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Note

Thermal decomposition studies on composite solid-propellants

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We have recently shown that a correlation exists between the thermal decomposition of polystyrene (PS)/ammonium perchlorate (AP) propellant and its burning rate[1]. In this particular study[2] we observed that the activation energy (*E*), 14 kcal mol^{-1}, for the propellant decomposition in the temperature range of 250–300°C corresponds to the AP thermal decomposition *E* (17±2 kcal mol^{-1}) in the same temperature range. AP thermal decomposition gives three *E* values, 30, 17 and 60 kcal mol^{-1} in the temperature ranges of 200–250°C, 250–350°C and 350–450°C, respectively[3]. It has been established that AP also undergoes sublimation and this process gives an *E* value of around 18 kcal mol^{-1} in all the above temperature ranges[4]. In our above-mentioned study, which we investigated the correspondence of *E* at the propellant and AP decomposition in the temperature range of 250–300°C, we could not distinguish wheather the correspondance was for the sublimation or for the decomposition process. The objective of the present communication, therefore, is to study the thermal decomposition of the propellant in the low-temperature range below 250°C to throw some light on this dilemma. Although the thermal decomposition study of the propellant in the high-temperature range above 300°C would also be useful, it could not be done in our present experimental set-up as the propellant ignites above 280°C.

It is well known that the propellant during storage undergoes changes in ballistic and mechanical properties. Thus, the understanding of the present low temperature decomposition studies will also help understanding the thermal stability of the propellant.

EXPERIMENTAL

PS/AP propellants were prepared as described earlier[5]. Recrystallised commercial AP of the particle size 172–204 μm was used in the propellant formulations. Fractionally distilled styrene monomer was used for preparing the binder. The

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propellant composition contained 25% PS and 75% AP by weight. Thermal decomposition of the propellant was studied on a home-made TG assembly as described elsewhere[6]. The propellant pieces of definite shape (vol/surface = 0.0512 cm) and weight (50 mg) were used in all the runs. The thermal decomposition was studied at 202, 215, 232, 240, 250 and 260°C. The temperature of the sample during decomposition could be kept constant to ±1 °C.

RESULTS AND DISCUSSION

The fractional weight-loss versus time plot of the thermal decomposition data of the propellant are shown in Fig. 1. A careful look at the curves show their non-smooth nature. Faced with this difficulty we did not make any attempt to fit these curves to any of the usual equations like Prout-Tompkins, Avrami-Erofeev[7], etc. Instead the rate was calculated for the decomposition of the propellant from 9 to 30%. The Jacobs and Kureishy method[8] was used for the calculation of E by plotting log

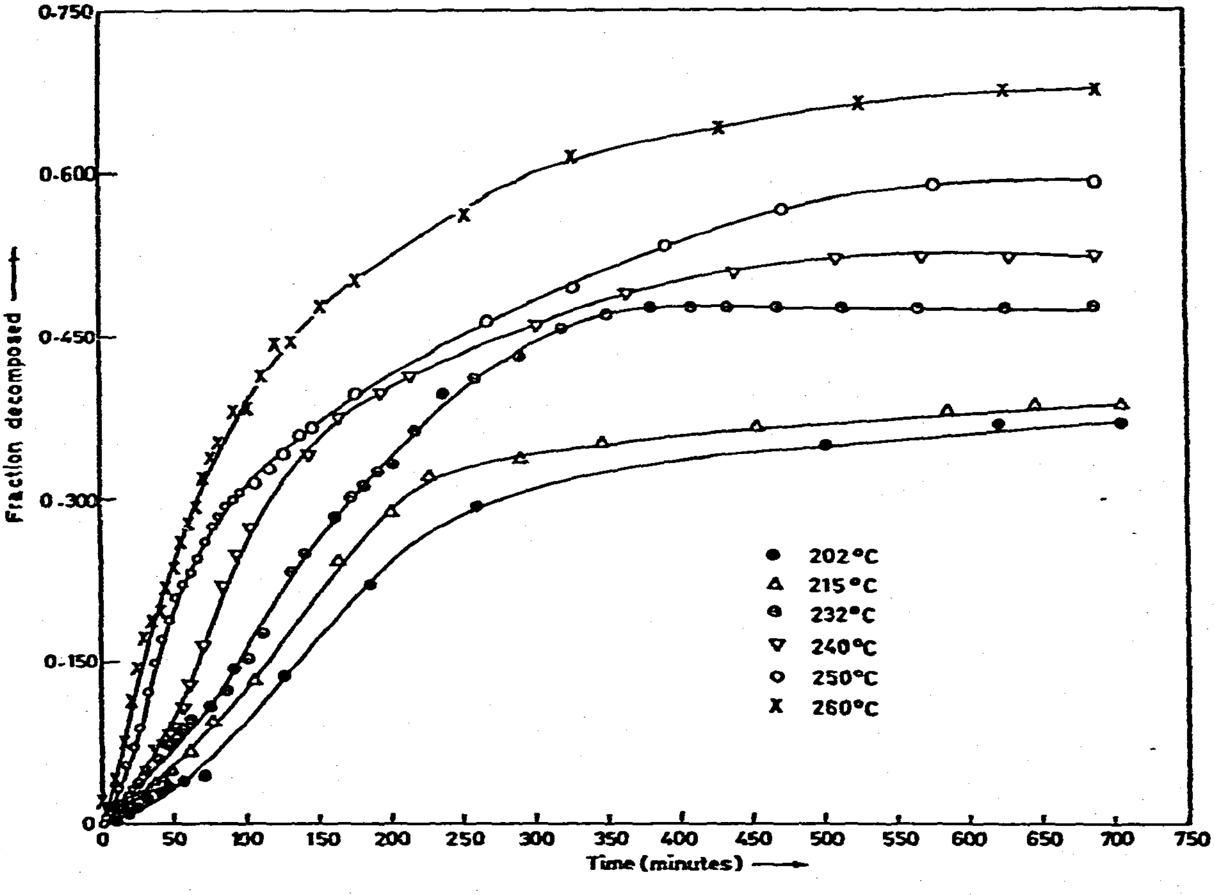

Fig. 1. The fractional weight-loss versus time plot of the thermal decomposition of the (PS/AP) propellant at various temperatures.

TABLE 1

ACTIVATION ENERGY DATA

Sample	*Activation energy (kcal mol^{-1})*			*Ref.*
	200–240°C	*240–350°C*	*350–450°C*	
PS/AP propellant	12±2	12±2	—	
PS decomposition	30±2	30±2	30±2	10
AP decomposition	30±2	17±2	60±2	3
AP sublimation	17±2	17±2	17±2	4
Heterogeneous thermal decomposition of $HClO_4$	9–14	9–14	—	11
$HClO_4$+methane	—	11.7	—	12

of the rate versus T^{-1}. The results are given in Table 1. The E of PS decomposition, AP decomposition and sublimation, heterogeneous gas-phase perchloric acid decomposition, perchloric acid reaction with methane and the propellant decomposition in different temperature ranges are also shown in Table 1. The very fact that the propellant decomposition E is the same throughout the temperature range 200 to 300°C (as shown in Fig. 2) suggests that it does not correspond to the AP decomposition E. However, neither does it correspond to the AP sublimation E, which remains the same in this temperature range. A quick glance on the Table 1 suggests that the propellant E corresponds to the heterogeneous thermal decomposition of $HClO_4$ or its reactions with an organic molecule. Recently, Korobeinichev et al. have shown that in a physical mixture of PS, AP and Fe_2O_3 (in powder form), the reaction between perchloric acid ($HClO_4$) and PS is important and they have confirmed

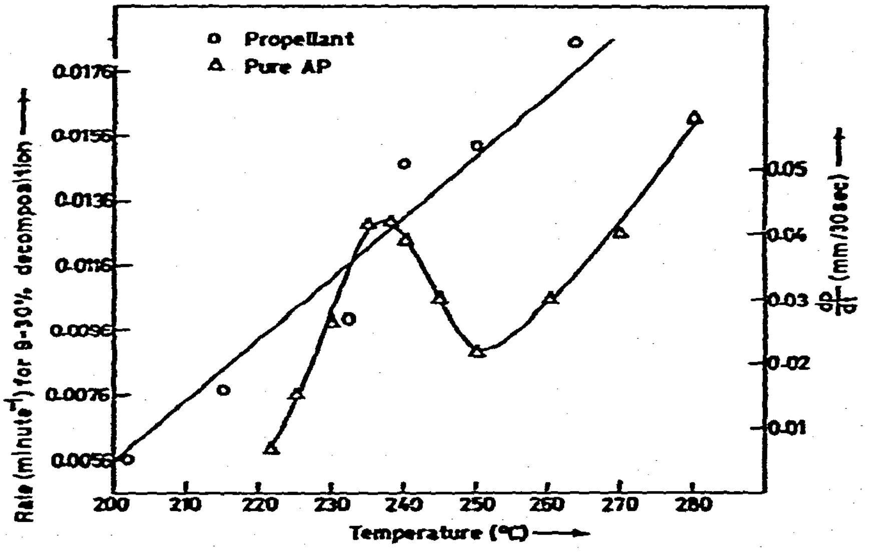

Fig. 2. Dependence of the rate of AP and PS/AP propellant decomposition on temperatures.

that the reaction in the above mixture is similar to the independent reaction of $HClO_4$ and PS[9]. That the thermal decomposition of the propellant does not follow the pattern of the thermal decomposition of AP can also be seen from Fig. 2. The rate of thermal decomposition of AP increases from 200 to 235°, then decreases till 250°C (phase-transition of AP from orthorhombic to cubic) and finally increases again[7]. In the propellant, the decomposition rate increases all the way from 200 to 250°C. It may be noted that the formation of $HClO_4$ results from the dissociation of AP and, therefore, our earlier assumption that the thermal decomposition of the propellant is governed by the thermal dissociation of the AP remains still valid. Our analysis of both the thermal decomposition residue and sublimate has shown that the decomposition is a complex phenomenon involving various intermediates.

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