

SOLID PROPELLANT DECOMPOSITION STUDIES BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

Decomposition of solid propellants, relevant in combustion processes, has been studied by differential scanning calorimetry (DSC). Enthalpy changes for decomposition of the polymers [polystyrene (PS) and styrene-oxygen copolymer (copolymer)], ammonium perchlorate (AP) and the corresponding propellants have been estimated from DSC thermograms. Energy of activation of the net decomposition process is estimated to be 41 ± 5 and 35 ± 6 kcal mol⁻¹ for PS and copolymer propellants, respectively. Isothermal decomposition studies of the propellants have also been made.

INTRODUCTION

The combustion of composite solid propellant is a complex phenomenon which involves several physico-chemical processes taking place in different phases. Combustion theories based on analytical models have been proposed in the past which ignore many such processes. It is becoming increasingly clear that combustion is controlled to varying degree by reactions taking place in flame zone, propellant surface or in the solid phase below the surface. Recent studies of propellant decomposition by differential scanning calorimetry (DSC) have proved the importance of solid-phase reactions during combustion of solid propellants¹⁻³. The data reported earlier¹ have been subjected to detailed analysis in this paper which yields valuable information regarding the enthalpy changes and the energy of activation of the net decomposition processes.

EXPERIMENTAL

Polystyrene and the copolymer of styrene-oxygen and the corresponding propellants were prepared as described earlier¹. Powdered AP (Fischer Scientific Co., U.S.A.) was used as such without further purification.

DSC thermograms were obtained by one of the authors (K.K.) at the University of Leeds, U.K., using a Perkin-Elmer DSC-IB instrument. The calorimeter temperature axis was calibrated using pure samples of indium, tin, and lead supplied by the above firm.

The propellant (approx. 0.8 mg) and polymer samples (approx. 2.5 mg) in the form of flakes and pure AP (approx. 2.0 mg) in the powdered form were used. The accurately weighed samples were placed in the aluminum pan and were sealed. A small hole was pierced at the top of the lid in order to allow the product gases to escape. The reference and the sample pans were placed at the centre of the sample holder cells and covered with aluminum domes. The thermograms were obtained by the procedure outlined by Brennan et al.⁴. The baseline of the thermogram was also drawn by the above-mentioned method.

The measurements were made at the scanning speeds 8, 16, 32 and 64 K min⁻¹ using range settings of 4, 8, 16 and 32 mcal sec⁻¹. Thermograms were obtained for PS and copolymer and the corresponding propellants (AP content 70, 75 and 80 per cent by weight) and for pure AP. After the decomposition, no residue remained in the pan. The typical thermograms for polymers, propellants and AP are shown in Fig. 1. Blank observations showed that no flame appears during decomposition.

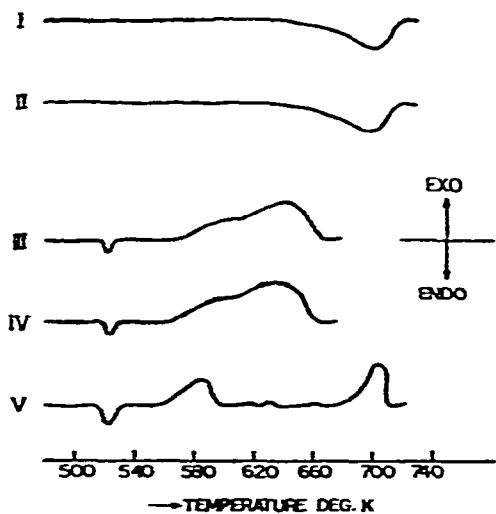


Fig. 1. DSC thermogram (I) PS; (II) copolymer; (III) PS/AP (70% by wt.) propellant; (IV) copolymer/AP (70% by wt.) propellant and (V) pure AP each at scan speed 16 K min⁻¹.

The enthalpy changes for the exothermic and endothermic processes were calculated using indium as the standard⁵. The area under the curves was measured by the Lynx (Indian) planimeter. The temperature range for endothermic and exothermic peaks for the propellants, polymers and AP samples is recorded in Table 1 and their enthalpy changes are given in Table 2. The energy of activation was calculated as follows:

The total area and the area under the segments at different time intervals were evaluated from the thermograms. α -time plots were drawn using these data (α = fraction decomposed). α varies with time as follows:

$$d\alpha/dt = k(1 - \alpha)^n \quad (1)$$

TABLE 1

TEMPERATURE RANGE OF ENDOTHERMIC AND EXOTHERMIC PEAKS OF PROPELLANTS, POLYMERS AND AP

Sample	AP (wt. %)	Scan speed	Temperature range (K)					
			Endothermic peak		Exothermic peak			
			Start	End	Start	End		
PS/AP	70	64	530	543	605	703		
		32	524	534	583	680		
		16	521	528	562	663		
		8	518	525	562	653		
	75	64	527	542	615	706		
		32	523	533	597	691		
		16	519	526	593	667		
		8	519	525	554	654		
	80	64	526	539	594	727		
		32	522	533	591	679		
		16	520	527	574	660		
		8	517	523	547	655		
Copolymer/AP	70	64	526	540	607	698		
		32	522	531	583	684		
		16	519	526	569	664		
		8	517	523	578	652		
	75	64	528	541	605	703		
		32	523	536	583	687		
		16	521	529	564	667		
		8	518	525	554	654		
	80	64	529	544	599	709		
		32	523	536	583	687		
		16	520	528	561	667		
		8	518	525	546	652		
PS	—	64	643	755	No. exotherm			
		32	632	729	No. exotherm			
		16	642	717	No. exotherm			
Copolymer	—	64	643	749	No. exotherm			
		32	636	736	No. exotherm			
		16	642	717	No. exotherm			
AP	—	64	524	First peak		Second peak		
		32	522	554	587	640	697	754
		16	518	542	570	618	691	733
		8	518	531	553	596	683	709
		2	517	529	—	—	—	—
			525	—	—	—	—	

TABLE 2

ENTHALPY CHANGE FOR THE ENDOTHERMIC AND EXOTHERMIC PROCESSES IN PROPELLANTS, POLYMERS AND AP

Scan speeds ($K \text{ min}^{-1}$) used: (a) = 8; (b) = 8, 16, 32 and 64; (c) = 8, 16 and 32; (d) = 2, 8, 16, 32 and 64; (e) = 16, 32 and 64.

Sample	AP (wt. %)	Enthalpy change ($\text{cal}^{-1} \text{ g}$)				
		Endothermic process		Exothermic process		
PS/AP	70	13.7	(a)	(b)	609 ± 79	
	75	15.2			608 ± 88	
	80	18.3			484 ± 62	
Copolymer/AP	70	14.9	(c)	(d)	582 ± 71	
	75	15.8			582 ± 62	
	80	16.3			660 ± 79	
PS	—	72.0 ± 10	(e)	(f)	—	
Copolymer	—	74.0 ± 10			—	
AP	—	20.6 ± 0.4 (d)	First peak	Second peak	72 ± 18 (e)	94 ± 18 (e)

where k is the rate constant and n is the effective order of reaction. Knowing the total mass decomposed, the rate of decomposition in g sec^{-1} of the sample was calculated. The heating rate ' S ' in cal sec^{-1} would simply be the product of the rate of decomposition at a particular time and the enthalpy change (ΔH) for the reaction. Using Arrhenius type relationship for the rate constant, we have:

$$S/\Delta H = A(1-\alpha)^n \exp. (-E/RT) \quad (2)$$

The energy of activation for different values of α was obtained by plotting $\log S/\Delta H$ vs. $1/T$.

The isothermal decomposition of propellant samples (AP 70% by weight) of both the propellants was also studied at 601, 611, 621, 631 and 641 K using range settings of 4, 8 and 16 mcal sec^{-1} . The baseline was found to be shifted after the

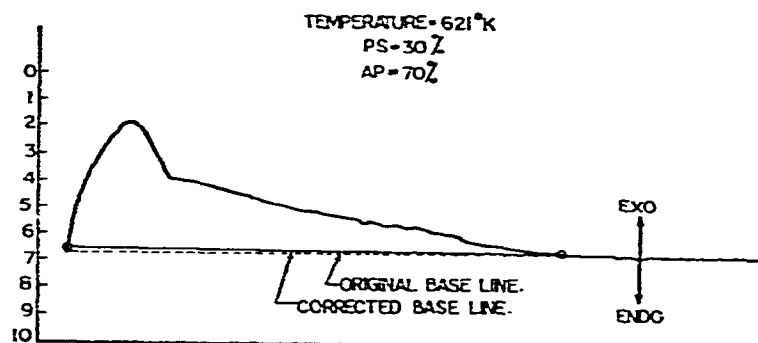


Fig. 2. Typical isothermal DSC thermogram of PS/AP (70% by wt.) propellant at 621 K.

experiment as indicated in Fig. 2. The difference in area under the peak due to shift was found to be less than 10% of the total area. Thus, the uncertainty in the enthalpy values estimated from the thermograms would be of the order of 10%. The results are recorded in Table 3. In view of the uncertainty in the experimental results, there does not appear to be a definite trend in the enthalpy values at different temperatures.

TABLE 3

ENTHALPY CHANGE FOR ISOTHERMAL
DECOMPOSITION IN PROPELLANTS (AP 70%)

Temp. (K)	Enthalpy change (cal g ⁻¹)	
	PS propellant	Copolymer propellant
601	400	550
611	420	417
621	430	417
631	500	436
641	530	555

DISCUSSION

The data on DSC thermograms are summarised in Tables 1 and 2. Thermal decomposition of propellants may involve: (i) thermal decomposition of binder; (ii) thermal decomposition of oxidiser; (iii) solid-phase reaction between binder and oxidiser; (iv) heterogeneous reaction between liquid binder and solid oxidiser and/or its decomposition products; (v) gas-solid reaction leading to thermo-oxidative degradation. The appearance of liquid phase has been reported in a recent study.¹ AP-binder sandwich experiments have been performed by several workers⁶⁻⁹ which further confirm the formation of liquid melt on the propellant surface during burning.

On comparing the thermograms of PS, copolymer, AP and the corresponding propellants (Fig. 1), it is obvious that the mode of decomposition of PS and copolymer propellants is the same and the first endothermic peak is essentially due to the phase transformation of AP. However, in propellants, only one exothermic peak in a broad range 545–710 K is obtained and the endothermic process in PS and copolymer in the temperature range 640–717 K is suppressed or overwhelmed by it. It should be noted that in pure AP, low temperature decomposition occurs in the range 552–595 K and high temperature decomposition occurs in the range 680–755 K. These peaks are submerged in the case of propellants in the range 545–710 K. It appears that in this temperature range, the decomposition of polymer, low and high temperature decomposition of AP and polymer-oxidiser interactions occur simultaneously. It has been observed that the polymer starts becoming a viscous fluid around 520 K. The endothermic peak in I and II (Fig. 1) would be due to simultaneous melting and degradation of polymers. Hence, the exothermic broad maxima in III and IV (Fig. 1) would be largely due to reaction between liquid polymer and solid-oxidiser and/or its

decomposition products. Recently, Ellsworths et al.¹⁰ have reported the species resulting from condensed phase decomposition of AP on the basis of time-of-flight and higher resolution methods of mass spectrometry. These are NH_4 , NH_3 , ClO_4 , ClO_2 , O_2 , NH , NH_2 , NO , ClO , Cl etc. Some of them attack the polymer chain with the evolution of heat or the interaction between them and the polymer degradation products takes place at the interface. That is why the rate of enthalpy production is much higher in III and IV (Table 2) as compared to what would have been expected for solid-solid reaction. The existence of faster reactions involving liquid phase is further supported by the fact that the material (III and IV) on the pan disappears completely at a lower temperature as compared to the corresponding I, II and V (Fig. 1) thermograms.

If $(\Delta H)_P$, $(\Delta H)_F$ and $(\Delta H)_{AP}$ are the enthalpy changes for the thermal decomposition of propellant, binder and AP, respectively, and if no solid-solid, solid-liquid and solid-gas reaction or pure liquid phase reaction is taking place, then

$$(\Delta H)_P = x(\Delta H)_F + (1-x)(\Delta H)_{AP} \quad (3)$$

where x is the weight fraction of binder and $(1-x)$ that of the oxidiser in the propellant. The estimated values of $(\Delta H)_P$, $(\Delta H)_F$ and $(\Delta H)_{AP}$ are recorded in Table 2, which clearly shows that eqn (3) is not satisfied proving thereby that polymer-oxidiser interaction must be taking place. The difference $(\Delta H)_R$ between the left- and right-hand side of eqn (3) is found to be $-461 \pm 62 \text{ cal g}^{-1}$ and $-502 \pm 27 \text{ cal g}^{-1}$ for PS and copolymer propellants, respectively. The low value for PS/AP propellant is due to the low value for one of the run (Table 2).

The important point which has to be discussed now concerns the processes which are responsible for such a large value of $(\Delta H)_R$ which is approximately half of the calorimetric value. It should be noted that the values are reproducible within experimental error and hence it cannot be exclusively due to the gas-phase reaction. Further, the exothermicity begins from approximately 500 K onwards at which temperature, the polymer is obtained in the molten form. At this temperature gas-phase reactions are not possible. Hence, it follows that a significant contribution to enthalpy change comes from the condensed phase reaction. Further it appears that solid oxidiser-liquid polymer reaction would also take place since it is observed that the particle size of ammonium perchlorate affects the burning rate. Since the particle size of the oxidiser has been kept fixed, the enthalpy change $(\Delta H)_C$ of the reaction in the condensed phase would be related to the number of such particles, i.e., the percentage of the oxidiser in the propellant. Thus the larger the amount of oxidiser, the greater would be the enthalpy change $(\Delta H)_C$. It should be noted that $(\Delta H)_C \approx (\Delta H)_R$ provided the decomposition of the separate components in their entirety is necessarily part of the decomposition of the propellant. Since the weight per cent of AP has only been varied between 70 and 80 during the investigation, the enthalpy values would only change by 12.5% which is evidently within experimental error. Hence, no definite trend in the dependence of $(\Delta H)_R$ on percentage of AP is evident (see Table 2).

In order to understand the kinetics of interface reactions, the thermo-kinetic

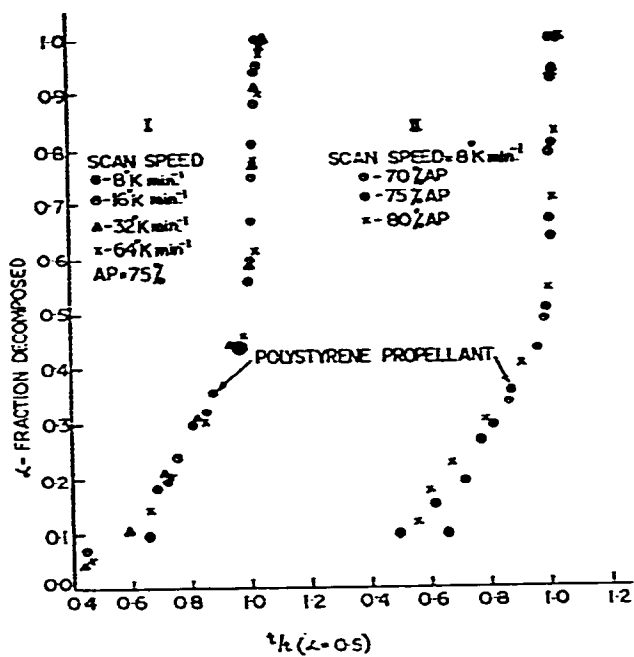


Fig. 3. α -reduced time plots PS propellants.

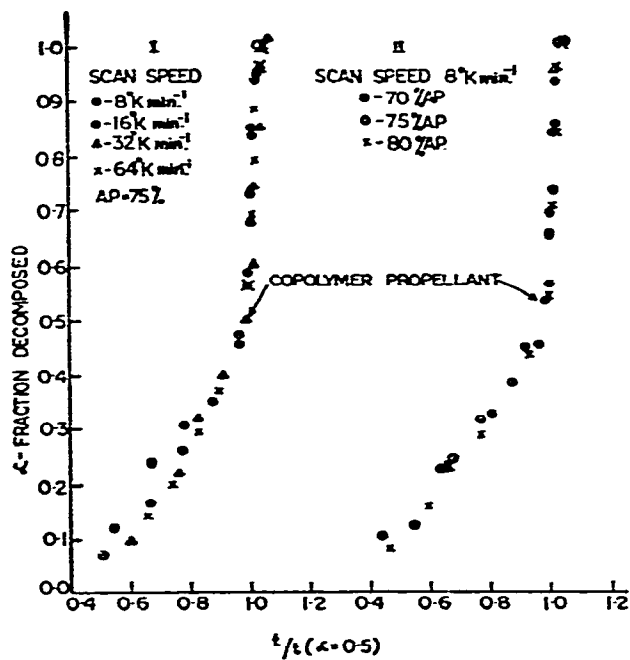


Fig. 4. α -reduced time plots copolymer propellants.

features were studied from thermograms. The energy of activation of the exothermic process was estimated for both the propellants containing 70, 75 and 80 per cent of AP at $\alpha = 0.2, 0.5$ and 0.8 where α is the fraction decomposed. The net energy of activation was found to be 41 ± 5 and 35 ± 6 kcal mol⁻¹ for PS and copolymer propellants, respectively. It should be noted that this value would be the resultant value for the entire decomposition process which may involve a number of steps. The α -reduced time plots (Figs. 3 and 4) show that the nature of decomposition was the same at different heating rates as well as for different AP compositions for both the propellants.

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