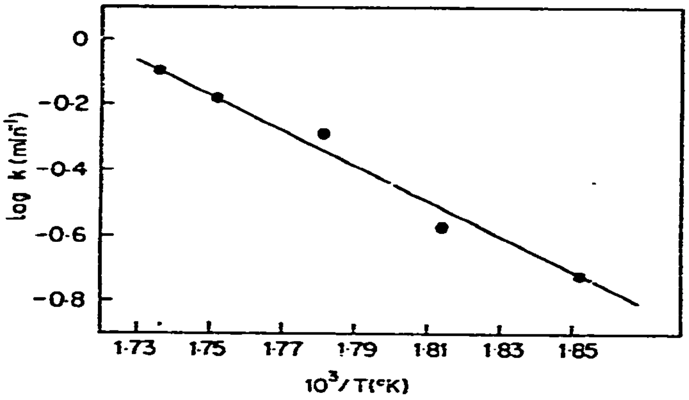

Fig. 16. Plot of log k vs. $1/T$(K) for LTE in isothermal operation.

value of the order to 120 kcal mol^{-1} for E in the LTE. A similar value was reported by Sammons for E of AP decomposition. The results are presented in Table 3. Our results indicate that considerable caution has to be exercised while attempting to derive E for decomposition from a single dynamic run.

The present method has confirmed the existence of few small exothermic peaks at the initial stages of HTE (see Fig. 1). This may not be due to noise as it is reproducible and secondly the corresponding empty pan thermograms do not show the presence of any such peaks. These peaks reduce in number as the heating rate is increased. These small peaks have been observed by some of the earlier workers[12] but have been ignored. However, the high heating rate runs may be misleading. But the very unsymmetrical nature of HTE even at high heating rates reveals that it is a composite peak which may be further resolved under suitable conditions. The actual nature of chemical reactions responsible for these secondary peaks is difficult to identify. The occurrence of these peaks may be attributed to the impurities present in the sample (commercial sample). Nevertheless it is this sample which is used in propellant formulations. The occurrence of these peaks as a result of reactions occurring at defect centers may not be ruled out. Earlier studies carried out by Sammons[12] indicate that pretreatment of AP samples, e.g., grinding, affects the general pattern of the thermograms obtained by DSC. The grinding is known to alter the concentration of gross imperfections in the lattice. Hence, it is likely that the peaks observed during the initial stages of HTE are due to decomposition reactions taking place at such sites. In short one can say that the appearance of these peaks may be due to the prehistory of the sample. In this respect the peaks are similar to LTE. It has been shown that the magnitude of LTE is dependent on the concentration of gross imperfections in the solid (AP)[13]. The gross-imperfections may result from the mechanical treatment and/or from the impurities present. The same explanation may also hold good for the existence of small peaks. However, it will be interesting to probe further into the nature of various reactions responsible for the generation of these peaks but even at a first glance it appears that it involves a complex decomposition process.

CONCLUSIONS

(1) The enthalpy values for LTE and HTE have been determined. It has been found that the extent of decomposition in LTE is approximately 30% both enthalpy-wise and weightwise.

(2) From the correspondence of our results with those of TG and DTA, we have concluded that DSC records only solid-state processes.

(3) A new method for obtaining the kinetic parameters from DSC thermograms has been developed. The E values for AP endotherm and exotherms obtained by this method agree well with the literature values.

(4) The value of E obtained by using several equations applicable to a single dynamic DSC run have been found to give a high value of E.

(5) The presence of small exothermic peaks at the initial stages of HTE have

been confirmed. These peaks may be attributed to either the presence of impurities or to the reactions taking place at gross imperfections in the lattice.

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