Ignition of Composite Solid Propellant Analogs

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Introduction

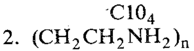
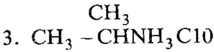
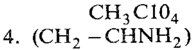
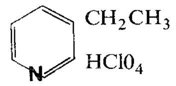
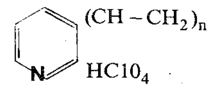
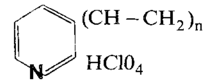
THE physico-chemical processes leading to the ignition and combustion of composite solid propellants have been studied widely during the last two decades.[1] Different theories are proposed and the experimental data are interpreted on the basis of various models. Even though there has been a lot of success in explaining many of the associated problems, no single theory has evolved which can explain the complex physical-chemistry of ignition and combustion. The thermal ignition theory,[2] granular diffusion flame theory,[3] and the heterogeneous ignition theory[4] are but a few of these generalizations. Our approach to the problem is essentially a novel one and consists of the preparation and thermal characterization of polymetric amine perchlorates having an analogous composition to that of composite solid propellants based on ammonium perchlorate (AP). In this Note we present the ignition temperatures of a few of these materials and extend the heterogeneous ignition mechanism to explain the case of ignition of these compounds. Perchloric acid salts of polyethylenimine, polypropylenimine, poly (vinyl pyridines) (2- and 4-) and poly (amino styrent) are prepared by treating the poly bases with 70% perchloric acid and washing off the excess acid. The bases are neutralized to the extent of 60-75% only, probably because of their polyelectrolyte character. Ignition temperatures of the polymeric amine perchlorates have been determined by differential thermal analysis (DTA).

Results

Table 1 shows the ignition temperatures of the various systems with those of the corresponding model compounds. These materials ignite with a visible flame when heated in a test tube. Therefore, the exotherm in the DTA trace (Fig. 1) is due to ignition of the perchlorates. In contrast to the low ignition temperatures of the polymeric perchlorate salts, the corresponding polymeric amines decompose at about 350-450°C as shown by DTA and TGA (thermogravimetric analysis) experiments in air. A mixture of AP with polymers also is found to decompose only above 300°C in DTA experiments.

The thermal decomposition of AP is studied extensively and there is fairly clear evidence to believe that proton transfer dissociation of AP into absorbed NH_3 and $HC10_4$ is the first reaction process to occur.[5] In the ignition of a composite solid propellant, the perchloric acid thus formed decomposes into oxides of chlorine and these oxidizing species attack either the solid polymeric matrix by a heterogeneous reaction or the polymer pyrolysis products in the gas phase, leading to ignition of the system. Levy's study on the thermal decomposition of $HC10_4$[6] and Pearson and Sutton's studies on the ignition of various polymers and model compounds of polymer pyrolsis products[7,8] render strong support to the theory that the decomposition of $HC10_4$ is heterogeneously catalyzed at temperatures below 325°C.

Table 1 Ignition temperatures and activation energies of polymeric amine perchlorates and corresponding model compounds

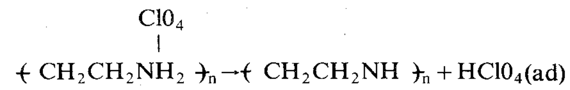
System	Ignition temperature °C	Activation energy Kcal/mole
1 $CH_3CH_2NH_3C10_4$ Ethyl amine perchlorate	301	40[a]
2.  $\overset{C10_4}{(CH_2CH_2NH_2)_n}$ Polyethylenimine perchlorate MW = 100,000	200 ± 10	20[a]
3.  $\overset{CH_3}{CH_3}-CHNH_3C10_4$ Isopropyl amine perchlorate	291	46[a]
4.  $(CH_2-\overset{CH_3C10_4}{CHNH_2})_n$ Polypropylenimine perchlorate MW = 15,000	240 ± 30	34[a]
5.  4-Ethyl pyridine perchlorate	340	50[b]
6.  Poly(4-Vinyl pyridine perchlorate) MW = 10^5	175	22[b]
 Poly (2-Vinyl pyridine perchlorate) MW = 10^5	228	15[b]

[a] Calculated from isothermal weight-loss experiments.
[b] Calculated from ignition delay experiments.

Recent studies[9,10] on the thermal decomposition of substituted ammonium perchlorates lead to the conclusion that proton transfer dissociation is the first step in the decomposition of these salts:

$$R_nNH_{(4-n)}C10_4 \rightarrow R_nNH_{(3-n)} + HC10_4 \rightarrow \text{products}$$

Based on these, it is highly probable that the polymeric amine perchlorates dissociate first to the polymeric amine and absorbed perchloric acid as shown below in the case of polyethylenimine perchlorate



$$\overset{\overset{C10_4}{|}}{\text{⟮} CH_2CH_2NH_2 \text{⟯}_n} \rightarrow \text{⟮} CH_2CH_2NH \text{⟯}_n + HC10_4(ad)$$

The $HC10_4$ thus formed can decompose into oxides of chlorine and this reaction is catalyzed by the polymer. One of the major products in the decomposition of $HC10_4$ is the C10 free radical. The thermal decomposition of most polymers is shown to follow the free radical route.[11] This combined with the fact that C10 and other chlorine oxides are strong oxidizing agents gives strong support to the conclusion that the polymeric bases are oxidatively pyrolyzed by the decomposition products of $HC10_4$, thus leading to ignition.

Another important finding from Table 1 is the effect of the chemical structure of the polymer on the ignition temperatures of the perchlorate salts. One explanation for the difference in the ignition temperatures of polyethylenimine and ploypropylenimine perchlorates can be the inductive effect of the CH_3 group which retards the ease of proton transfer. Such an explanation, however, cannot account for the difference of

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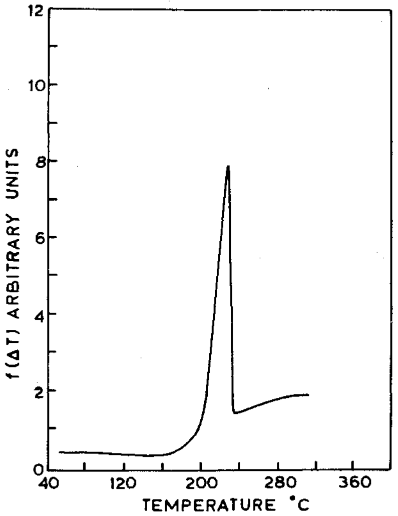

Fig. 1 DTA trace of polyethylenimine perchlorate.

about 50°C in the ignition temperatures of the two poly (vinyl pyridine) salts. The most plausible explanation is that there is some sort of hydrogen bonding between the vinyl→C–H and O of the ClO_4 group in the case of poly (2-vinyl pyridine) perchlorate due to the proximity of the two groups. This given an additional stability for this compound which ignites at a higher temperature than poly (4-vinyl pyridine) perchlorate. Such a trend is noticed again in the case of ortho and para poly (amino styrene) perchlorates. The assumption of hydrogen bonding in these compounds finds support from the recent theoretical[12] and experimental[13] studies on hydrogen bonding where the hydrogen is attached to a carbon atom.

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Relaxation Distance and Equilibrium Electron Density Measurements in Hydrogen-Helium Plasmas

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Introduction

THE physical properties of shock-heated hydrogen-helium plasmas which surround an entry probe during outer planet entry present a challenging area for theoretical and experimental investigation. In the present Note, electron density measurements are reported for 84.17% H_2–15.83% He for a wide range of shock velocities (26km/sec to 46 km/sec at an initial pressure of 1 torr). Two completely independent diagnostic techniques, namely, pulsed laser interferometry and high-resolution spectral measurements of the Stark-broadened H_β line profile from the transient plasma are used. The flow behind the incident shock wave within the shock tube simulates the flow behind the bow shock wave of an outer planet entry probe. The radiative emission of this shock-heated, hydrogen-helium plasma and consequent heat flux at an entry probe heat shield is directly related to the electron temperature and density.

Holographic Interferometry Measurements

The shock wave is produced in the annular arc accelerator (ANAA) shock tube[1] which consists of a cold gas driver, an expansion section, high-voltage electrode sections, and the shock tube test section (see Fig. 1). The shock speed is monitored by fast-rise photo-multiplier tubes at nine stations along the test section so that any shock attenuation can be measured accurately. Good quality flow with various shock velocities is achieved. The holographic interferometer consists of a pulsed ruby[4] laser system, a beam splitter, a scene beam expander, two spherical collimating mirrors, a reference beam expander, and the hologram film holder. All of these components are mounted about the ANAA shock tube on tables or optical stands with the optical axis of the scene beam in a horizontal plane 1.5 m above the floor. The scene beam passes through the test section which is composed of a 15.3-cm inside diameter tube. The fringe shift from the first exposure with a neutral 84.17% H_2–15.83% He gas in the test section to the second exposure with the shock heated plasma in view is the integral $\int(\mu\text{-}1)d\ell/\lambda$ where the refractive index μ is a function of the particle species encountered along a ray of length ℓ and the laser wavelength λ. Each species of molecule, atom, ion, or electron has a different refractive index. Through the previous integral, they all contribute to the total fringe shift. The free electrons cause a fringe shift of opposite sign and are more than 40 times more effective in changing laser phase than the neutral species. These properties allow us to interpret the hologram for electron density with a minimun of uncertainty.

Spectroscopic Measurements

In constrast to stationary plasmas where spectroscopic measurements can be made with little time limitation so that one can scan across a line profile at a large number of wave-

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