

SYNOPTIC: Heterogeneous NH_4ClO_4 Decomposition Using Isothermal and Pulsed Laser Mass Spectrometry, G. L. Pellett, NASA Langley Research Center, Hampton, Va.; *AIAA Journal*, Vol. 8, No. 9, pp. 1560-1566.

**Combustion in Heterogeneous Media; Properties of Fuels and Propellants;
Thermochemistry and Chemical Kinetics**

Theme

This paper presents a mass spectrometric study of the low- and high-temperature decomposition of ammonium perchlorate (AP) and certain catalyzed AP systems relevant to solid propellant combustion. Although some product distributions are given for the pure salt, emphasis is placed upon high-temperature heterogeneous decomposition of AP in the presence of "burning rate catalysts," and certain doped AP's that exhibit intermediate reaction behavior. Details of the pulsed ruby (and also CO_2) laser pyrolysis-mass spectrometry techniques employed are given to encourage use of these new approaches in chemical studies of other high-temperature and/or rapid pyrolyses.

Content

The present use of pulsed lasers to decompose solid samples in the low-pressure ion source chamber of a Bendix Time of Flight mass spectrometer permitted study of rapid high-temperature decompositions without the attendant disadvantages of many conventional heating techniques. For a major portion of the present work, a pulsed (0.8 ms) ruby laser allowed selective study of heterogeneous reactions that occur when hot substrates (light absorbing) contact AP (relatively transparent at 6943 Å) and rapidly surface-heat the oxidizer by conduction. Reference is also made to the recent application of a CO_2 gas laser (variable square-pulse duration and power output), used to obtain high-temperature time resolved decomposition histories of the pure salt, which absorbs strongly at 10.6 μm ; results from this technique provided independent confirmation of the conclusion that the site of HClO_4 decomposition (crystal vs substrate surface) was at least as important as temperature and effective residence time in determining the predominant chemical pathways.

The major features of the present results can be summarized as follows. Consistent evidence indicated that in pulsed ruby laser pyrolyses (LP) of AP mixed with finely divided carbon black, copper chromite, Fe_2O_3 or MnO_2 substrates, the predominant decomposition pathways involved high-temperature heterogeneous reactions. Since open sample geometries and initial pressures below 10^{-6} torr were employed, desorption was favored and gas phase reactions probably had a negligible effect on the product distributions.

The first decomposition step appeared to be proton transfer dissociation of AP into NH_3 and HClO_4 . Both were always observed initially, but there was generally a large stoichiometric deficiency of HClO_4 in the gas phase. Adsorbed HClO_4

appeared to have undergone a rapid heterogeneous decomposition on the substrate material, wherein ClO_2 and HCl were evolved in relatively large quantities. Small quantities of ClO_3 were also detected, suggesting some HO-ClO_3 cleavage, but not in the comparatively high abundance found in CO_2 laser pyrolyses of AP. Relatively little decomposition of the ClO_2 appeared to occur under LP conditions, since ClO and Cl_2 were evolved in comparatively small quantities. Chemisorbed oxygen and/or other oxygen carriers such as OH and ClO were most probably formed on the substrate simultaneously, however. These could react with substrate, as in the case of carbon, and also abstract hydrogen from adsorbed NH_3 and its dehydrogenated fragments to form H_2O and NO , which were observed as major decomposition products; N_2 , N_2O , and NO_2 were found to be minor products. HOCl was a significant and characteristic product of heterogeneous decomposition.

Low-pressure isothermal decompositions (ID) of AP, KMnO_4 and $\text{CrO}_4^{=}$ doped AP, and AP/substrate mixtures, heated in a glass capillary up to 380°C, are also presented. Comparisons of results obtained from the two pyrolysis techniques indicated significant differences in product distribution, and hence decomposition mechanism; e.g., ClO_2 and HOCl were not major products of pure AP decomposition in the present ID, or in high-temperature CO_2 laser pyrolyses. Further LP vs ID comparisons, in which the Cl_2/HCl ratio varied by two orders of magnitude, provided additional evidence for a transition in pyrolysis behavior relating to the extent of heterogeneous HClO_4 decomposition. As indicated above, the site of HClO_4 decomposition appeared to be at least as important as temperature and effective residence time in determining the predominant chemical pathways. Recent CO_2 -laser pyrolyses of pure AP, KMnO_4 -doped AP, and AP/metal oxide mixtures at heating rates between 40 and 220 $\text{cal/cm}^2\text{sec}$ fully support this conclusion. Previously published results, derived from application of different analytical techniques to similar systems, are referenced to provide supplementary confirmation.

The roles that various chlorine oxides play in the decomposition and combustion of AP are pivotal to our understanding. Unfortunately these compounds are difficult to observe by less direct sampling means because of their high reactivity. Reference is made to proposed mechanisms, based on the probable chlorine oxides, that have been formulated to explain the role of HClO_4 vapor in ignitions of uncatalyzed and catalyzed solid propellant fuels, and, more generally, the fate of HClO_4 and NH_3 during AP decomposition and combustion under a variety of experimental and practical conditions.