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NOTE

Effect of Electric Field on Ammonium Perchlorate Decomposition

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A novel method of detecting the charge-carrying species in inorganic decomposable salts is described. In ammonium perchlorate it is observed that the charge-carrying species at temperatures 150 and 230°C are oppositely charged; i.e., they are negatively charged (ClO_4^- ions) at 230°C and positively charged (H^+ or NH_4^+) at 150°C.

Introduction

Studies on electrical conductivity of ammonium perchlorate (AP) have been carried out by several investigators (*1–13*) with a view to shedding light on the charge transport processes, which in turn may play a role in the thermal decomposition of AP.

Zirkind and Freeman (*1*), Wise (*2*), Boldyrev (*3*), and Jacobs and Ng (*4*, *5*) all seem to agree on a proton transfer mechanism. Maycock *et al.* (*6*, *7*), Owen *et al.* (*8–10*) favor ionic conduction with NH_4^+ interstitials as the charge-carrying species. Keenan and Ohanian (*11*, *12*) argue in favor of proton transfer at low temperatures. Doping experiments have revealed that SO_4^{2-} dopants enhance the conductivity (*10*). Keenan's experiments on Sr^{2+} doping at low temperatures point to an increase in conductivity. Owen *et al.* (*8–10*) state that Ba^{2+} doping does not affect the conduction in AP. An analysis of the results, however (lowering of the knee temperature on doping with Ba^{2+}), indicates that the conductivity must have been lowered. This complexity might arise (i) because conduction in AP is complex or (ii) because the material decomposes during conduction measurements. Recently Pai Verneker *et al.* (*13*) have shown that preferential decomposition at a selective electrode can be used as a technique for identifying the charge-carrying species. Thus, when NaN_3 is decomposed in an electric field, the decomposition takes place at the negative electrode, whereas $PbNO_3$ under identical conditions decomposes at the positive end. The decomposed portion of the crystal becomes opaque or colored depending upon the material under investigation. The undecomposed end of the crystal remains transparent. The inference is that in NaN_3, Na^+ is the charge-carrying species whereas in $PbNO_3$, NO_3^- is the charge-carrying species. Using this approach Pai Verneker *et al.* (*13*) have argued that a preferential decomposition of AP at the positive electrode at 230°C indicates that ClO_4^- is the charge-carrying species at that temperature. Zakharov and Scheckov (*14*) have also stated that negative charge carriers are predominant in AP. The approach of Pai Verneker *et al.*(*13*) for identifying the charge-

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carrying species is only visual in nature. One of the objectives of the present investigation is to see whether one can experimentally determine the difference between the two ends of a crystal (one at the positive electrode and the other at the negative electrode).

The second, and more important, objective is based on the assumption that the mechanism of conduction, and therefore of decomposition, may be different in different temperature ranges; i.e., at a low temperature (150°C) proton transfer may occur (substantiated by Boldyrev's experiment (*3*, *15*) on gas evolution at the electrode), whereas at a high temperature (230°C), ClO_4^- may be the charge-carrying species. If this assumption is correct then the objective is to see whether, contrary to what happens at 230°C, there occurs preferential decomposition at the negative electrode at low temperatures.

Experimental

AP was pelletized using a pressure of 1500 kg/cm^2. The resultant pellet had a density of 1.81 g/cm^3. Before experiments were carried out on pellets, single crystals of AP were investigated (density, 1.98 g/cm^3). The AP crystal or pellet was held in position by the usual spring-based conductivity cell. Platinum electrodes were used, and an electric field of 100 V/cm was applied across the crystal. The entire cell was placed in a thermostatically controlled furnace (±1°C) at the desired temperature for a desired length of time. At the end of the experiment, the crystal or pellet was removed and the change in appearance was noted. The two ends of the crystal were scraped with a clean blade, and the resultant powders were collected and sieved to obtain particles in the range 45 to 104 m*M*; isothermal thermogravimetric (TG) runs at 285 and 230°C were carried out using 20 mg of these samples. To observe a significant change at one of the ends it was necessary to heat the crystal for 1 hr at 230°C using an electric field of 100 V/cm. With the same electric field, it took about 140 hr. at 150°C. Similar results could be obtained at 50 V/cm, but it was necessary to heat the crystal for a much longer time. No measurable weight loss could be observed after the crystal was removed from the electric field.

Results and Discussion

Earlier work (*13*, *16*) has shown that Na^+ ions are the charge-carrying species in NaN_3. Isothermal TG measurements at 375°C of NaN_3 scraped from either side of the pretreated crystal (100 V/cm at 300°C for 2 hr) show that the material scraped from the surface near the negative electrode decomposes much faster than a similar material scraped from the surface near the positive electrode (Fig. 1). This technique, isothermal TG measurements of pretreated crystals, gives us a means of establishing the charge-carrying species in the decomposing crystal.

It was observed that the portion of the crystal at the positive electrode became opaque, whereas the portion near the negative electrode as well as the rest of the crystal remained perfectly transparent when a single crystal of AP was kept at 230°C under an electric field of 100 V/cm for 1 hr. This is just a repetition of earlier work (*6*). Figure 1 shows a plot of percentage weight loss versus time of heating at 230°C using 20 mg of AP scraped separately from either end of the AP pellet, which was previously heated under an electric field of 100 V/cm for 1 hr at 230°C. The AP sample taken from the positive electrode is seen to decompose faster than the AP sample from the pellet at the negative end. When AP is doped with 10^{-4} mole% $(NH_4)_2SO_4$, the decomposition at the positive electrode is sensitized, whereas when the dopant is 10^{-4} mole% $Ba(ClO_4)_2$ a drastic desensitization at the positive electrode takes place. The dopant concentration refers to the concentration of the dopant in the solution in which AP is recrystallized. Measurement of the decomposition rates at 230°C of scraped samples at the

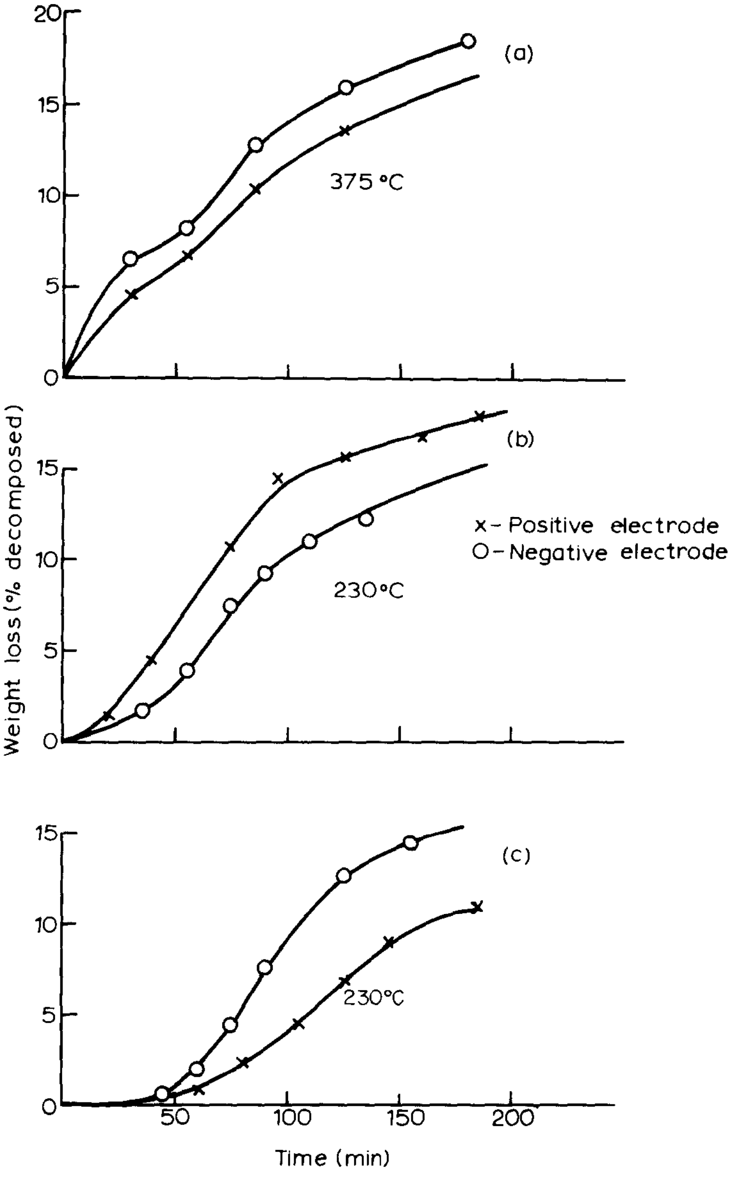

FIG. 1. Plot of weight loss versus time for the samples, scraped from positive and negative sides, subjected to an electric field of 100 V/cm. (a) NaN_3: Electric field at 300°C for 2 hr (TG at 375°C); (b) NH_4ClO_4: electric field at 230°C for 1 hr (TG at 230°C); (c) Nh_4ClO_4: electric field at 150°C for 140 hr (TG at 230°C).

two ends of an AP pellet subjected previously to an electric field thus provides us with a method of measuring the differences in the reactivities of the two ends of the crystals or pellets.

When an AP crystal is heated under an electric field for 140 hr at 150°C, the end of the crystal near the negative electrode turns opaque, whereas the rest of the crystal including the end near the positive electrode remains transparent. Figure 1, thus, gives the quantitative measurements of the AP pellet subjected to the electric field as above. Twenty milligrams of AP was scraped from either end of the pellet and subjected to isothermal decomposition at 230°C. The sample from the end near the negative electrode can be seen to be more reactive than the sample taken from the end near the positive electrode.

The inference of the electric field experiment carried out at 150°C versus that carried out at 230°C is that the charge-carrying species at the two temperatures are oppositely charged; i.e., while the charge-carrying species at 230°C is negative and is therefore likely to be ClO_4^- (also supported by the fact that Ba^{2+} desensitizes and SO_4^{2-} sensitizes (*7*)), the species at 150°C is positively charged and can be either a proton or NH_4^+ ions.

It should be borne in mind that the method of identifying the charge carrier is rather empirical in nature. More stringent and elaborate experiments will have to be carried out for quantifying the data and for establishing the precise identity of the conducting species.

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