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 $O^=$ 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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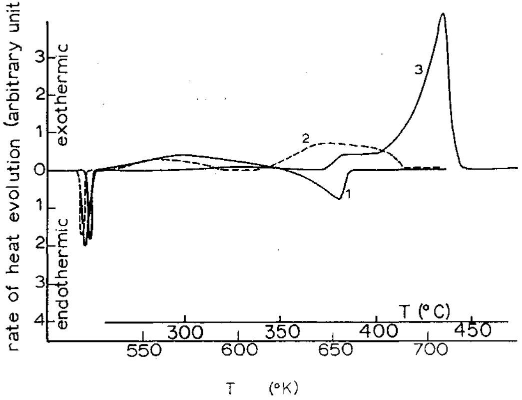

Fig. 1 Differential scanning calorimetry of pure AP. Curve 1, in vacuo; curve 2, 1 atm. nitrogen, conventional sample pan; curve 3, 1 atm. nitrogen, casserole pan with pierced lid.

MP and of mixtures of MP + AP, have been described in a separate paper.[9] Here we concentrate on information derived from differential scanning calorimetry (dsc).

II. Experimental Technique

All the results to be described were obtained using a Perkin Elmer DSC-1B differential scanning calorimeter. The general procedure adopted was that recommended in the equipment manual provided by the makers. More specifically, the technique adopted follows closely that of Wenograd and Waesche.[10] The effects of ambient gas pressure, heating rate and type of sample pan were examined. The type of pan used had a considerable influence on the dsc curves. The normal type of pan in which the lid is tightly crimped down on the pan proved to be unsuitable as sample tended to ooze out during the rapid stage of the decomposition so that the results were irreproducible. The best type of pan proved to be one in the shape of casserole dish with a small pin hole pierced in the center of the lid. This design of pan is designated "casserole pan, pierced" in the description of the results and was in fact used in all the experiments quoted except when specifically stated otherwise. The "normal" pan was used only for comparative purposes (e.g., the data in Figs. 1 and 2 later).

The sample mixture was crushed in an agate mortar with a little acetone and enough of the slurry placed in a pan, previously weighed on a Cahn electrobalance, to give 3–5 mg of sample in the pan after the acetone had evaporated. It is believed that this procedure gave an even, thin layer of sample on the bottom of the pan with good heat transfer characteristics. After evaporation of the acetone the pan was reweighed and the lid crimped into place.

The purge gas was nitrogen and the apparatus was always flushed for 10 min prior to an experiment, including those in which the dsc curves were determined at reduced pressure. Runs designated "in vacuum" mean that the pressure registered was less than 1 torr. The actual pressure in the reaction vessel is not known precisely as it is evacuated through a small orifice and there may have been some leakage around the seals of the reaction vessel. The pressure in the reaction vessel would probably have been in the range 1–10 torr which is low enough to facilitate sublimation.

Mixtures of AP and MP (as the hexahydrate) were ground together, well-mixed and stored in a desiccator.

III. Results

Ammonium Perchlorate

The results of three dsc runs are shown in Fig. 1. The heating rate was 10 deg/min in each case and the differences are due to the ambient pressure and type of pan. Curve 1 shows the results of a run in vacuo (owing to the nature of the design of the dsc apparatus, this is perhaps better described as reduced pressure), curve 2 a run under 1 atm of N_2 with the conventional sealed pan, and curve 3 a run under the same pressure of N_2 with the sample in the pierced casserole pan. All three runs show the expected phase transition: under equilibrium conditions this should occur at 240°C or 513°K. The first exotherm is due to low temperature decomposition of AP; after this, curve 1 shows an endotherm, curve 2 an exotherm. This is clearly due to the pressure difference: in vacuo AP sublimes without decomposition but under nitrogen the diffusion of $HClO_4$ molecules is slowed down sufficiently for exothermic reactions to occur in the gas phase within the sample pan and the heat evolved to be registered by the thermocouple in contact with the bottom of the pan. In the normal pan the combined pressure of NH_3, $HClO_4$ and their reaction products cannot increase without limit and the gases will vent through the spaces that will naturally be present between the pan and the crimped lid. If no such spaces were present the contents of the pan could not be evacuated (cf. curve 1). If such spaces are too small to permit the gases to escape at a rate equal to their production, the gas pressure in the pan will rise until gas vents are forcibly formed or enlarged. The diffusion path length is shorter in the normal pan, where the lid is close to the sample, than in the casserole pan where the controlled exit of gases is provided at the top of the dome. Thus the exotherm is accentuated by the new type of pierced casserole

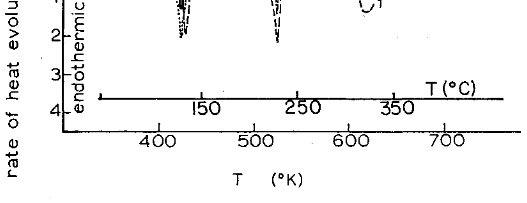

Fig. 2 Differential scanning calorimetry of pure MP. Curve 1, normal pan, 1 atm. nitrogen; curve 2, normal pan, in vacuo; curve 3, pierced casserole pan, in vacuo.

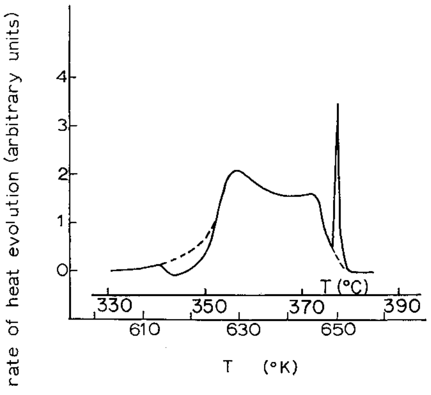

Fig. 3 DSC exotherm for AP containing 1.75 mole % MP. The dotted lines show the exothermic character of the reaction alone. The superimposed endotherm between 613 and 625°K is ascribed to melting and the sharp exotherm at 650°K to solidification.

pan which permits only slow effusion of products from the pan.

Magnesium Perchlorate

The dsc results for pure MP hexahydrate are shown in Fig. 2. The heating rate is again 10°/min. The series of endotherms represent successive stages of dehydration. Curve 1 shows that dehydration is not completed until 367°C if the normal pan is used and the nitrogen pressure is 1 atm. Curve 2 shows dehydration completed by about 285°C if the salt is heated in vacuo in the conventional pan. Curve 3 shows that dehydration is completed by 227°C if the pan has the pierced lid. The exothermic decomposition of anhydrous MP occurs above 370°C.

Mixtures of Ammonium Perchlorate and Magnesium Perchlorate

To avoid complications due to sublimation of AP and/or incomplete dehydration of MP interfering with the exothermic reactions we wished to study, the following technique was adopted. The samples were heated in vacuo at rates of 20–40°/min up to a temperature of 210–220°C. Nitrogen was then admitted until the pressure became 1 atm and the run continued at a heating rate of usually 10°/min. Sometimes rates of 5°/min were used for comparison.

The exotherm obtained for a mixture containing 1.75 mole % MP hexahydrate is shown in Fig. 3. Reaction commences about 332°C; between 340° and 352°C there is an endothermic process superimposed on the exothermic reaction. This we associate with melting. The exotherm has two peaks at 354° and 372°C; a third very sharp peak occurs at 377°C just before the end of the reaction. This sharp peak we associate with solidification. The dotted lines in Fig. 3 show the general form of the exotherm with the perturbations due to melting and solidification removed.

The extent of the catalysis of the AP decomposition by MP is shown by the exotherms in Fig. 4 which includes data for pure AP, and mixtures containing 0.09, 1.75, and 6.31 mole % of the hydrated MP. The effects of melting and solidification have been suppressed, as indicated by the dotted lines, for clarity. Clear evidence of melting was lacking for the lowest concentration studied (0.09 mole %). The shift of the exotherm to lower temperatures with increasing concentration of MP is clearly apparent.

The question naturally arises as to whether this really is the catalyzed decomposition of AP that is being observed. Accordingly we have calculated the heat evolved per g of AP in the mixture and this is plotted against % composition in Fig. 5. Although the results are probably not very accurate they do indicate a linear decrease in the heat evolved with increasing molar concentration of MP, as would be expected if this figure referred to the decomposition of AP.

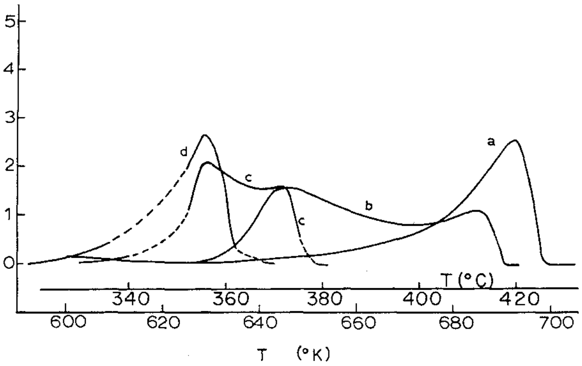

Fig. 4 The effect of catalyst concentration on the reaction temperature as revealed by DSC. The dotted lines emphasize that the effects of melting and solidification have been removed for clarity. a) pure AP; b) AP + 0.09 mole % MP; c) AP + 1.75 mole % MP; d) AP + 6.31 mole % MP.

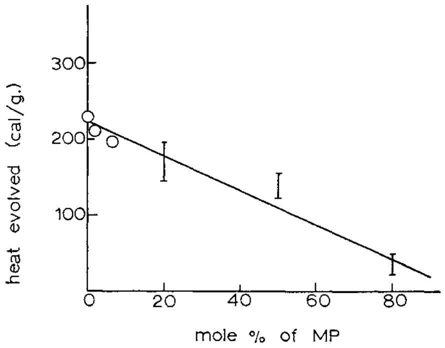

Fig. 5 The dependence of the heat of reaction on catalyst concentration. (The heat produced in the low-temperature decomposition of AP is not included.[3]

IV. Discussion

Ammonium Perchlorate

Although this was not an immediate objective of the work the availability of numerous dsc curves for pure AP made possible a redetermination of ΔH for the orthorhombic to cubic phase transition in AP. The result of 2.46 ± 0.10 kcal/mole (95% confidence limits) is in good agreement with the value of 2.3 ± 0.2 kcal/mole obtained by Stone[11] from differential thermal analysis. Reasons have been advanced previously[2] as to why Stone's figure was to be preferred to other values in the literature. At heating rates of 5–20°/min the phase transition was succeeded by a reaction of small exothermicity. The wide temperature range over which it occurs under these conditions (257–317°C at 5°/min, 287–337°C at 10°/min, and 302–352°C at 20°/min), concurrent sublimation, and the fact that this reaction occurs partly in the gas phase, make the determination of ΔH from dsc rather difficult. This "low-temperature" reaction is succeeded by a reaction of well-marked exothermicity (when the pierced casserole pan is used). The heat of reaction was found to be 238 cal/g. which corresponds to $\Delta H = -28$ kcal/mole. Now the fraction of AP which decomposes in the low temperature reaction is close to 30%, so that if we assume that the high temperature reaction refers to 70% of the available AP, a total heat of reaction of 340 cal/g. (equivalent to $\Delta H = -40$ kcal/mole) is calculated. Such a figure for the heat release must be regarded as approximate, but it is nevertheless in rather good agreement with the result of 348 ± 11 cal/g. obtained by Manelis and Rubtsov[12] by a direct calorimetric procedure.

Magnesium Perchlorate

Dsc of MP hexahydrate shows a small endotherm at ~40°C which is attributed to the removal of surface moisture. Dehydration is a multistage process extending from 50–227°C when the pierced casserole pan is used. The sharp peak at 154°C may indicate a phase transition in the partially hydrated MP, or it may indicate removal of part of the water (~1 mole) under conditions approaching equilibrium. The former conclusion is more probable. The kinetics of the decomposition of MP have been measured in separate (isothermal) experiments and are described elsewhere.[9]

Mixtures of AP with MP

Samples containing 1.64, 1.75, 6.3, 6.6, 18.8, and 56 mole % MP all exhibited an endotherm, which is believed to indicate melting, and at a higher temperature an exotherm which can then be associated with solidification. The general exothermic

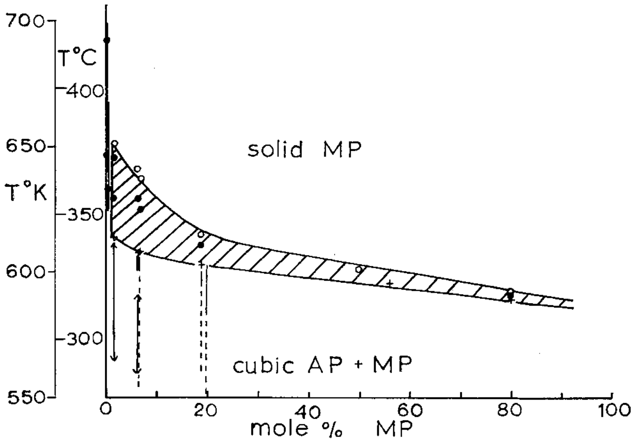

Fig. 6 'Phase diagram' for mixtures of AP + MP. The shaded area shows the temperature-concentration region in which the mixtures are molten. Vertical lines show the temperature range in which a solid state thermal decomposition was observed. Where these are dotted, the reaction is believed to be the low temperature decomposition of AP. +, melting point of the mixtures; O, freezing point of the mixtures (ignoring concentration changes due to loss of AP which cannot be estimated); ●, temperature at which the maximum decomposition rate was observed. Arrows indicate the temperature range of isothermal kinetic studies.

character of the reaction, but not the clear indication of melting and solidification was also observed by differential thermal analysis. A rapid loss in weight of the sample accompanies the exotherm, as shown by thermogravimetric analysis.[9] Just prior to melting an exothermic reaction occurs and during and following the melting process, the reaction occurs at an increasing rate. At the lower concentrations, when reaction was approaching completion it suddenly accelerated again (Figs. 3 and 4) and was then completed within 30 sec. In one case, 18.8 mole % MP, reaction continued briefly after solidification. Some mixtures did not follow this course. Mixtures containing 18.8 and 19.85 mole % MP showed a long period 287–323°C when reaction was slow. This may be due to catalysis of the low temperature reaction without melting. In the 19.85% mixture the reaction was complete before the freezing point of the 18.8% mixture was reached, indicating excessive consumption of material in the catalyzed low temperature reaction. The mixtures containing 50% and 80% MP showed only a very fast reaction associated with the melt.

All this information is summarized in the form of a "phase diagram" in Fig. 6. The temperature-concentration range in which AP + MP is molten is shown as a shaded area. The continuous vertical lines show the range in which a solid-state thermal decomposition was observed. The dotted vertical lines indicate the range of thermal decomposition which is believed to refer to the low temperature reaction (of AP, but probably catalyzed). Plus signs indicate the observed melting point and open circles the observed freezing point. Filled circles indicate the temperature of maximum decomposition rate. The arrows indicate the temperature range in which isothermal kinetic studies were made.[9] The "phase diagram" shows that in these experiments the whole reactant was not molten. However, it is probable that local partial melting occurs at the interface between the two reactants at temperatures below those at which the whole sample is molten. It is important to appreciate that this is not a true (equilibrium) phase diagram since the composition of the mixtures is changing all the time as the temperature increases, due to decomposition. Rather Fig. 6 is to be viewed as plot of the temperature range in which certain phenomena (melting, decomposition, etc.) occur vs the initial composition of the mixture. Specifically, the concentration of MP at the temperature at which freezing occurs will be much greater than that shown on the abscissa. It is significant that the temperature range in which the catalyzed reaction could be studied isothermally lay well below the melting point indicated by dsc (Fig. 6).

Mechanism of the Catalyzed Reaction

It is known from previous work that has been recently reviewed[1,2] that MgO is a catalyst for the AP decomposition and that ZnO, CdO, and PbO, which behave similarly, promote melting[5,6] and form perchlorates[8] during the catalyzed reaction. Furthermore it is known[9] that MgO is a product of the thermal decomposition of MP. The initial step in the uncatalyzed decomposition of AP is proton transfer from NH_4^+ ions to ClO_4^- ions forming NH_3 and $HClO_4$.[13] The latter decomposes to form radicals (including ClO) which oxidize the ammonia.[3] This information strongly suggests that the mechanism of decomposition of AP catalyzed by MgO (and also ZnO, CdO and PbO) involves reaction of the oxide with $HClO_4$ to form MP, the formation of a molten layer between the MgO particles and the AP, and the occurrence within that molten layer of the following reactions:

$$ClO_4^- \rightarrow ClO_3^- + O \qquad (1)$$

$$ClO_3^- \rightarrow ClO_2^- + O \qquad (2)$$

$$ClO_2^- \rightarrow ClO^- + O \qquad (3)$$

$$O + O \rightarrow O_2 \qquad (4)$$

$$2ClO^- \rightarrow O^= + Cl_2 + O \qquad (5)$$

These equations represent the decomposition of perchlorate anions to oxide ions, chlorine, and oxygen; this is essentially the mechanism proposed[9] for the solid phase decomposition of MP. Oxide ions will act as proton acceptors,

$$O^= + NH_4^+ \rightarrow OH^- + NH_3 \qquad (6)$$

$$OH^- + NH_4^+ \rightarrow H_2O + NH_3 \qquad (7)$$

These reactions result in the liberation of water and ammonia. Thus the net process Eqs. (1–7) is the decomposition of two moles of AP into chlorine, oxygen, water, and ammonia. The oxygen being liberated first as atoms, oxidation of ammonia will proceed via O atoms rather than by ClO radicals, as in the uncatalyzed reaction. The function of the MP is thus to promote the formation of a molten phase in which these reactions proceed more readily than they can do in the crystal lattice. It should be noted that it is an essential fea-

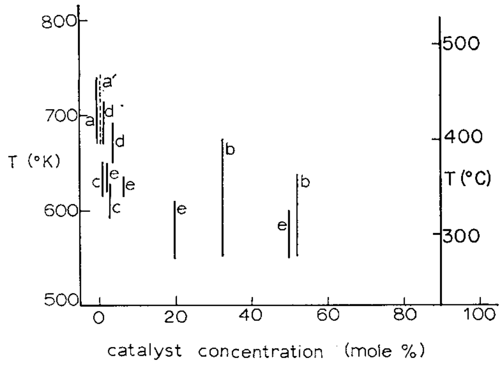

Fig. 7 Temperature range of thermal decomposition of AP in the presence of various additives. a denotes pure AP (Fisher), a′ denotes purified AP (from American Potash and Chemical Corp.), b denotes carbon black, c denotes copper chromite, d denotes iron oxide (Fe_2O_3) and e denotes MP. All results except a and e are from Wenograd and Waesche, Ref. 10.

ture of this mechanism that the perchlorate decompose to oxide ions. If reaction (5) is replaced by

$$2ClO^- \rightarrow 2Cl^- + O_2 \qquad (8)$$

then no proton acceptor results and there will be no catalysis. Melting is not of itself a sufficient criterion. Barium perchlorate (BP)[14] behaves rather similarly to MP on thermal decomposition except in one vital respect; it forms the chloride instead of the oxide. Thus catalysis of the AP decomposition by BP does not occur,[14] since no oxide ions are produced to act as proton acceptors.

Comparison of Catalytic Efficiencies

The temperature range over which thermal decomposition of AP occurs in the presence of various additives, when heated at a constant rate of 10 deg/min, is shown in Fig. 7. This diagram provides a qualitative picture of the efficacy of various catalysts and shows that MP is about as effective a catalyst as copper chromite and more effective than iron oxide or carbon black.[10] It is, of course, not implied that the mechanism presented in the previous subsection is the only route by which the AP decomposition is catalyzed. It can apply only under the special circumstances indicated. Jacobs and Russell-Jones have explained[15] the catalytic action of copper chromite as being due to its promoting the heterogeneous decomposition of $HClO_4$. That copper chromite and other transition metal oxides can act in this way has recently been confirmed.[16, 7]

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