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Thermoanalysis of Ammonium Perchlorate and Sodium Nitrate Mixture

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A binary mixture of ammonium perchlorate–sodium nitrate in molar proportion undergoes partial fusion at 223°C and the transformation of the mixture to sodium perchlorate–ammonium nitrate occurs in the broad endothermic region. The mixture was heated and quenched at various temperatures in a differential thermal analysis assembly. Thermogravimetric analysis, X-ray diffraction, and infrared spectroscopic techniques were used to determine the composition of the quenched sample in order to explain the overall thermal phenomenon. Visual observations of the morphological changes that occur during the course of heating were made using a hot-stage microscope, 30–350°C.

Introduction

Thermal decomposition plays a dominant role during aging of composite solid propellants (*1–6*) and significantly affects the steady-state burning of the propellant (*7–10*). Mixed oxidizers in composite solid propellants are useful in altering (i) burning rate, (ii) aging behavior, (iii) specific impulse, and (iv) ignition characteristics. Recently, combustion and decomposition of a mixed oxidizer, viz., ammonium perchlorate–sodium nitrate (AP–SN), have been studied (*11, 12*). However, the detailed solid-state interaction of the two (AP and SN) has not been studied. Hogan and Gordon (*13*) have made a thermoanalytical evaluation of binary mixtures of oxidant systems such as potassium perchlorate (KP)–alkali or alkaline earth metal nitrates. The decomposition phenomenon was attributed to the physicochemical behavior of the ingredients and their mixtures. The authors have shown that a mixture of KP and SN undergoes eutectic formation followed by complete fusion in the temperature region 260–265°C and 480–485°C, respectively. It is also understood that the binary mixture quenched after heating to a clear melt and cooled to room temperature is a system of a stable salt pair.

In the present work, a binary mixture of AP and SN in molar proportion was heated in order to understand and explain the behavior of a nonmetal perchlorate like AP with SN. Pure AP decomposes between 200 and 400°C without melting (*14*). SN melts at 306°C and decomposes appreciably after 700°C.

Experimental

Recrystallized AP and SN (Sarabhai M. Chemicals) in molar proportion were mixed in a mortar to a particle size range of 212–250 μm. Two hundred milligrams of

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the mixture in a platinum cup was heated at the rate 10°C min^{-1} in air in a DTA assembly. Residues left after heating the mixture of AP–SN up to 200, 260, 312, 350, and 530°C were cooled to room temperature and subjected to conventional chemical analysis to identify the constituents. X-Ray diffraction and infrared (ir) spectroscopic techniques were used to identify the intermediates. A thermogravimetric (TG) curve of the mixture was obtained on a Stanton Redcroft thermobalance (Model TG 750/770) at a heating rate of 10°C min^{-1}. Visual observations of the changes in the morphological and textural properties of AP–SN mixture during the course of heating were followed using a hot-stage microscope in the temperature range of 30–350°C at a heating rate of 4°C min^{-1}.

Results and Discussion

The DTA curve for the mixture of AP–SN in molar proportion is shown in Fig. 1, which also exhibits the thermograms of AP, SN, sodium perchlorate (SP), ammonium nitrate (AN), and a mixture of SP–AN in molar proportion. It may be seen that the DTA curve of AP–SN shows an endotherm at 223°C and an exotherm at 312°C which cannot be assigned to any of the thermal reactions exhibited by the ingredients and is quite different from the additive DTA of AP and SN. The TG curve of the mixture was obtained and the change in the stoichiometry of the mixture was ascertained from the curve shown in Fig. 2. The 40% weight loss within the temperature region 248–350°C conforms to the decomposition of AN and the 31.5% weight loss between 530 and 602°C to that of SP decomposition. The residual weight percent after 602°C corresponds to sodium chloride.

Hogan and Gordon (*13*) in their study of binary mixtures of KP–SN (0.21 and 0.57 mole% KP), have shown that they undergo partial and complete fusion between 260 and 265°C and 480 and 485°C, respectively. Also TG data for the KP–SN mixture indicate that the weight loss corresponding to nitrate and perchlorate decomposition occurs at higher temperature between 750 and 780°C and 620 and 680°C, respectively. Thus the nitrate is rendered more stable by potassium in KP–SN mixture. Besides, the X-ray diffraction result of KP–SN mixture

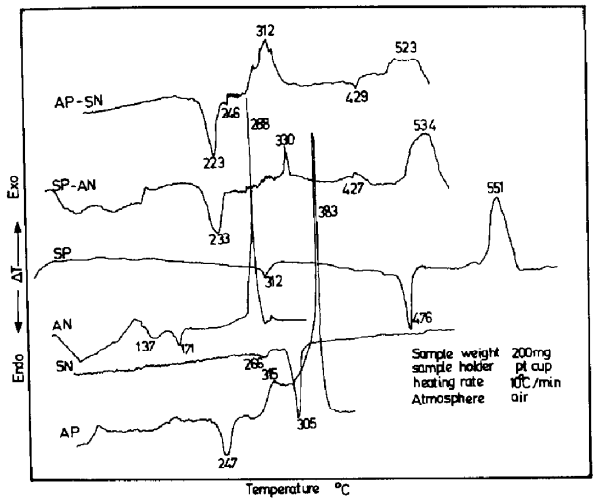

FIG. 1. DTA traces for AP, SN, AN, SP, SP–AN, and AP–SN.

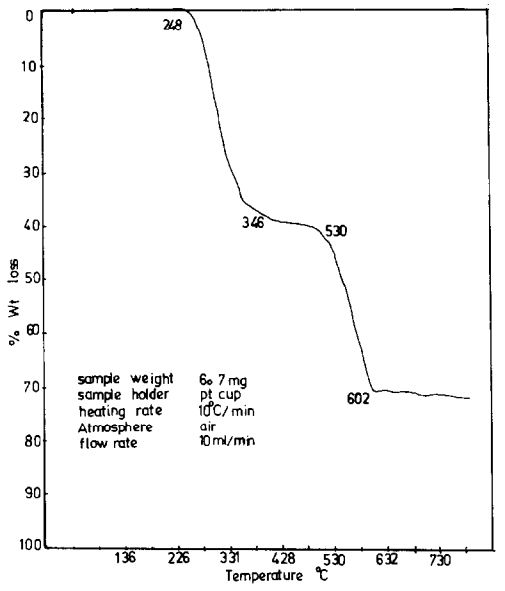

FIG. 2. TG curve for AP–SN binary mixture.

heated to a clear melt and cooled to room temperature has indicated the presence of original salts, suggesting the system to be of a stable salt pair.

In contrast to KP–SN binary mixture, the TG data for AP–SN mixture are indicative of the fact that the nitrate is rendered unstable by the NH_4^+ at a lower temperature, between 248 and 350°C. Otherwise, as pure SN, it would show appreciable weight loss after 700°C. Accordingly, X-ray diffraction results of Fig. 3 for the mixture of AP–SN heated to 200 and 260°C and cooled to room temperature show the presence of original salts. At 260°C, the residue shows the presence of SP in addition to the original salts. Between 223 and 260°C, the material sublimes and gets deposited on the cooler parts of the furnace. Qualitative tests indicated the presence of NH_4^+ and NO_3^-. The ir spectrum (Fig. 4) confirms the sublimate to be AN. The DTA exotherm around 312°C for AP–SN mixture was speculated to be the exothermic decomposition of the unsublimed AN. The DTA of AN shown in Fig. 1 also supports this. After the exotherm, the decomposition product was quenched at 350°C and the residue was subjected to ir and X-ray analysis. The ir results shown in Fig. 5 indicate the presence of SP. X-Ray analysis also (Fig. 3) shows the presence of SP, suggesting that the DTA curve of the mixture of AP–SN, after the exotherm at 312°C, is characteristic of SP. A further point of similarity between AP–SN and SP–AN mixtures is the DTA evidence. The DTA curve of SP–AN, ground separately, dried, and mixed in molar proportion to a homogeneous blend, was also obtained to check the reproducibility of the characteristic peaks compared to those obtained in the case of AP–SN

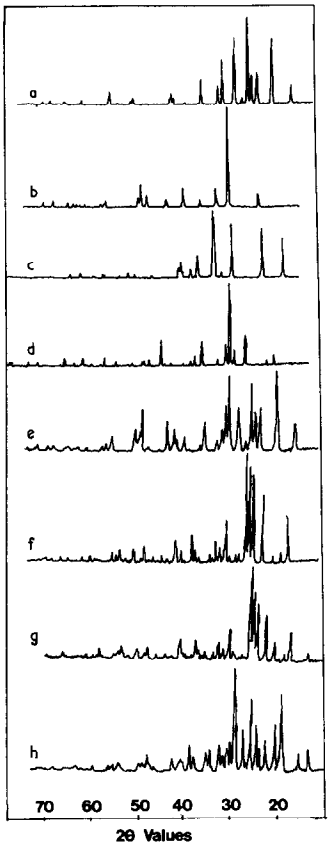

FIG. 3. X-Ray diffraction patterns of (a) AP, (b) SN, (c) AN, (d) SP, (e) AP–SN, 200°C, (f) AP–SN, 260°C, (g) AP–SN, 312°C, and (h) AP–SN, 350°C.

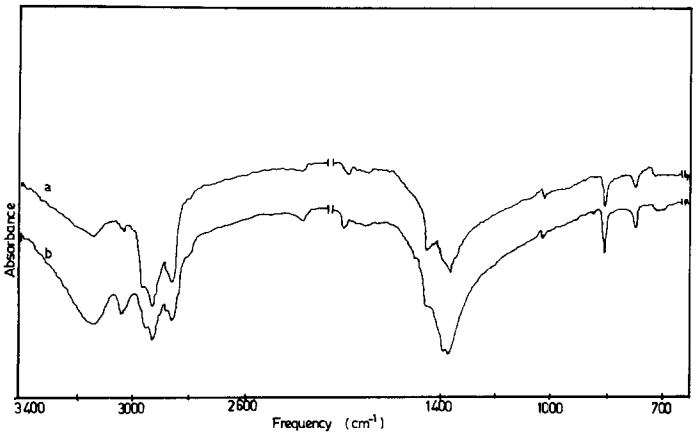

FIG. 4. Infrared spectrum of (a) sublimate of AP–SN mixture at 240°C, and (b) neat AN crystals.

mixture. The DTA of SP–AN mixture matches that of the AP–SN mixture (Fig. 1). A careful look at the broad endotherm at 223°C in the DTA of the AP–SN mixture shows a small endotherm at 246°C which, however, is not seen in the corresponding endotherm at 233°C in the DTA of SP–AN. The endotherm at 246°C in AP–SN may be ascribed to the phase transition of AP. This result indicates that AP–SN undergoes partial fusion in the broad endotherm region at 223°C, while SP–AN forms a solid solution at 233°C.

In order to gain insight into the reaction process manifest in the melt phase, visual observations of the transformations occurring during the course of heating in the fusion region of 223°C, where AP–SN mixture is converted to SP–AN, were made using a hot-stage microscope. Microphotographs (Fig. 6) of the changes observed were obtained and specific areas of interest are indicated by the arrow marks. Microphotograph 1 shows that SN with AP suffer depression in the melting point to 218°C at which fusion occurs. The melt phase becomes extensive with AP crystals in the melt as shown in microphotograph 2. At 220°C, formation of a eutectic was visualized as in microphotograph 3 and few AP crystals are indicated by the arrow marks. Eventually between 220 and 260°C, AN crystals were observed to grow abruptly in its cubic form and the increase in number of such cubic forms was gradual. Because of the impending thermal strain, AN crystals were observed to melt immediately as shown in microphotograph 4. The melt later

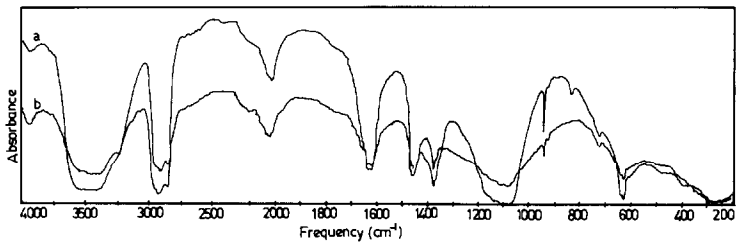

FIG. 5. Infrared spectrum of (a) neat SP crystal, and (b) AP–SN mixture quenched at 350°C.

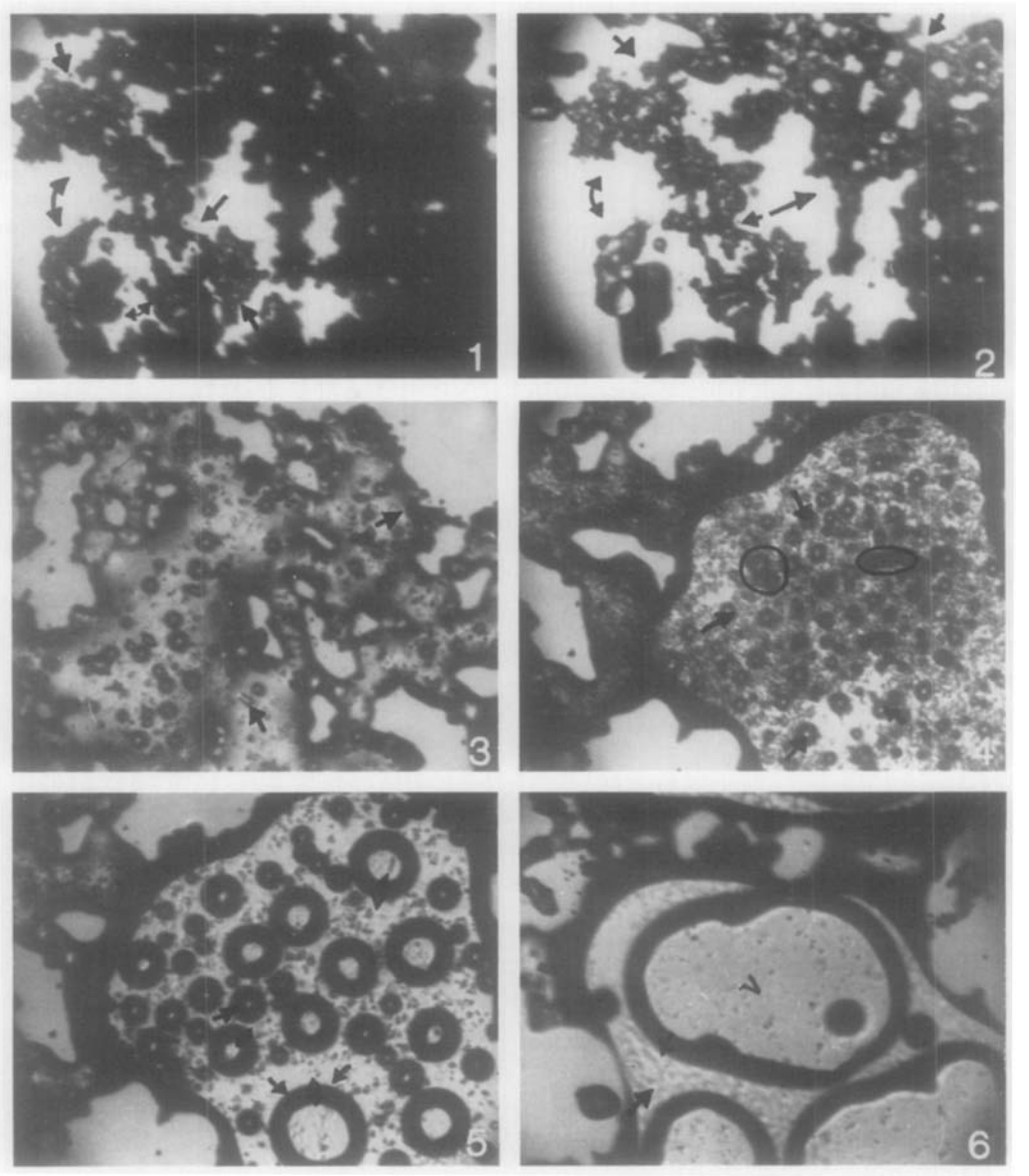

FIG. 6. Microphotographs of AP–SN mixture. (1) Fusion of SN at 218°C. (2) Melt of SN becoming extensive at 220°C. (3) Eutectic formation of AP–SN mixture at 220°C. (4) Formation and simultaneous melting of AN between 220 and 260°C. (5) Agglomeration of AN melt to larger melts between 220 and 260°C. (6) Segregation of SP.

agglomerated to larger melts. The sites of agglomeration are indicated in microphotograph 5. As evidenced in microphotograph 6, SP was observed to segregate and grow around 270°C, while voids (V), which are the sites of AN vaporization, were also observed.

Conclusion

In conclusion, it may be said that the thermoanalytical study made of the binary mixture of the oxidant system AP–SN in molar proportion indicates that it is a system of an unstable salt pair, in contrast to KP–SN which is a system of a stable salt pair as reported in the literature. The reactivity of AP–SN mixture is manifest in the endothermic fusion region to form the decomposition product SP–AN. It also appears that there is flux growth of AN from the melt of AP–SN mixture after the cooperative rearrangement of NH_4^+, Na^+, ClO_4^-, and NO_3^-.

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