REACTIONS OF BARIUM CHLORIDE DIHYDRATE IN POTASSIUM HALIDE MATRICES: A DIFFERENTIAL SCANNING CALORIMETRY STUDY

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ABSTRACT

The deaquation of $BaCl_2 \cdot 2H_2O$ in pressed KCl, KBr, and KI disks was followed by TG and DSC at pressures ranging from one to 34 atmospheres. Resolution of the DSC peaks of the first deaquation reaction and subsequent water vaporation was not improved by use of the matrix; for the second deaquation reaction, resolution was greater in the matrix. Evidence of a ternary eutectic involving $BaCl_2$, KI, and H_2O, which melted at 219 °C, was obtained.

INTRODUCTION

The use of a potassium halide matrix in pressed disk or pellet form to study the thermal dissociation reactions of various inorganic compounds has been extensively investigated by Hisatsune and coworkers[1-5]. They found that many reactions were initiated by heating the disks to elevated temperatures (up to 600 °C) and that the kinetics of these reactions could be followed conveniently by infrared spectroscopy. The thermal decomposition kinetics of Ag_2CO_3 in thallium bromide disks was studied by Wydeven and Leban[6]. Continuous, in situ determination of the infrared active reactants and products was possible by the use of a heated cell. More recently[7-9], pressed KCl, KBr, KI, and RbI disks have been used to study the reactions of $KMnO_4$ and KIO_3 with the matrix material up to 100–110 °C and the behavior of $KMnO_4$ in MX disks (M = Na, K, Cs; X = Cl, Br, I) has been reported[10]. As in the other investigations, infrared spectroscopy was used to follow the reactions and to evaluate the kinetics.

One of the first studies to use the technique of differential scanning calorimetry (DSC) to monitor decomposition reactions taking place in a potassium halide disk was that by Collins and Wendlandt[11]. They found that dispersing certain pharmaceutical compounds in a matrix in the form of a thin disk improved the thermal contact between the sample and the sample holder thus yielding more definitive DSC

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curves. In a continuation of the use of KCl, KBr and KI matrices to study decomposition reactions, the deaquation and matrix reaction of $BaCl_2 \cdot 2H_2O$ are presented here.

EXPERIMENTAL PART

Powdered or finely ground materials of reagent grade quality were used in this investigation. The instruments employed for the DSC study were the DuPont Models 900 and 990 thermal analysis systems. The high pressure DSC curves were obtained using the DuPont high pressure cell with the Model 900 console. The TG curves were obtained using a Cahn Model RG electrobalance converted to a thermobalance. All samples were heated at $10°C$ min^{-1}. Unless noted otherwise, a dynamic nitrogen atmosphere was used.

Sample preparation

Samples of $BaCl_2 \cdot 2H_2O$ or anhydrous $BaCl_2$ weighing 8–10 mg were studied in the pure state and in pressed disks containing 45–65 mg of matrix material. After intimate mixing, the latter were pressed in a home-built die at 4×10^4 psi to form disks 6.25 mm in diameter by approximately 1.5 mm thick. Both the disks and pure materials were placed in DuPont aluminum sample pans during the heating cycle.
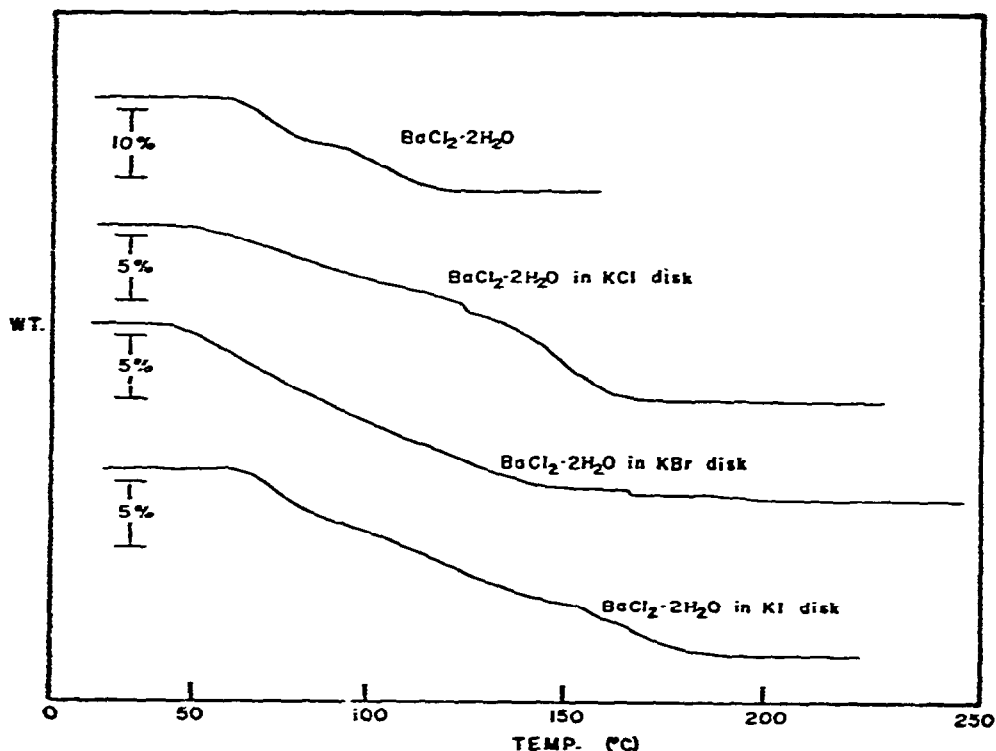

Fig. 1. TG curves of $BaCl_2 \cdot 2H_2O$ in KX matrices.

RESULTS AND DISCUSSION

The TG and DSC curves of the deaquation reactions of $BaCl_2 \cdot 2H_2O$ are shown in Figs. 1–4. Among other things, they indicate that the deaquation process in the disk is significantly affected by the decreased diffusability of the evolved water vapor. The mass-loss (Fig. 1), entirely attributable to the evolution of water, occurred over a much greater temperature range in the disk than in the pure sample. The DSC peaks are much less sharp and repeatable than those which would be expected for
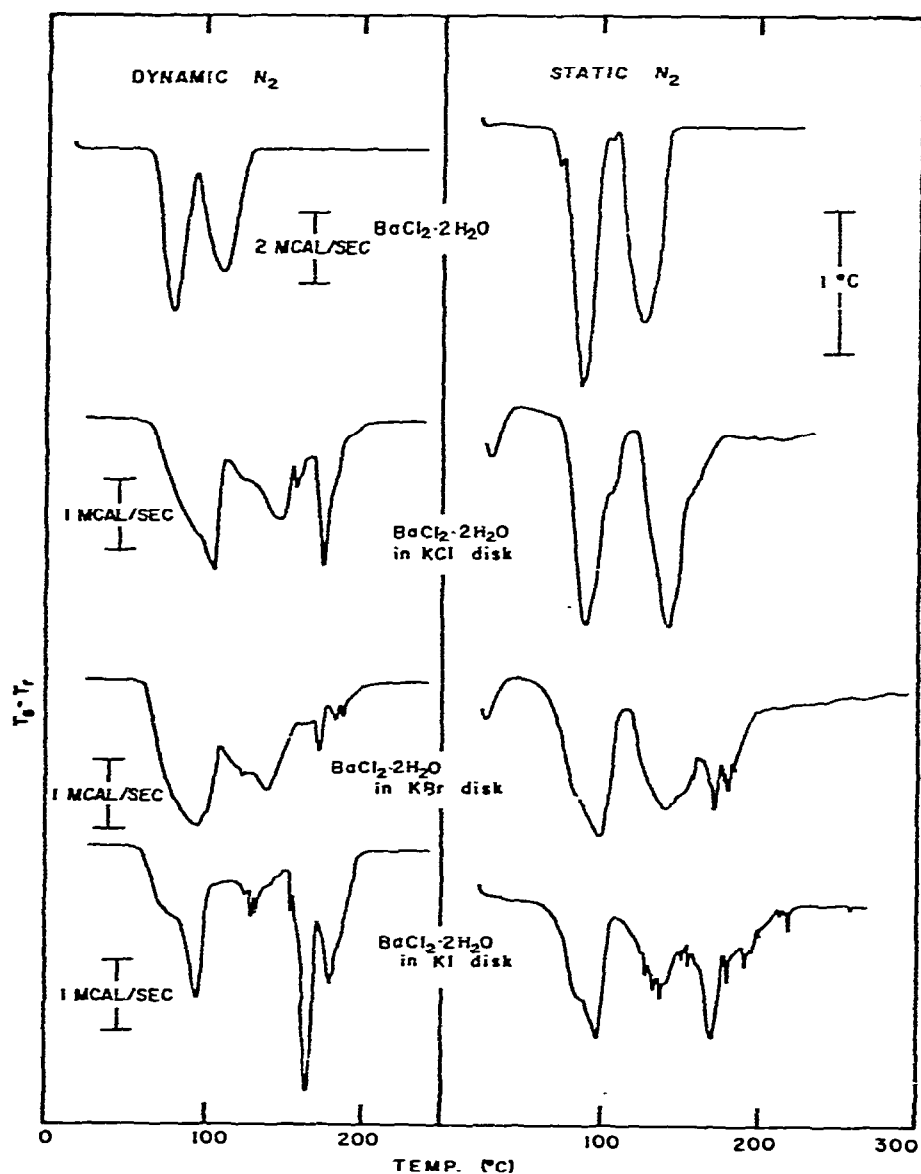
Fig. 2. DSC curves of $BaCl_2 \cdot 2H_2O$ in KX matrices.

transitions which do not involve gaseous reactants or products. The diffusability of water, in turn, depends on the nature of disk material and the nature of the disk pressing. Unfortunately, the latter is difficult to standardize precisely and this complicates the study of these reactions.

Comparisons between the two atmospheres, dynamic versus static nitrogen, and the nature of the matrix materials are shown in Fig. 2. Neither the disk composi-
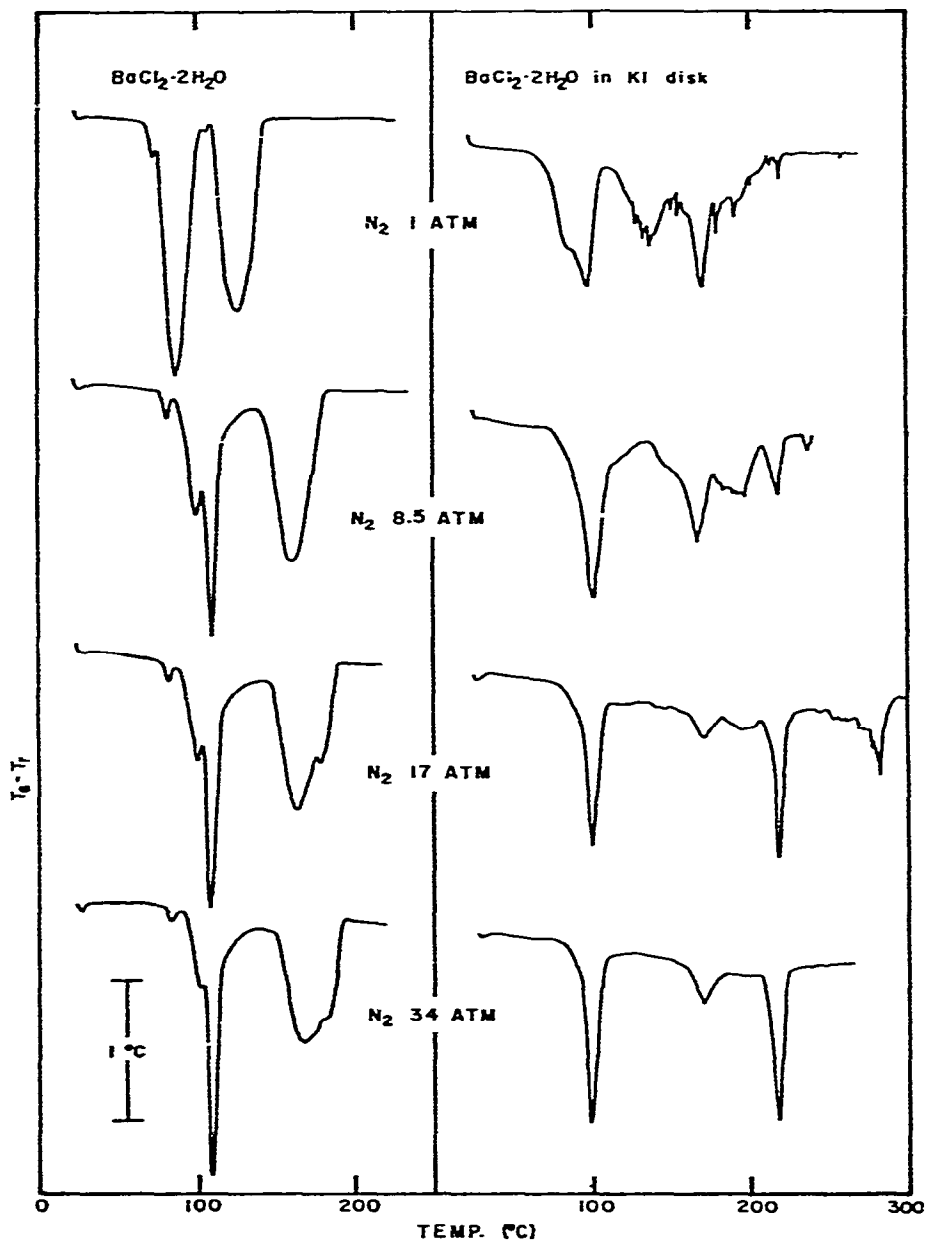

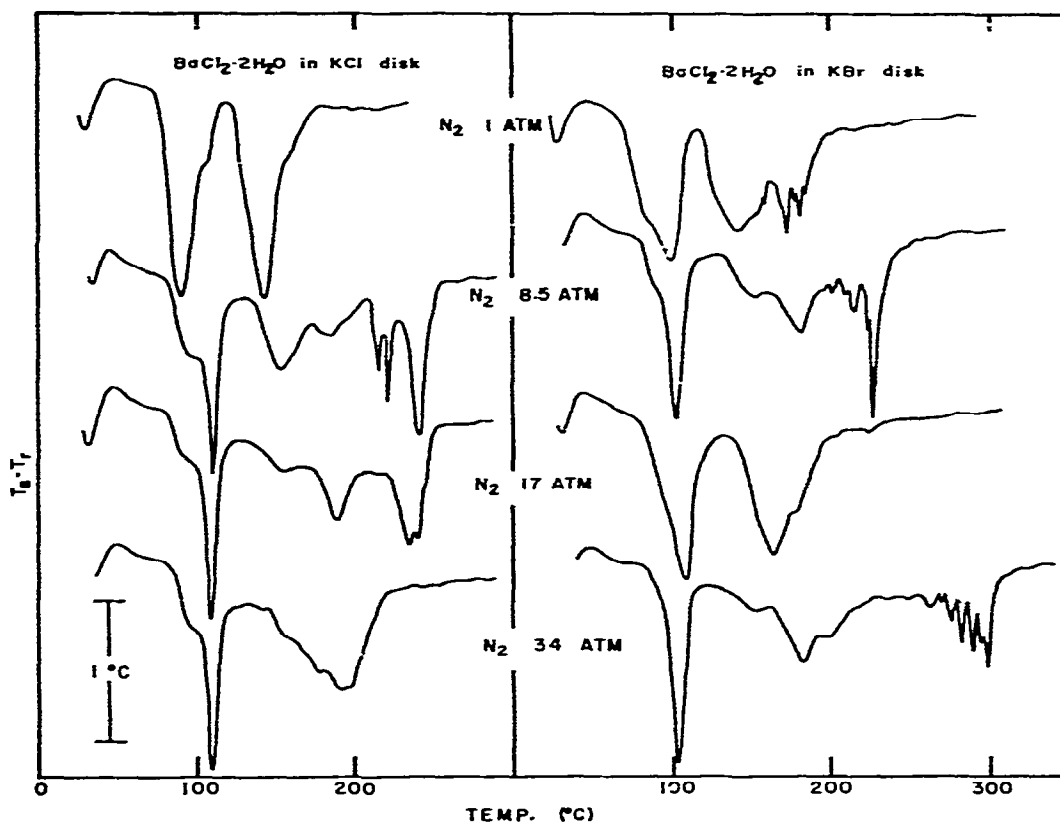Fig. 3. DSC curves of $BaCl_2 \cdot 2H_2O$ in the free state and in KI matrix at various pressures.

Fig. 4. DSC curves of $BaCl_2 \cdot H_2O$ in KCl and KBr matrices at various pressures.

tion nor the type of atmosphere had much effect on the first major peak, arising from the initial deaquation step and vaporization of water. Except for the KCl disk in static nitrogen, however, a separation between the second deaquation and water vaporization can be observed.

The effect of increasing pressure on the DSC curves of $BaCl_2 \cdot 2H_2O$ in a KX matrix are shown in Figs. 3 and 4. At a specific pressure, evolution of the first mole of water and its subsequent vaporization is resolved better in the pure sample than in any of the matrix samples. Resolution between deaquation and vaporization of the second mole of water was generally enhanced both by increased pressure and by the use of a matrix. Of particular interest are the two peaks which appear in the KI matrix for which ΔT_{min} are 170 and 217°C, respectively. As pressure is increased, the former becomes smaller while the latter increases. No evidence of either peak was obtained when anhydrous $BaCl_2$ was used (Fig. 5). Therefore, it is unlikely that they arose from any chemical reaction between $BaCl_2$ and KI, although the reaction, $BaCl_2 + 2KI \rightarrow BaI_2 + 2KCl$, is endothermic. A melting reaction is suggested by the sharpness and repeatability of the 217°C peak as well as by the absence of any change in mass (Fig. 1). It is felt that a ternary eutectic, involving $BaCl_2$, KI and
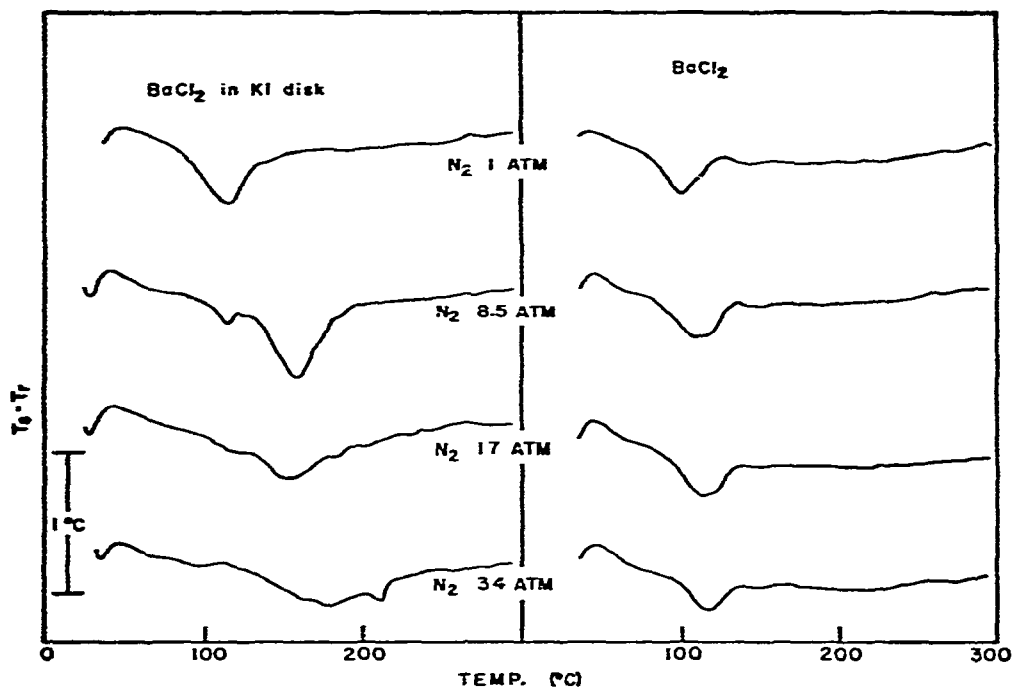
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Fig. 5. DSC curves of BaCl₂ (anhydrous) in the free state and in a KI matrix at various pressures.

H_2O, was present at 217 °C. If so, the enhancement of this peak by increasing pressure is consistent with the anticipated slower loss of water due to decreased diffusability of the latter.

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