

THERMAL DECOMPOSITION OF $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ **P.K. GALLAGHER***Bell Laboratories, Murray Hill, NJ 07974 (U.S.A.)*

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ABSTRACT

Thermogravimetry (TG), differential thermal analysis (DTA), and mass spectrographic evolved gas analysis (EGA) were used to study the thermal decomposition of $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$. Single crystals were found to contain considerable amounts of free water. The dehydration occurs in two steps and there are several phase transitions below the melting point of the anhydrous material $\sim 250^\circ\text{C}$. Decomposition of the anhydrous nitrite occurs primarily in two stages over the temperature range $500\text{--}750^\circ\text{C}$. The volatile products are $\text{NO} > \text{NO}_2 \approx \text{N}_2 > \text{O}_2$.

INTRODUCTION

The thermal stability of $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ is of interest because of its piezoelectric and pyroelectric properties [1]. Differential thermal analysis (DTA), thermogravimetry (TG), and mass spectrographic evolved gas analysis (EGA) are used to investigate the thermal decomposition in both single crystals and powder. Earlier work describes dehydration [2] and phase transitions [2,3] up to the melting point of the anhydrous compound.

EXPERIMENTAL PROCEDURES AND RESULTS

Crystals of $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ were grown by slow evaporation from aqueous solution at room temperature. Actual samples were chips from larger crystals, powder shaved from crystals, fine powder prepared by crushing and lightly grinding the crystal in an agate mortar, and finer powders made by more prolonged grinding.

A Perkin-Elmer (Model TGS-1) thermobalance modified for digital data acquisition and processing [4] was used to obtain the TG data. Temperatures are based upon magnetic calibration [5]. The heating rate was $10^\circ\text{C min}^{-1}$ in a flow of N_2 at $40 \text{ cm}^3 \text{ min}^{-1}$. Figure 1 presents the TG curves for these samples.

Platinel ring thermocouples were used with the Columbia Scientific Ind. (Model 202) DTA. Alumina served as the reference material and Pt sample pans were used. The heating rate was $10^\circ\text{C min}^{-1}$ in a flow of N_2 at $100 \text{ cm}^3 \text{ min}^{-1}$. Figure 2 presents the results.

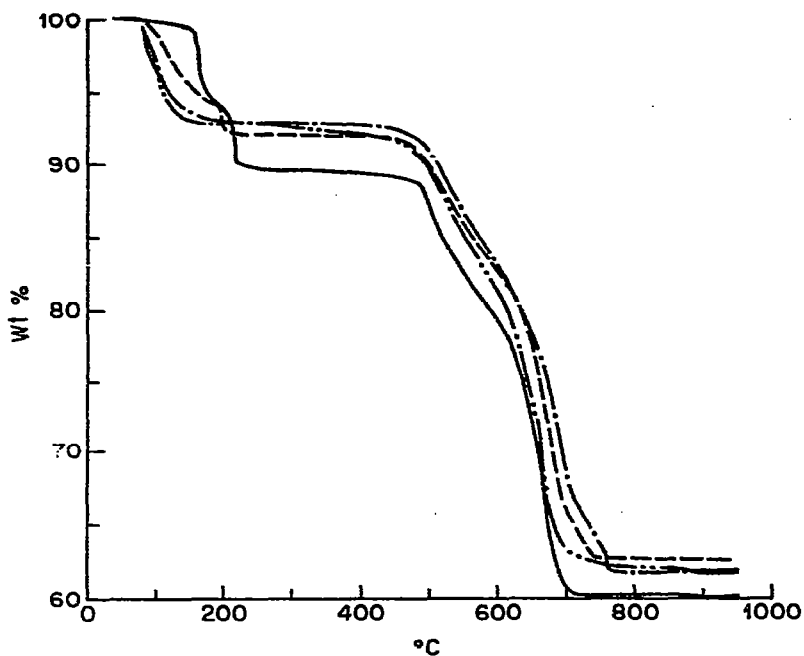


Fig. 1. Thermogravimetric curves for $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ of varying particle sizes ($10^\circ\text{C min}^{-1}$ in N_2). —, Single crystal fragment, 5.685 mg; ---, coarse powder, 5.822 mg; - · -, lightly ground powder, 5.322 mg; · · ·, more heavily ground powder, 3.171 mg.

The basic EGA apparatus has been described elsewhere [6] except for the following modifications. The temperature controller was changed to a more compact Netzch (Model 411). A Fluke (Model 2190A) digital thermometer with analog output coupled with a Spectrum (Model 1021) filter/amplifier ($10\times$) was used for temperature recording. Finally, a UTI (Model 2054) programmable peak selector was used to control the mass spectrometer scan and provide data acquisition. The heating rate was $10^\circ\text{C min}^{-1}$ and the vacuum ranged from about 1×10^{-7} to 5×10^{-6} torr depending upon the extent of the decomposition. The EGA results are summarized for selected atomic mass numbers in Figs. 3 and 4.

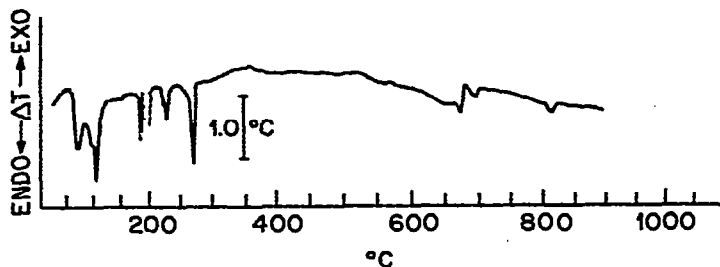


Fig. 2. Differential thermal analysis of ground $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$, 6.068 mg at $10^\circ\text{C min}^{-1}$ in N_2 .

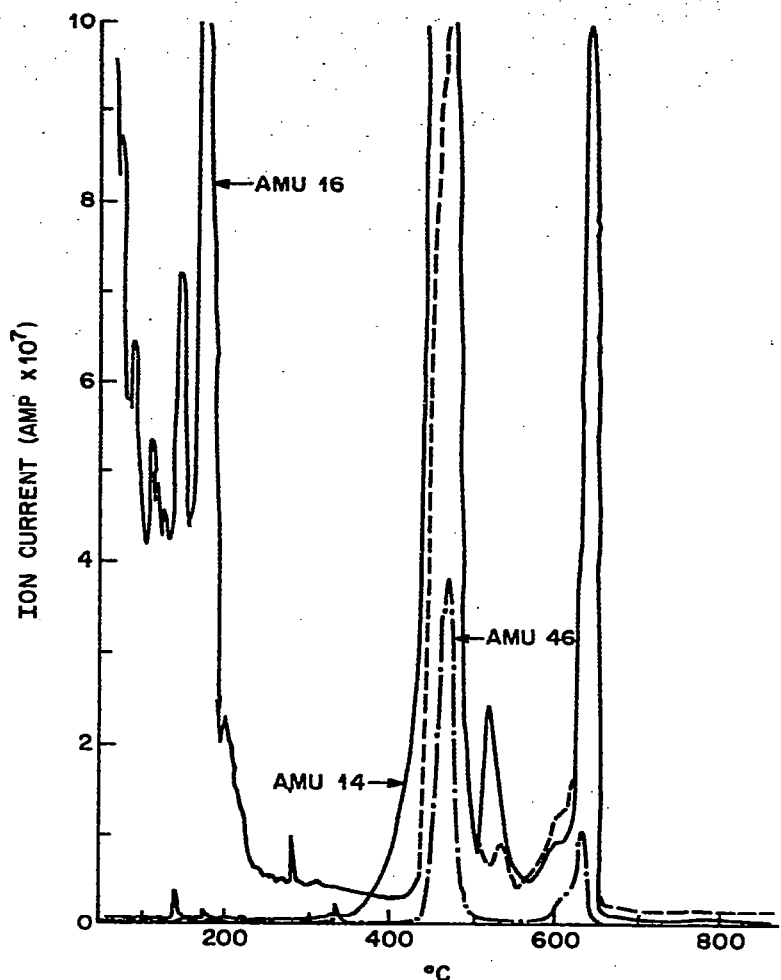


Fig. 3. Mass spectrographic evolved gas analysis of crystalline fragments of $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$, 3.856 mg heated at $10^\circ\text{C min}^{-1}$ in vacuum.

DISCUSSION

It is clear from the TG curve for the large fragments in Fig. 1 that there was weight loss in excess of the theoretical amount calculated from the formula, $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$. If one accepts the weight at temperatures greater than 800°C as BaO , then the plateaus in the temperature range from 200 to 400°C correspond well for all the samples with the weight calculated for anhydrous $\text{Ba}(\text{NO}_2)_2$. The weight loss below 200°C agrees with the loss of a single H_2O (-7.3 wt. %) for the powders. The crystal fragment, however, shows a weight loss closer to $1.5 \text{ H}_2\text{O}$. Earlier detailed X-ray studies [1] indicate that this must be free non-crystalline water which is readily lost at room temperature from the ground powders. Detailed discussions of the dehydration and phase transition in the hydrate were described earlier [2]. Similarly, transitions of the anhydrous material below 300°C are described

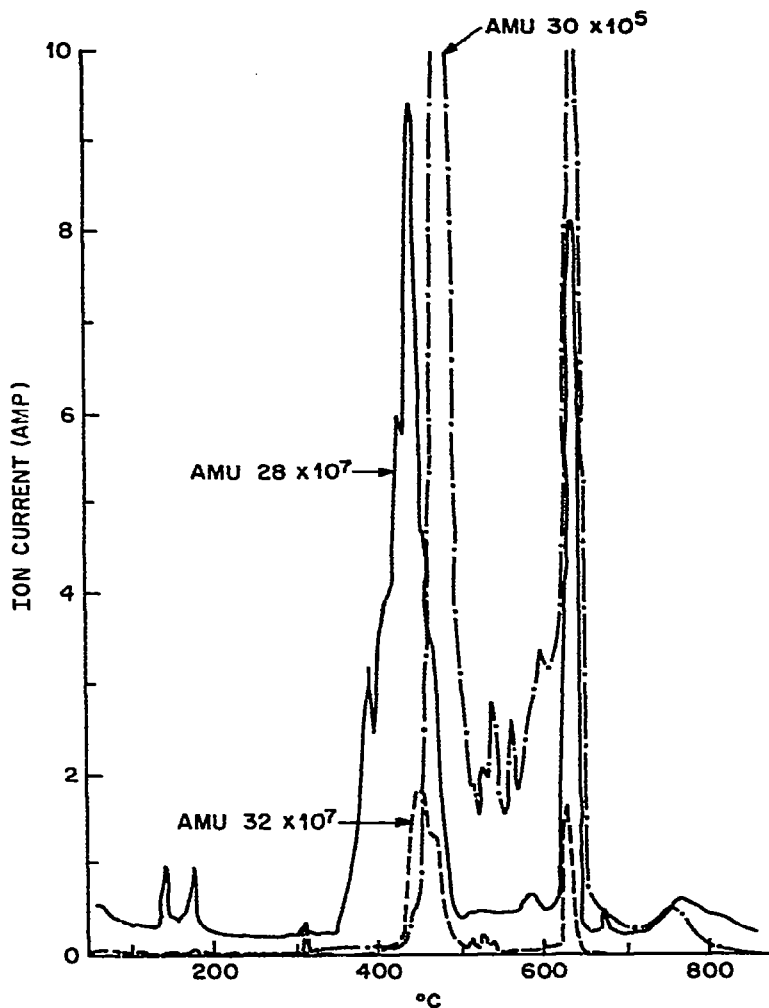


Fig. 4. Mass spectrographic evolved gas analysis of crystalline fragments of $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$, 3.856 mg heated at $10^\circ\text{C min}^{-1}$ in vacuum.

elsewhere [3]. Inspection of the DTA curve, Fig. 2, reveals considerable complexity below 250°C .

The decomposition of the anhydrous compound is complex. Prior melting will have removed any effects of the original particle size or morphology. Both the TG data in Fig. 1 and the DTA data in Fig. 2 indicate that it is a multistage process. It is particularly obvious from the EGA results in Figs. 3 and 4. In comparing the EGA results with the TG and DTA data, it must be remembered that the EGA takes place in vacuum which enhances the loss of volatiles and generally displaces the decompositions to lower temperatures. A separation of about 150°C between the two major steps of the decomposition is evident in both the TG and EGA results.

Species associated with N_2 , O_2 , NO and NO_2 are present. The N_2 and O_2 peaks around 400°C slightly precede the NO and NO_2 indicating that they do not arise solely from cracking patterns of the latter. The 14 and 16 peaks,

however, do seem to correspond in temperature with those of the NO and NO₂. The cracking pattern of NO₂ has mass 30 as the predominant peak, however, there is a far greater amount of 30 than can be accounted for on that basis. The products are NO ≫ NO₂ ≈ N₂ > O₂. This order is in accord with the chemical analysis of Oza and Jha [7]. Although there appears to be some brief transient intermediate around 600°C, it is not evident from the thermal analysis what that might be.

The appearance of the N₂ and O₂ prior to that of NO and NO₂ implies that either an evolution of trapped or occluded air took place at that point or some reduction mechanism occurred. The prior melting of the sample makes the evolution of air highly unlikely. It is suggested that perhaps some disproportionation of Ba(NO₂)₂ occurs [see eqn. (1)] prior to the major decomposition.



The oxygen would then come from the equilibration of barium peroxide



Obviously, these reactions need to proceed to only a slight extent to explain the small amounts of nitrogen and oxygen in Fig. 4.

CONCLUSIONS

Single crystals of Ba(NO₂)₂ · H₂O may contain considerable excess free water which is easily removed by grinding and exposure at room temperature.

The decomposition of Ba(NO₂)₂ is complex, occurring primarily in two stages over the temperature range 500–750°C. The products are NO ≫ NO₂ ≈ N₂ > O₂. The early appearance of N₂ and O₂ suggests that some disproportionation may precede the major decomposition.

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