SYNOPTIC: Thermal Decomposition of Ammonium Perchlorate + Magnesium Perchlorate Mixtures, R. J. Acheson and P. W. M. Jacobs, Department of Chemistry, The University of Western Ontario, London, Ontario; *AIAA Journal,* Vol. 8, No. 8, pp. 1483–1487.

Solid Propellants

Theme

Describes a continuation of previous kinetic work on the thermal decomposition of ammonium perchlorate (AP) mixed with barium and magnesium perchlorates, using the experimental technique of differential scanning calorimetry.

Content

The experimental technique employed was designed to minimize the complications due to 1) sublimation of AP and 2) dehydration of magnesium perchlorate (MP). D.s.c. curves for pure AP, pure MP, and various mixtures are presented. The results show clear evidence of a vigorous exothermic reaction in the mixtures; this is the thermal decomposition of AP catalyzed by MP. The d.s.c. curves for the mixtures show a weak endotherm superimposed on the leading edge of the main exotherm, and also a very sharp exotherm superimposed on the trailing edge of the main exotherm. The latter is extremely sharp with a half-width of <1°C. It is concluded that the main chemical reaction occurs in the melt and that the features just described are due to the melting of the reacting mixture and the freezing of the residue from which most of the AP has been lost.

A general mechanism for the catalytic action of the oxides of Mg, Zn, Cd, and Pb on the decomposition of AP is proposed. This comprises 1) reaction of the oxide with the AP to form a superficial layer of the metallic perchlorate; 2) formation of a molten layer at the interface between the oxide particles and the AP due to the lowering of the melting point of AP by the metallic perchlorate; 3) decomposition of perchlorate ions ClO_4^- in the molten layer to form oxide ions, $O^=$; and 4) proton transfer from ammonium ions, NH_4^+, in the melt to $O^=$ to yield NH_3 and H_2O.

A necessary feature of the mechanism is that the metallic perchlorate formed, e.g., $MgClO_4$, decompose to yield the oxide. Barium perchlorate (BP) decomposes to the chloride and so BP is not an effective catalyst for the decomposition of AP.

Thermal Decomposition of Ammonium Perchlorate + Magnesium Perchlorate Mixtures

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A study has been made of the thermal stability of mixtures of ammonium perchlorate (AP) with magnesium perchlorate (MP) using the technique of differential scanning calorimetry. Clear evidence of vigorous, exothermic decomposition of AP, catalyzed by MP, is presented. It is shown that while a catalyzed reaction can proceed without complete formation of a molten phase, over a wide concentration range of the constituents the decomposition proceeds in the melt. A mechanism is proposed which involves the decomposition of ClO_4^- ions to $0^=$ ions which then act as proton acceptors.

I. Introduction

THERE has been a tremendous interest in the thermal decomposition of ammonium perchlorate[1,2] because of its extensive use as the oxidizer in solid fuel rocket propellant compositions. Low-temperature thermal decomposition studies are useful because of the information they provide about the mechanism of the many chemical reactions that occur under combustion conditions. Recently, a detailed mechanism for the thermal decomposition of ammonium perchlorate (AP) has been formulated;[3] it was also shown that comparatively few modifications were necessary in applying this mechanism to the combustion of pure AP. The chemistry is basically the same; the reaction rates are, of course, much faster under combustion conditions.

Catalysts are extensively used in propellant compositions to promote various desirable characteristics, usually to extend the pressure limits, to increase the burning rate, or to modify the burning rate vs pressure characteristic. Whereas considerable progress has been made[3] towards understanding the mechanism of the decomposition and combustion of pure AP, the comparable situation with respect to catalysts is not so favorable. This paper deals with a certain class of catalysts that promote melting of the AP: this class includes the oxides of magnesium, zinc, cadmium, and lead.[2,4–6] Since it is known that AP can react with metal oxides of this type to form perchlorates[7,8] we chose magnesium perchlorate (MP) for detailed study. The kinetics of decomposition of

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