

COMBUSTION AND THERMAL DECOMPOSITION CHARACTERISTICS OF COMPOSITE SOLID PROPELLANTS

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ABSTRACT

The role of thermal decomposition of the binder and the oxidiser in the thermal decomposition, ageing and combustion of composite solid-propellants has been investigated. The present study shows that the burning rate and ageing of polystyrene and ammonium perchlorate propellant are related to the thermal decomposition of the propellant itself and ammonium perchlorate.

INTRODUCTION

The combustion of a solid composite propellant is a complex process. A wealth of data exists on the burning of the propellant. Yet, the mechanism of combustion is poorly understood. The reasons for this lack of understanding are basically: (I) Combustion is a very fast process and, therefore, it is extremely difficult to identify the intermediates and the rate-determining step; and (II) a real propellant consists, in addition to an oxidant and a fuel, of various other additives, thereby complicating the study of the reaction of the oxidant and the fuel by various side reactions.

Basically combustion is discussed in terms of either a gas-phase theory¹⁻³ or a condensed-phase theory⁴⁻⁷. The present investigation aims at studying the role of condensed-phase reactions, if any, in the combustion of propellants, which has relatively received less attention. The reason for studying the condensed-phase reactions is the following: Firstly, most of the actual burning takes place in the gaseous state and the components of a solid-propellant are relatively non-volatile, an extensive amount of decomposition must first take place in the solid state. Secondly, considering the gas-phase reactions to be quite fast compared to the thermal decomposition process occurring in the solid phase, the rate-controlling process may hopefully lie in the condensed-phase decomposition reactions. In addition, the study of the condensed-phase makes it easier to identify the intermediates.

The propellant investigated in this work consists of only two ingredients: ammonium perchlorate (AP) as an oxidiser and polystyrene (PS) as fuel cum binder. The essence of the present work thus amounts to the study of the thermal decomposition of the propellant made from AP and PS. Burning-rate studies on the propellant have also been undertaken to seek a correlation, if any, with thermal decomposition data. Thermal decomposition of propellant ingredients, namely PS and AP, has

also been carried out to determine the relative role of oxidiser and binder decomposition in the overall decomposition of the propellant.

A significant amount of the work, on the burning of the propellant⁸⁻¹⁰, the thermal decomposition of the propellant¹¹⁻¹³, the thermal decomposition of the oxidiser¹⁴⁻¹⁹ and the binder²⁰, has already been published separately. Together with some new data on the sublimation of pre-treated AP and ageing studies of the propellant, the present paper reviews all the earlier data in totality establishing certain definite relationships between the combustion of the propellant and the thermal decomposition of its ingredients.

EXPERIMENTAL

Doped AP was prepared by coprecipitating a saturated aqueous solution, containing definite proportions of AP and the dopant, by slow cooling. The exact amount of the dopant in AP was not analysed. Therefore, the amount which we are referring to is in solution. The particle size of undoped and doped AP was kept constant. The details of other pre-treatments like precompression and preheating together with the thermal decomposition studies by DTA, pressure-time and differential scanning calorimetry (DSC) techniques are described in detail elsewhere^{14-17,27}. The details of activation-energy (E) calculations and enthalpy measurements are also available in the respective references. For sublimation studies, the DTA technique described in refs. 2 and 3 was used with a little additional arrangement in which sample could be decomposed in vacuo (pressure $\approx 40 \pm 5 \mu\text{m}$). The details of PS degradation are given in one of our recent papers²⁰.

Preparation, determination of burning rate and thermal degradation studies of PS/AP propellant were done as described earlier^{4,8,13}. The ageing studies of propellants were carried out at 60, 100, 120, 150 and 200°C. Times for different percentages of burning-rate changes were calculated (extrapolation was done wherever necessary) at a particular temperature. E for the changes in burning rate was calculated from the Arrhenius plot and then used to calculate the safe-life time at 25°C in air.

RESULTS AND DISCUSSION

Study of the oxidiser

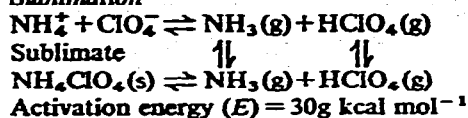
It has been observed that AP undergoes sublimation and decomposition both on heat treatment, depending upon the experimental conditions^{9,18}. Thus, both sublimation and decomposition of AP have been studied. The proton-transfer mechanism for both sublimation and decomposition has been advocated by one school¹⁸. However, our findings show that the decomposition is controlled by ionic diffusion mechanism¹⁵ and the sublimation by proton-transfer at the subliming surface²². The proposed mechanism of AP decomposition and sublimation is summarised in Table 1. Ionic diffusion mechanism gets strong support from con-

TABLE 1

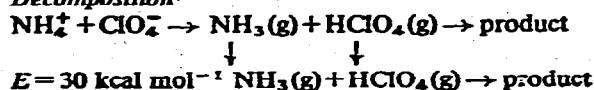
MODELS FOR SUBLIMATION AND
THERMAL DECOMPOSITION OF AMMONIUM PERCHLORATE

1. Proton-transfer model for sublimation and thermal decomposition (ref. 18)

(a) Sublimation



(b) Decomposition



Essential features of proton-transfer model

- (i) Only one value of E for decomposition, throughout the temperature range 200–460°C
- (ii) E for thermal decomposition and sublimation are same supporting that same mechanism holds good.

2. Ionic-diffusion|electron-transfer model for thermal decomposition (refs. 14–16)

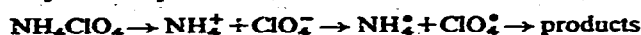
Essential features

- (i) Three values of E for thermal decomposition of AP

$$E = \begin{array}{ccc} 200\text{--}250^\circ\text{C} & 250\text{--}350^\circ\text{C} & 350\text{--}450^\circ\text{C} \\ \hline 30 \text{ kcal mol}^{-1} & 20 \text{ kcal mol}^{-1} & 60 \text{ kcal mol}^{-1} \end{array}$$

- (ii) Activation energies for thermal decomposition and sublimation are different
Sublimation (200–380°C), $E = 20 \text{ kcal mol}^{-1}$ (below 20 torr)

Model for decomposition



Steps involved:

- (i) Migration of NH_4^+ to a preferential site for decomposition. (rate-determining step in low temp. range decomposition).
- (ii) Electron-transfer from ClO_4^- to NH_4^+ (rate-determining step in high temp. range decomposition).
- (iii) Reaction between ClO_4^- and NH_4^+ to give the products of decomposition.

ductivity measurements¹⁵ and from electric field experiments²⁴. It has also been observed that pretreatments like precompression, preheating and doping have a considerable effect on the decomposition and sublimation behaviour of AP (Table 2). Our proposition that decomposition and sublimation follow a different mechanism is supported by the results presented in Table 2. It is evident from Table 2 that the thermal decomposition of AP can be altered by various means.

Since AP undergoes an exothermic decomposition process, the enthalpy change associated with it has been calculated. E values in various temperature ranges have also been calculated. The results are presented in Table 3. It may be mentioned that the enthalpy values for the two exotherms of AP have been calculated separately

TABLE 2
COMPARISON OF THE DECOMPOSITION AND
SUBLIMATION BEHAVIOUR OF AP

<i>Pretreatment</i>	<i>Thermal decomposition (250–350°C)</i>	<i>Sublimation (250–350°C)</i>
Precompression (50–100 kg cm ⁻²)	Sensitisation (refs. 16, 21)	Sensitisation
Particle size (600–50 μm)	Decomposition rate increases with the decrease of particle size and passes through a maximum at 110 μm (Refs. 17, 25)	Sublimation rate increases with the decrease of particle size and passes through a maximum at 195 μm
Preheating (110°C for 24 h)	Sensitisation (refs. 16, 21)	Desensitisation
Doping		
(i) Ca ⁺²	At 340°C the rate decreases upto a conc. of 10 ⁻² mol % and then increases (ref. 15)	Desensitisation (reaches a saturation value at 10 ⁻³ mol %)
(ii) SO ₄ ²⁻	At 340°C the rate increases upto a conc. of 10 ⁻² mol % and then decreases (ref. 15)	Desensitisation (reaches a saturation value at 10 ⁻³ mol %)
(iii) PO ₄ ³⁻	At 230°C the increase is upto a conc. of 10 ⁻⁴ mol % and then decreases (ref. 23)	Desensitisation (reaches a saturation value at 10 ⁻³ mol %)

TABLE 3
ENTHALPY DATA AND ACTIVATION-ENERGY OF AP DECOMPOSITION

<i>Enthalpy data: (ref. 14)</i>	
(i) Low-temperature exotherm (250–350°C)	(a) 9.9 kcal mol ⁻¹ (isothermal DSC) (b) 10.3 kcal mol ⁻¹ (scanning DSC)
(ii) High-temperature exotherm (320–450°C)	20.3 kcal mol ⁻¹ (scanning DSC)
(iii) Total heat evolved in both exotherms	32.6 kcal mol ⁻¹ (scanning DSC)
(iv) % decomposition of AP in low-temperature range	~30 (enthalpy wise) ~30 (weight wise)
<i>Activation energy data (refs. 14–16)</i>	
(i) Low-temperature exotherm (250–350°C)	22 kcal mol ⁻¹ (scanning DSC) 21 kcal mol ⁻¹ (isothermal DSC) 20 kcal mol ⁻¹ (DTA) 20 kcal mol ⁻¹ (Pressure-time)
(ii) High-temperature exotherm (320–450°C)	60.5 kcal mol ⁻¹ (scanning DSC) 60.0 kcal mol ⁻¹ (DTA) 60.0 kcal mol ⁻¹ (calculated)

by us for the first time. We have also shown that AP undergoes 30% decomposition enthalpywise in a low temperature range further supporting the earlier observations of earlier workers that 30% decomposition weightwise takes place in low temperature range.

Study of the binder

Following the lines in which the oxidiser has been discussed, some studies on binder decomposition have also been made. The binder selected was PS. Although it does not represent the real binder system, it has certain inherent advantages like:

- (i) Easy preparation.
- (ii) No complication of the addition of curing agents (which some time interacts with AP to give side-reactions).
- (iii) No char formation during decomposition.
- (iv) Thermal decomposition and thermodynamic data are readily available.
- (v) The products of decomposition and the mechanism of degradation have been well studied.

Moreover, the knowledge gained on the mechanism of PS/AP system can also be used for other systems because a general mechanism will not show whether a particular system contains PS, polybutadiene or polyurethane. Although a great number of degradation data on polystyrene is available in the literature, the E values are in much variance from author to author as shown in Table 4. This may be due to the use of different techniques or the use of different equations. In order to check this,

TABLE 4
REPORTED VALUE OF ACTIVATION ENERGY FOR
POLYSTYRENE DEGRADATION (taken from ref. 20)

<i>Author</i>	<i>Technique</i>	<i>E (kcal mol⁻¹)</i>
Jellinek (1948)	Melt-viscosity measurements	24.5
Jellinek (1949)	TG	44.7
Papkov & Solninskii (1966)	TG	76, 83
Kysel (1965)	Gas chromatography	52
Bonn & Challa (1965)	Melt-viscosity measurements	20, 39
Madorsky (1952)	TG	58
Reich (1966)	DTA	64, 70
Anderson & Freeman (1961)	TG	46, 60
Coats & Redfern (1965)	TG	35
Lengelle (1970)	TG	65
Wegner & Patet (1970)	Melt-viscosity measurements	48

we have used three different techniques like DSC, TG and mass spectrometry and have used equations to calculate E which do not assume any order of reaction. Since the greater part of the study on degradation process concerns the change in condensed bulk, we have also calculated the E (using Jacobs-Kureishy method²⁶) of gaseous species formation like styrene and benzene. TG and DSC results together

with mass-spectrometric results on styrene formation give E values of around 30 kcal mol^{-1} (Table 5) showing that it is the most relevant value of styrene degradation. However, for benzene, E was 54 kcal mol^{-1} which suggests that the rate-controlling process in the conversion of solid PS into the gaseous monomer and benzene results from secondary reactions.

solid PS \rightarrow styrene monomer (gas) \rightarrow secondary reactions

TABLE 5

ACTIVATION ENERGY VALUES FOR
THE THERMAL DEGRADATION OF POLYSTYRENE (taken from ref. 20)

Technique	Temp. range ($^{\circ}\text{C}$)	E (kcal mol^{-1})
(1) DSC	370-380	32 ± 3
(2) TG		
(a) in air	320-390	29 ± 2
(b) in N_2	290-390	32 ± 2
(c) in O_2	340-375	28 ± 2
(3) Mass spectrometry		
(a) Styrene formation	360-430	30 ± 2
(b) Benzene formation	360-430	44 ± 2

The theoretical calculations²⁷ from solid PS to gaseous monomer reveals that the value is 28 kcal mol^{-1} confirming further the experimental validity of our results. It was further observed that E remains the same irrespective of the atmosphere under which PS decomposes. This suggests that hopefully the E of PS degradation in propellant (oxidative degradation) should also be 30 kcal mol^{-1} .

Study of the propellant

We have already pointed out the justification of the thermal decomposition studies of the propellant. The present PS/AP system shows a correlation between the thermal decomposition of the propellant to that of its burning rate⁹. Similar results are also obtained for the polyester/AP system (Table 6, Fig. 1). However, a great deal of work employing various systems is needed to obtain a general picture.

The thermal decomposition of the propellant involves the decomposition of AP and binder both. The DSC thermograms of PS, AP and propellant are shown in Fig. 2. The propellant thermogram seems to be a composite one. E calculation (by the method used earlier¹⁴) reveals that for a low temperature range the value is 20 kcal mol^{-1} and for a high temperature range it is about 55 kcal mol^{-1} . The E values of AP, PS and propellants are compared in Table 7, which shows that E of the propellant corresponds to that of AP and not to that of PS. One is, therefore, tempted to say that the rate-controlling process in the propellant decomposition is the decomposition of AP. Further, it should be noted that the thermal decomposition of the propellant is related to the thermal decomposition of AP (Fig. 3) and not

the sublimation of AP. This is evident from the fact that whereas E for AP decomposition and propellant decomposition has two values (20 and 60 kcal mol⁻¹ for the low and high temperature regions), the E value for the sublimation of AP is 20 kcal mol⁻¹ throughout the whole temperature range covering both low and high temperature ranges. This derives further support from the data presented in Table 6, i.e., 1 M % CrO₄²⁻ doped AP sensitises the thermal decomposition of AP at 350°C; the thermal decomposition of the propellant using 1 M % CrO₄²⁻ doped AP is also

TABLE 6

BURNING RATE AND THERMAL DECOMPOSITION OF
POLYESTER/AP PROPELLANT (taken from ref. 9)

Pressure	Burning rate (cm sec ⁻¹)	
	Undoped	1 M% CrO ₄ ²⁻ doped
300	0.410	0.435
500	0.461	0.538
700	0.563	0.717
900	0.589	0.819

	Thermal decomposition ^a	
	Undoped	1 M% CrO ₄ ²⁻ doped
% decomposed at 350°C of propellant	25	45
% decomposed at 350°C of AP	12	30

^a Dynamic TG (4°C min⁻¹).

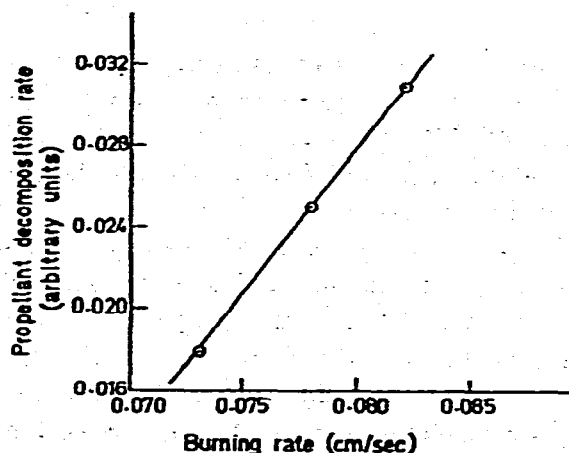


Fig. 1. Dependence of burning rate on the thermal decomposition of the PS/AP (75%) propellant.

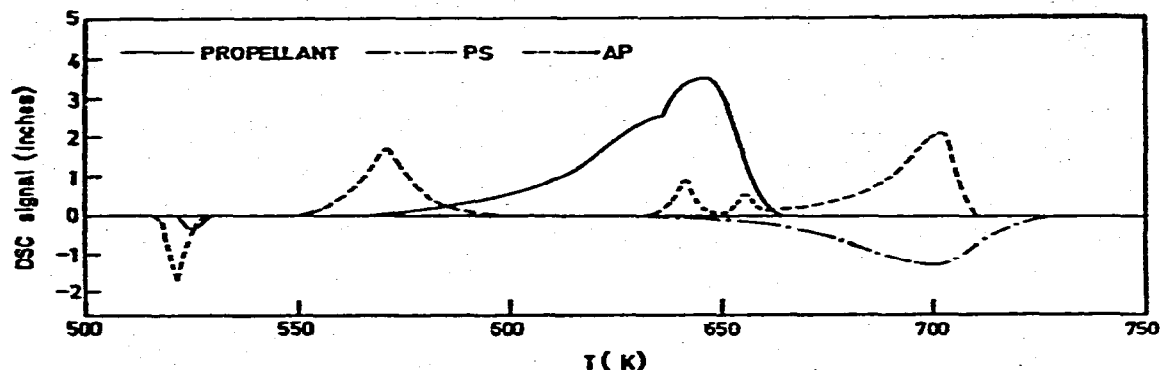


Fig. 2. DSC thermograms of AP, PS and PS/AP (70%) propellant at the scan speed of 16 K min^{-1} . Weight of the samples: PS = 2.466 mg; AP = 1.7216 mg and propellant = 1.392 mg.

TABLE 7

COMPARISON OF THE DECOMPOSITION ACTIVATION ENERGIES OF AP, POLYSTYRENE AND PS/AP PROPELLANT

	Activation energy		Technique (isothermal and scanning)
	250–350°C	350–450°C	
Ammonium perchlorate (AP)			
(i) Sublimation	20	20	DTA, theoretical
(ii) Decomposition	20	60	DSC, TG, DTA, MS*, theoretical
Polystyrene (PS)	30	30	DSC, TG, MS*
PS/AP propellant	20	55	DSC (isothermal & scanning both)
	17 ± 2	Explodes	TG

* MS = mass spectrometry.

sensitised at that temperature. In Fig. 1, we have shown that the thermal decomposition of the propellant is related to its burning rate. Figure 3 presents data on the relation between the thermal decomposition of AP and the burning rate of the propellant containing AP. It is evident that the burning rate of the propellant can be changed by changing the decomposition behaviour of AP.

It has been observed that the mechanical and ballistic properties of the propellant change during storage. Whereas the changes in the mechanical properties of the propellant may be due to the deterioration in the mechanical properties of the binder, the changes in the ballistic properties may, from the above discussed data, well be due to the slow thermal decomposition of the propellant as a whole. If this is the case, it may be interesting to see if the rate-determining step in the ageing process is the same as that in the thermal decomposition of the propellant and AP at higher temperature (300°C).

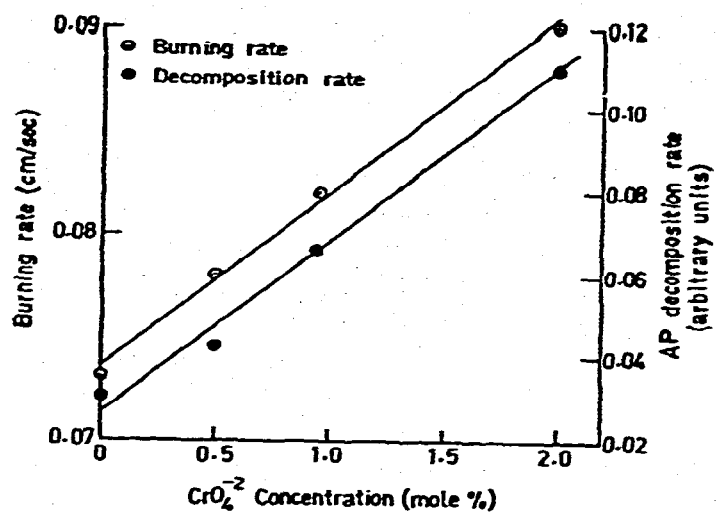


Fig. 3. Dependence of the burning rate of PS/AP (75%) propellant and the thermal decomposition of AP (Isothermal; 276°C) on the concentration of the dopant.

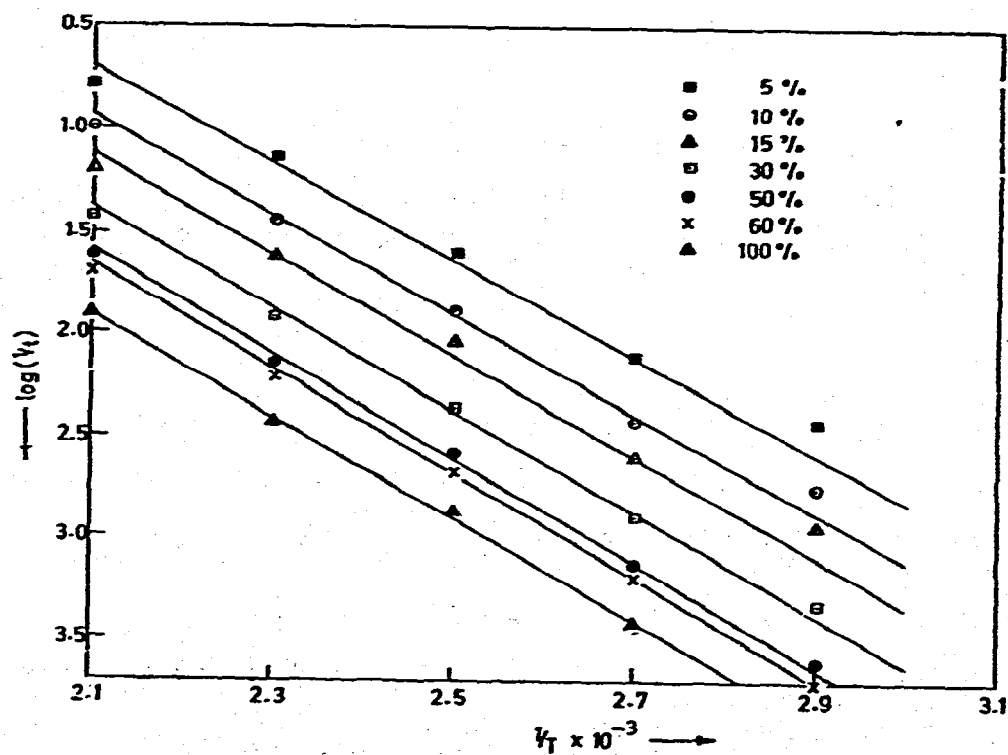


Fig. 4. Arrhenius plot between the rate (storage time (t)⁻¹) and the storage temperature at different percentage change of burning rate of PS/AP (75%) propellant.

Ageing of the PS/AP propellant for changes in the ballistic properties has, therefore, been studied in the temperature range 60 to 200°C. The data are presented in Fig. 4. A single E of 14 kcal mol⁻¹ is obtained over the whole temperature range 60 to 200°C. The obvious inferences are: (i) the mechanism of ageing at low storage temperature is the same as that of the decomposition at higher decomposable temperatures; and (ii) the value of the E for ageing corresponds to that of the propellant decomposition (17 kcal mol⁻¹) and therefore to AP decomposition. The aged propellant and the residue of the propellant decomposition at 300°C have been qualitatively analysed. In both cases, a yellow-coloured product is obtained having an absorption at 278°C. TLC analysis of the decomposition residue shows a number of bands indicating thereby the formation of a large number of intermediates¹³ (Table 8).

TABLE 8

R_f VALUES OF SOME OF THE BANDS OF DECOMPOSITION RESIDUE OBTAINED IN BENZENE+25% METHANOL SOLVENT (taken from ref. 13)

Colour of the bands in UV light	Vacuum residue	Air residue
Yellow	0.97	1.0
Light blue	0.83	0.83
Brown	0.08	0.08
Light yellow with orange tinge	0.37	—
No fluorescence (absorbs I ₂)	0.62	0.61

In summary, it may be concluded from the present work that the thermal decomposition of AP plays a significant role in the ageing as well as the combustion of the propellant.

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