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Thermal Decomposition and Combustion Studies on Potassium Perchlorate/Polystyrene Propellant Systems

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Abstract

STUDIES on potassium perchlorate/polystyrene (KP/PS) propellant systems have been carried out by using such techniques as thermogravimetry (TG), differential thermal analysis (DTA), and mass spectrometry (MS). It has been found that the thermal decomposition (TD) behavior of the KP/PS propellant is similar to that of the AP/PS propellant studied earlier.¹ It has also been observed that the TD of KP in the melt has a correlation with the burning rate (\dot{r}) of KP/PS propellant at atmospheric pressure.

Contents

It has been shown in recent years that condensed-phase reactions occur in Ammonium Perchlorate (AP) based propellants at ambient pressure. The present studies were carried out with a view to examine the TD behavior including the occurrence of condensed-phase reactions of another propellant system, KP/PS. KP was chosen because it is the simplest oxidizer and decomposes to give O_2 which is its only gaseous species, whereas AP releases many gaseous species during decomposition. Another objective was to compare the TD behavior of KP/PS and AP/PS propellants.

Experimental Method

Dynamic DTA³ and TG⁴ techniques (heating rated at $7^\circ C \text{ min}^{-1}$) along with MS studies ($400^\circ C$) were employed to study the TD behavior of KP/PS propellants. KP/PS propellants were prepared in a manner described previously² for AP/PS propellants. The oxygen/fuel ratio was maintained at 4. \dot{r} measurements at atmospheric pressure were made as described earlier.⁵

Results and Discussion

MS studies¹ and the analysis of intermediates⁶ for AP/PS propellants gave some information regarding the chemical nature of condensed-phase reactions. MS studies were carried out on KP/PS propellants. A comparison of the MS data (Table 1) for AP/PS¹ and KP/PS propellants showed that the MS of the propellant is not equivalent to the sum of MS of the individual components. Some peaks (mass Nos. 22, 29, and 51) seen in the propellant are not present in PS or KP individually. Since the sum of the KP and PS MS is not

equivalent to the MS of the propellant it may be inferred that there are reactions occurring between the products of KP and PS in the propellant matrix as shown for AP/PS propellants.¹

Pai Verneker et al.,⁷ have shown that the TD of KP is desensitized by the presence of $KClO_3$ at $535^\circ C$. In order to see whether this behavior is reflected in the combustion of the KP based propellants, KP/PS propellants with an appropriate amount of $KClO_3$ as the additive were prepared and the \dot{r} (at ambient pressure) was determined. The results showed that $KClO_3$ enhanced the \dot{r} contradictory to what was expected. This may be due to the formation of a melt (which is observable) during the combustion of KP based propellants. The effect of $KClO_3$ on the TD of KP in the liquid phase was therefore expected to be different. Hence TD studies were carried out on KP and KP + $KClO_3$ systems at $570^\circ C$ where KP decomposes in the melt. At this temperature $KClO_3$ was found to sensitize the TD of KP. It may then be concluded that in KP/PS propellants \dot{r} is correlated to the TD of KP in the melt but not in the solid state.

DTA and TG studies (Fig. 1) brought into focus the following features. The phase transition of KP in the propellant was found to remain unaltered except for a slight shift which is similar to that observed in AP/PS propellants.⁸ The KP/PS propellant DTA thermogram shows the presence of two exotherms around 385 and $475^\circ C$ which are absent in the DTA of KP. PS decomposes around $400^\circ C$ endothermically. Thus the two exotherms in KP/PS propellant in the solid state may be attributed to the occurrence of the condensed phase reactions. A wide endotherm at 525 – $540^\circ C$

Table 1 Mass numbers corresponding to peaks obtained in various decomposition experiments at $400^\circ C$

AP/PS	AP	PS	KP	KP/PS
12	—	12	—	12
14	14	14	—	14
15	—	15	—	15
16	16	16	16	16
17	17	—	17	17
18	18	—	18	18
22	—	—	—	22
26	—	26	—	26
27	—	27	—	27
28	28	28	—	28
30	30	—	—	29
32	23	—	32	32
—	35	—	—	—
—	36	—	—	—
—	37	—	—	—
—	38	—	—	—
44	44	44	—	44
—	—	—	—	51
—	—	52	—	52
—	70	—	—	—
—	72	78	—	78
—	74	92	—	92
—	—	104	—	104

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Index categories: Combustion and Combustor Designs; Ablation, Pyrolysis, Thermal Decomposition (including Refractories); Thermochemistry and Chemical Kinetics.

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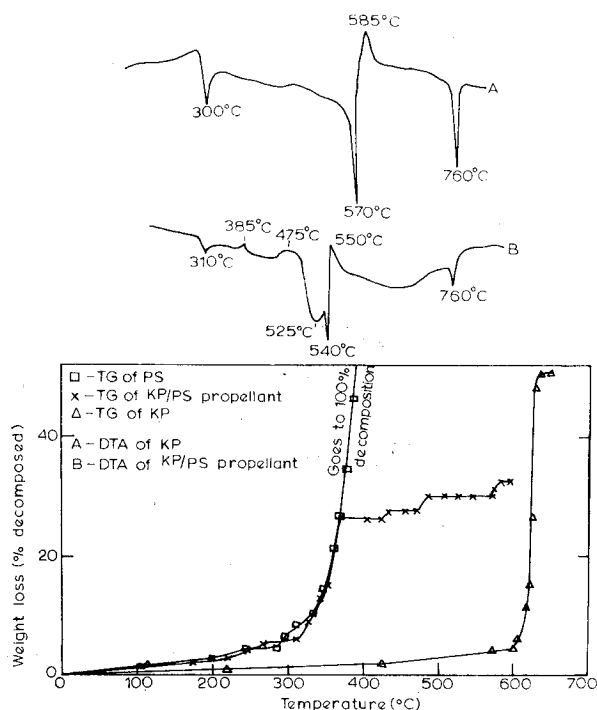


Fig. 1 DTA and TG thermogram of PS, KP, and KP/PS systems.

and the exotherm at 550°C (after fusion) in the propellant may be compared to the endotherm and exotherm of KP.

The dynamic TG plot of KP/PS propellant shows four steps. The first two steps in the temperature range 300–450°C correspond to the first exotherm in the DTA thermogram involving the following reactions: 1) PS degradation, 2) KP decomposing to give KClO_3 , and 3) heterogeneous reactions of KP and PS decomposition products. Isothermal TG studies in the temperature range 230–370°C yield a value of 27 Kcal/mole for the energy of activation (E). Most of the weight loss up to 400°C (~20%) is due to PS degradation. This has been confirmed by the analysis of the propellant residue obtained after decomposing it at 440°C. Earlier studies⁹ have shown that the TD of PS in air or O_2 gives an E of 30 Kcal/mole⁻¹, therefore lending support to the observation that PS degrades in this temperature region. TG studies could not be carried out above 400°C because the decomposition (up to ~20%) was very rapid. Therefore, kinetic studies were carried out by MS. The objective was to compare the value of E for the decomposition of the propellant with those of KP and PS. Mass numbers corresponding to styrene, oxygen, and carbon dioxide were followed as a function of time and temperature. The concentration of O_2 evolved was very little, hence the kinetics of oxygen evolution could not be studied quantitatively. E was calculated for the rate of evolution of all the species by the Jacobs-Kureishy technique.⁹ All of them gave values of $E \sim 30$ Kcal/mole⁻¹. Since E for PS degradation⁹ and KP decomposition^{7,10} is also 30 Kcal/mole⁻¹ it was not possible to make out whether the rate controlling step is governed by KP decomposition or PS degradation.

The growth and decay of styrene and benzene were followed as a function of time under isothermal conditions from MS. The MS results of the AP/PS system were explained by assuming that AP particles are surrounded by the binder film.¹¹ On heating, the binder and oxidizer decomposed but only the decomposition products of PS were recorded first; later when the film ruptured the decomposition products of the oxidizer and the interaction products of the binder and the oxidizer were recorded. With the AP/PS propellant, styrene (the degradation product of PS) was the first product obtained, confirming the speculation that oxidizer particles are surrounded by PS film.¹¹ In the KP/PS system MS was not recorded at low temperature; however, conventional chemical analysis showed styrene to be the only decomposition product, indicating that the physical model of the condensed-phase holds good for the KP/PS propellant also.

Conclusion

MS and DTA studies on KP/PS propellant has shown that there is occurrence of exothermic reactions in the propellant matrix and that these reactions are different from those which occur in KP or PS individually. r of the KP/PS propellant (at ambient pressure) has been found to be related with the TD of KP in the melt.

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