

REACTIONS OF SILVER(I) SALTS IN POTASSIUM HALIDE MATRICES

A DIFFERENTIAL SCANNING CALORIMETRY STUDY

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ABSTRACT

Reactions of AgCl , Ag_2SO_4 , and Ag_2CO_3 in and with pressed KCl , KBr , and KI disks as well as those of unpressed mixtures were followed by TG and DSC. Except for Ag_2CO_3 and Ag_2SO_4 in KI , the curves obtained were readily interpreted in terms of eutectic melting, decomposition, and complex formation.

INTRODUCTION

Differential scanning calorimetry (DSC) has been previously used in this Laboratory to monitor reactions occurring in and/or with potassium halide (KCl , KBr , and KI) matrices in disk form. Applications of this technique include the characterization of pharmaceutical products¹, deaquation reactions of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ², and the study of solid-state reactions of several copper(I, II) salts³. In this investigation, the solid-state reactions of AgCl , Ag_2SO_4 , and Ag_2CO_3 in KCl , KBr , and KI matrices were studied and discussed. As in the case of the copper(I, II) salts³, eutectic melting, decomposition, and complex-forming reactions were observed.

EXPERIMENTAL PART

All the compounds used were of reagent-grade quality. Samples were studied as the pure material, pressed in KX ($\text{X} = \text{Cl}$, Br , or I) disks as described previously², and mixed with KX but not pressed, designated herein as the free state. All samples were heated in open, aluminum sample containers (DuPont). The heating rate was 10 deg min^{-1} and, unless otherwise noted, the atmosphere was dynamic nitrogen. The mass of salt taken was 5-12 mg which was mixed with 50 mg of KCl and 60 mg of KBr or KI and pressed into disks. In the free state, the salt samples were diluted with about 20 mg of KCl and 30 mg of KBr or KI . The DSC curves were obtained using the DuPont Model 990 thermal analysis system. In the case of Ag_2CO_3 , the

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DuPont high pressure cell in conjunction with the Model 900 console was also used. The TG curves were obtained utilizing the DuPont 951 thermogravimetric analyzer.

RESULTS AND DISCUSSION

The DSC and TG curves of AgCl in KCl are illustrated in Fig. 1. An endothermic peak corresponding to the eutectic melting temperature of 319°C ⁴ was observed both in the free state and in the disk. This was followed by a highly exothermic reaction for which ΔT_{max} is 338°C . In the disk, the latter peak was obscured

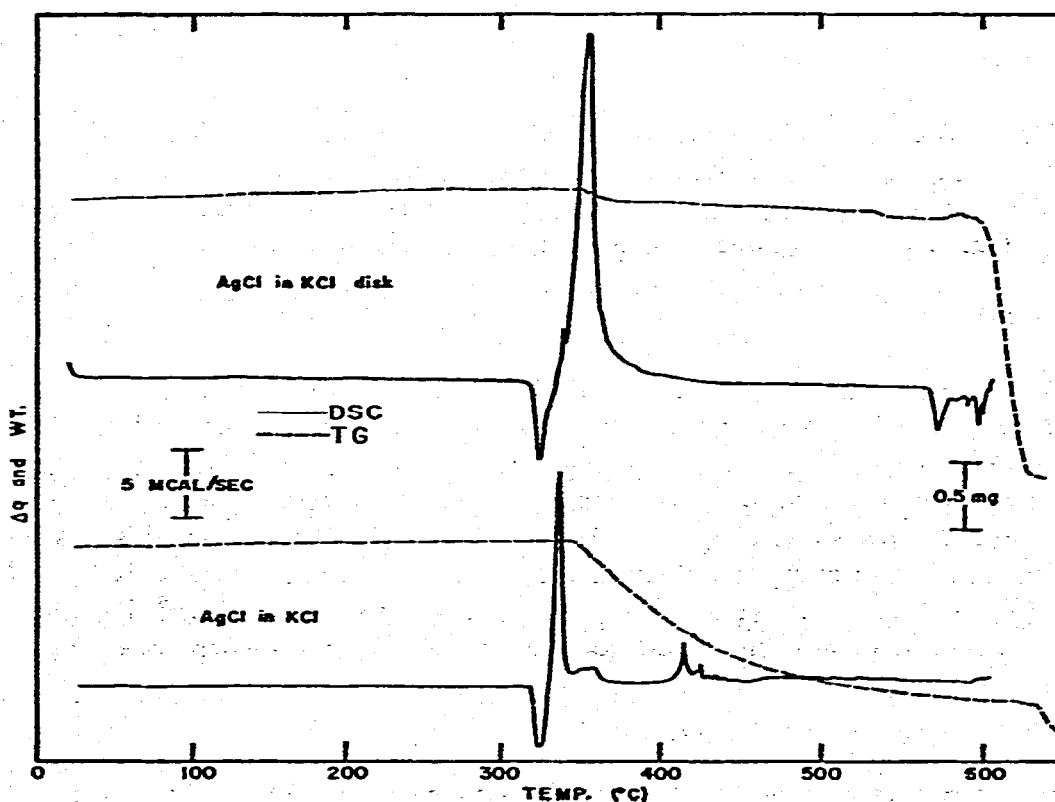


Fig. 1. DSC and TG curves of AgCl-KCl mixtures.

by the occurrence of an even more highly exothermic reaction for which ΔT_{max} is 356°C . In the free state, the development of the first exothermic peak was followed by a gradual loss of mass which attained 12.2% at 635°C . This corresponds to the evolution of 0.25 mol of Cl_2 per mol of AgCl and suggests the formation of an equivalent of silver subchloride, Ag_2Cl , the existence of which has been both reported and denied⁵. In the disk, only a very small loss of mass was observed above 338°C . It is felt that the 338°C peak marks the onset of decomposition of AgCl but that in the disk, the decreased diffusability of Cl_2 and a relatively high concentration

of KCl favor the formation of a chloro complex (e.g., KAgCl_2). The 356°C peak is attributed to the latter phenomenon. Above 595°C rapid decomposition occurred in the disk. The mass loss (22%), the endothermic nature of the process, and the darkening of the disk suggested the formation of elemental silver. A similar mass loss in the free state sample started at 635°C but could not be followed to completion due to the temperature limit of the experiment.

The DSC and TG curves of Ag_2SO_4 and Ag_2SO_4 in KCl are shown in Fig. 2. Pure Ag_2SO_4 exhibited a single endotherm at a $\Delta T_{\text{min.}}$ of 436°C which is due to a $\text{solid}_1 \rightarrow \text{solid}_2$ phase transition⁶. In the disk, there was no mass loss over the

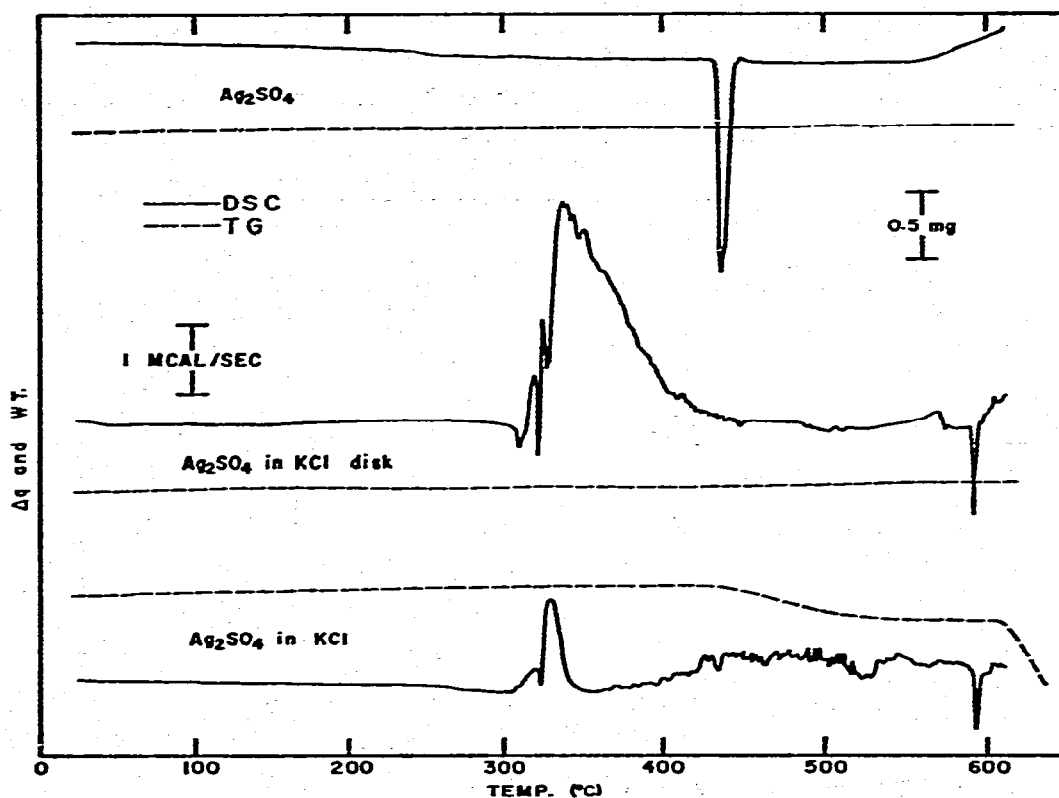


Fig. 2. DSC and TG curves of Ag_2SO_4 and of Ag_2SO_4 -KCl mixtures.

temperature range studied, although several reactions occurred between 300 and 450°C . The small endothermic peak starting at 304°C with a $\Delta T_{\text{min.}}$ of 309°C suggests $\text{AgCl-Ag}_2\text{SO}_4$ eutectic melting, the reported temperature for which is 304°C ⁷. Thus, the formation of some AgCl at temperatures below 304°C is indicated. This was followed by an exothermic transition for which the $\Delta T_{\text{max.}}$ was 325°C and which is thought to have been the formation of additional AgCl , the rate of which was accelerated by the presence of a liquid phase. During the course of this reaction, AgCl-KCl eutectic melting occurred, evidence for which is given by the endothermic peak with a $\Delta T_{\text{min.}}$ of 321°C . This was followed by a broad exothermic peak which is

believed to arise from the formation of a chloro complex such as that proposed in the case of AgCl in the KCl disk. The total heat flow per mol of Ag was essentially the same in both cases. The fact that the peak in Fig. 2 is much less sharp than its counterpart in Fig. 1 can be attributed to the less intimate contact between AgCl and KCl caused by the presence of K_2SO_4 . In the free state, the exothermic peak starting at 305°C and with a ΔT_{max} of 330°C , interrupted by eutectic AgCl-KCl melting at 321°C , is ascribed to the conversion of Ag_2SO_4 to AgCl. As with the free state sample of AgCl in KCl, complex formation apparently did not occur. The mass loss observed by temperatures greater than 430°C amounted to 3.0% of the mass of the Ag_2SO_4 initially present. The nature of this reaction is not known; if either Ag_2Cl or Ag was formed, the conversion of Ag_2SO_4 was far less than complete. The origin of the endothermic peak for which ΔT_{min} is 592°C is also unclear.

The DSC curves of Ag_2SO_4 in KBr, presented in Fig. 3, indicate behavior much like that noted for Ag_2SO_4 in KCl. In the disk as well as in the free state, the exo-

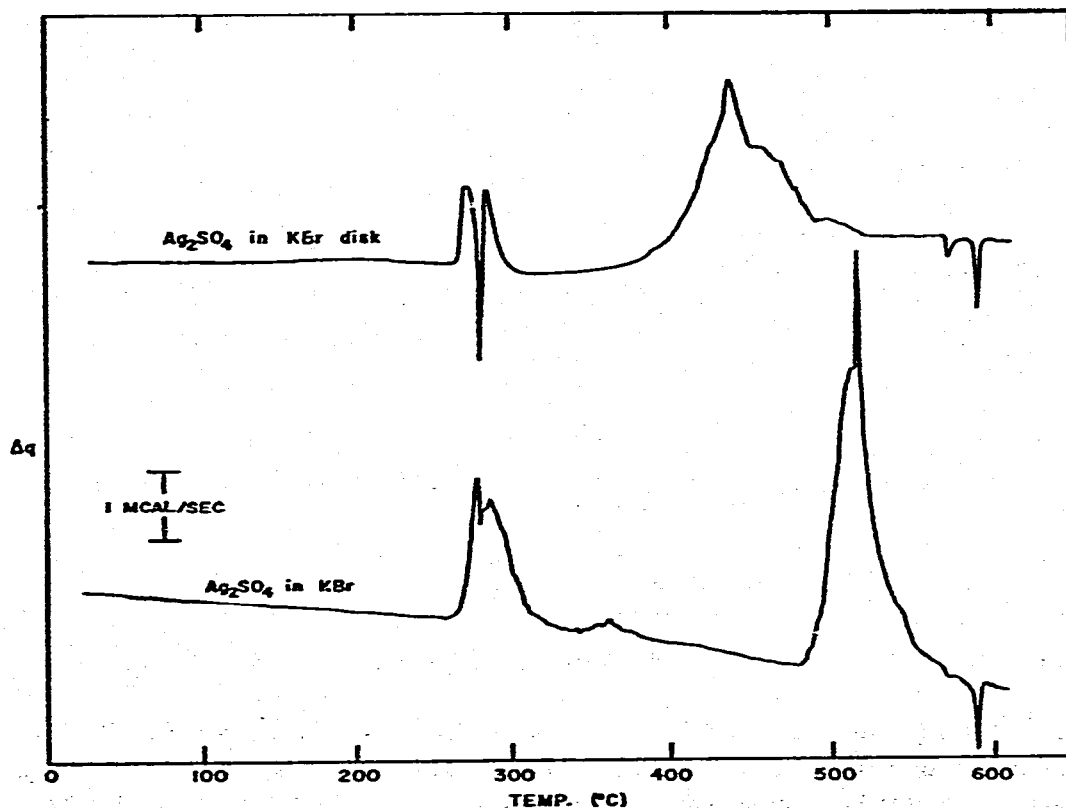


Fig. 3. DSC curves of Ag_2SO_4 -KBr mixtures.

thermic peak between 260 and 320°C is assumed to be due to the conversion of Ag_2SO_4 to AgBr. In both cases, this reaction was interrupted by AgBr-KBr eutectic melting, the reported temperature of which is $285^\circ\text{C}^{8,9}$. In the disk, the large

exothermic peak with a ΔT_{\max} of 433°C is thought to arise from the formation of a bromo complex analogous to the chloro complex postulated for Ag_2SO_4 in KCl. In contrast to the behavior of Ag_2SO_4 in KCl, there is evidence in the form of an exothermic peak for which ΔT_{\max} is 517°C for the formation of a bromo complex in the free state sample. As in the case of Ag_2SO_4 in KCl, an unexplained endothermic peak at 592°C was found.

The DSC curves of Ag_2SO_4 in KI are shown in Fig. 4. In the disk, an endothermic peak with a ΔT_{\min} of 245°C corresponds to the reported AgI-KI eutectic

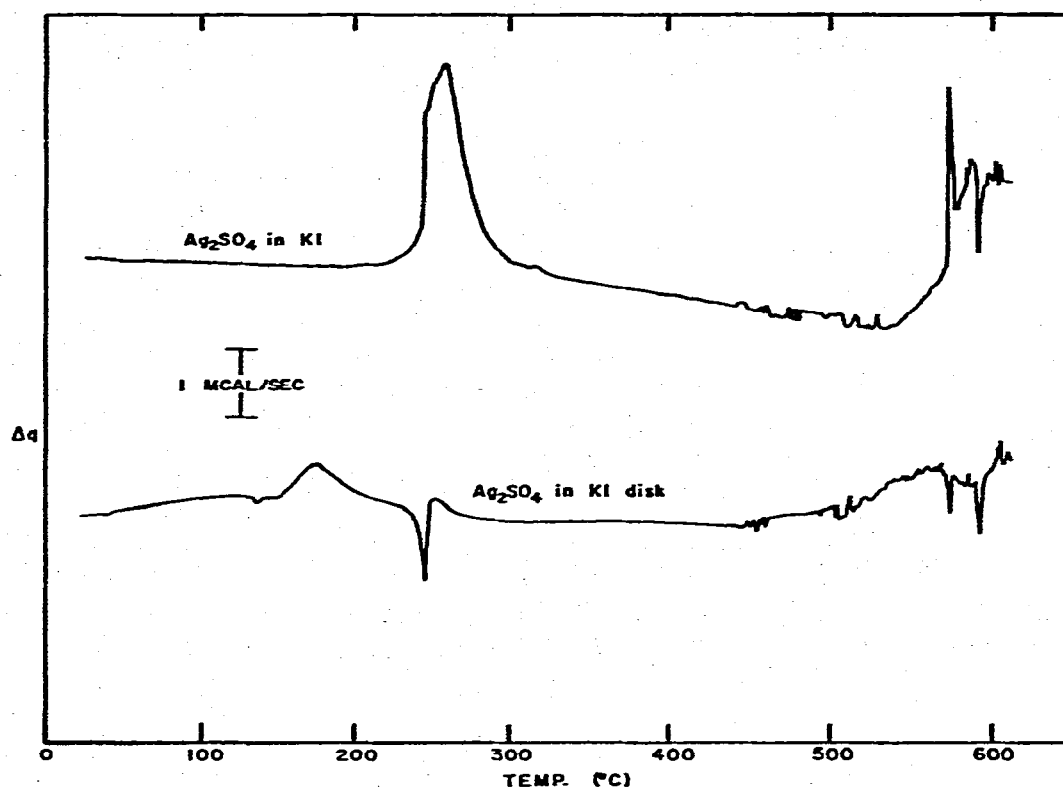


Fig. 4. DSC curves of Ag_2SO_4 -KI mixtures.

melting temperature¹⁰. It appears that at least partial conversion of Ag_2SO_4 to AgI occurred during the pressing of the disk and that no exothermic transitions of any significance were observed until decomposition took place at higher temperatures. In the free state, however, an exothermic transition between 240 and 310°C was observed and it is attributed to the formation of AgI. Although an endotherm arising from AgI-KI eutectic melting was not obtained, a clear change of slope at 245°C is indicative of this phenomenon. As with KCl and KBr, the unexplained endotherm at 592°C can be noted.

The DSC and TG curves of Ag_2CO_3 and Ag_2CO_3 , in KCl are given in Fig. 5. For pure Ag_2CO_3 , an endothermic peak with a ΔT_{\min} of 197°C marks the onset of

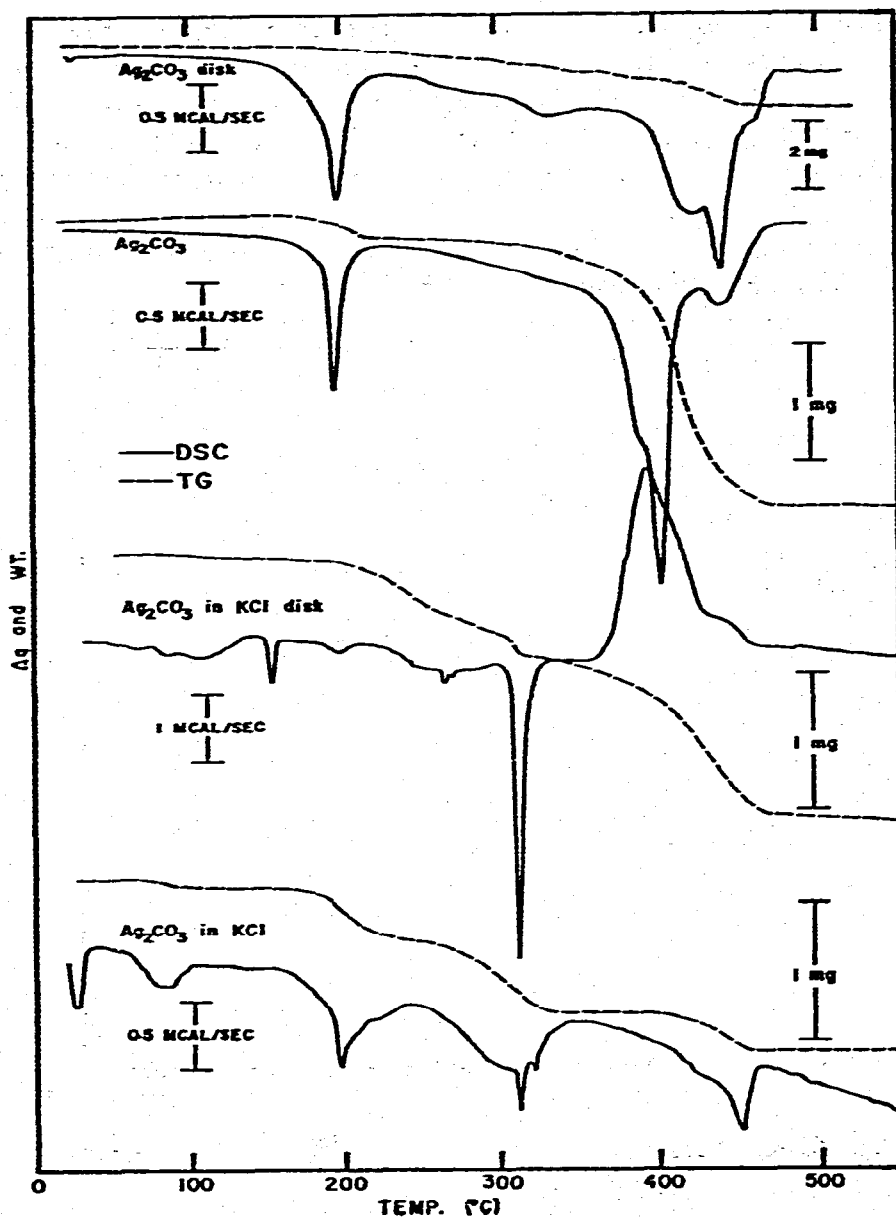


Fig. 5. DSC and TG curves of Ag_2CO_3 and of Ag_2CO_3 -KCl mixtures.

about 10% conversion of Ag_2CO_3 to Ag_2O , an observation noted elsewhere¹¹. Between 250 and 475°C complete conversion to Ag_2O and the subsequent formation of Ag occurred. An endothermic peak for which ΔT_{min} is 403°C (and which actually appears to be two overlapping peaks) corresponds to the production of Ag_2O while the broad exothermic peak with a ΔT_{min} of about 442°C is associated with the reduction of the latter to Ag. Pure Ag_2CO_3 in disk form underwent much the same decomposition reaction except that the expected decreased diffusability of CO_2

caused the mass loss to be slower and somewhat irregular with some variation in the higher temperature peaks. The formation of Ag_2O was clearly accompanied by the generation of two endothermic peaks for which the $\Delta T_{\text{min.}}$ were 423 and 442°C and the peak indicating reduction to Ag became a high temperature shoulder on the latter. For the Ag_2CO_3 -KCl mixtures, both in the free state and in disk form, the overall decrease in mass corresponds to the loss of one mol of CO_2 per mol of Ag_2CO_3 . For both samples, endothermic peaks with a $\Delta T_{\text{min.}}$ of 313°C, close to the AgCl-KCl eutectic melting temperature noted earlier, indicated the formation of AgCl. Otherwise, significant differences are evident. In the free state, as in the pure Ag_2CO_3 , an endothermic peak with a $\Delta T_{\text{min.}}$ of 197°C suggests conversion to Ag_2O . Since the mass loss indicates that this occurred to an extent greater than 10%, it is felt that this reaction was promoted by the transformation of Ag_2O to AgCl. The endothermic peak with a $\Delta T_{\text{min.}}$ of 452°C is believed to manifest final decomposition of the Ag_2CO_3 and the ultimate production of AgCl. In the disk, an endothermic peak for which $\Delta T_{\text{min.}}$ is 153°C is probably due to the initial decomposition of Ag_2CO_3 . The fact that this occurred at a temperature considerably lower than those previously cited can be attributed to the effect of the high KCl concentration in the disk and the attendant enhanced conversion of Ag_2O to AgCl. Once again, the decreased diffusability of CO_2 resulted in a slow mass loss. It is interesting to note that the rate of mass loss increased markedly upon formation of a liquid phase at 313°C. The origin of the large exothermic peak with a $\Delta T_{\text{max.}}$ of 393°C is thought to be due to the formation of a chloro complex (perhaps KAgCl_2). The accompanying mass loss shows that evolution of CO_2 occurred and suggests that the latter reaction involves Ag_2O and not Ag_2CO_3 . This is supported by the fact that when samples were run in a high pressure DSC cell (Fig. 6), the exothermic peak was not observed even at 17 atm pressure. In this static system which provides a self-generated atmosphere, CO_2 produced at temperatures lower than 355°C apparently inhibited the decomposition of Ag_2CO_3 to Ag_2O and the absence of the latter precluded complex formation.

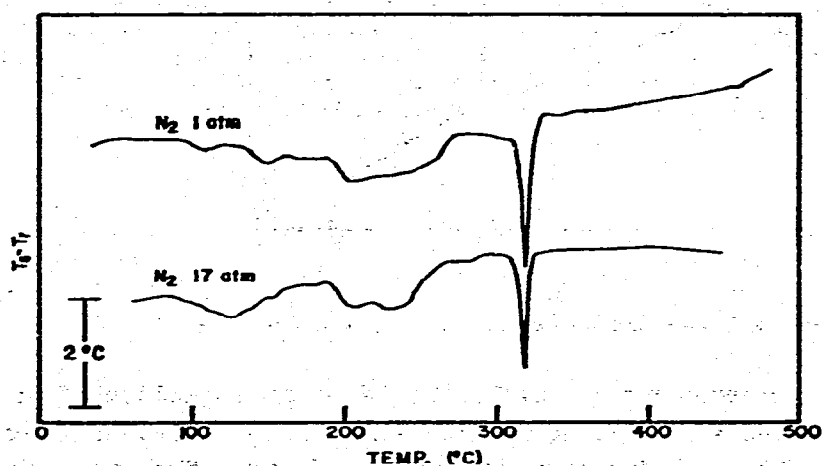


Fig. 6. DSC curves of Ag_2CO_3 -KCl mixtures.

The DSC and TG curves of Ag_2CO_3 in KBr, shown in Fig. 7, indicate behavior similar to that of Ag_2CO_3 in KCl. For samples in both the free state and in disk form, the overall loss of mass corresponds to the evolution of one mol of CO_2 per mol of

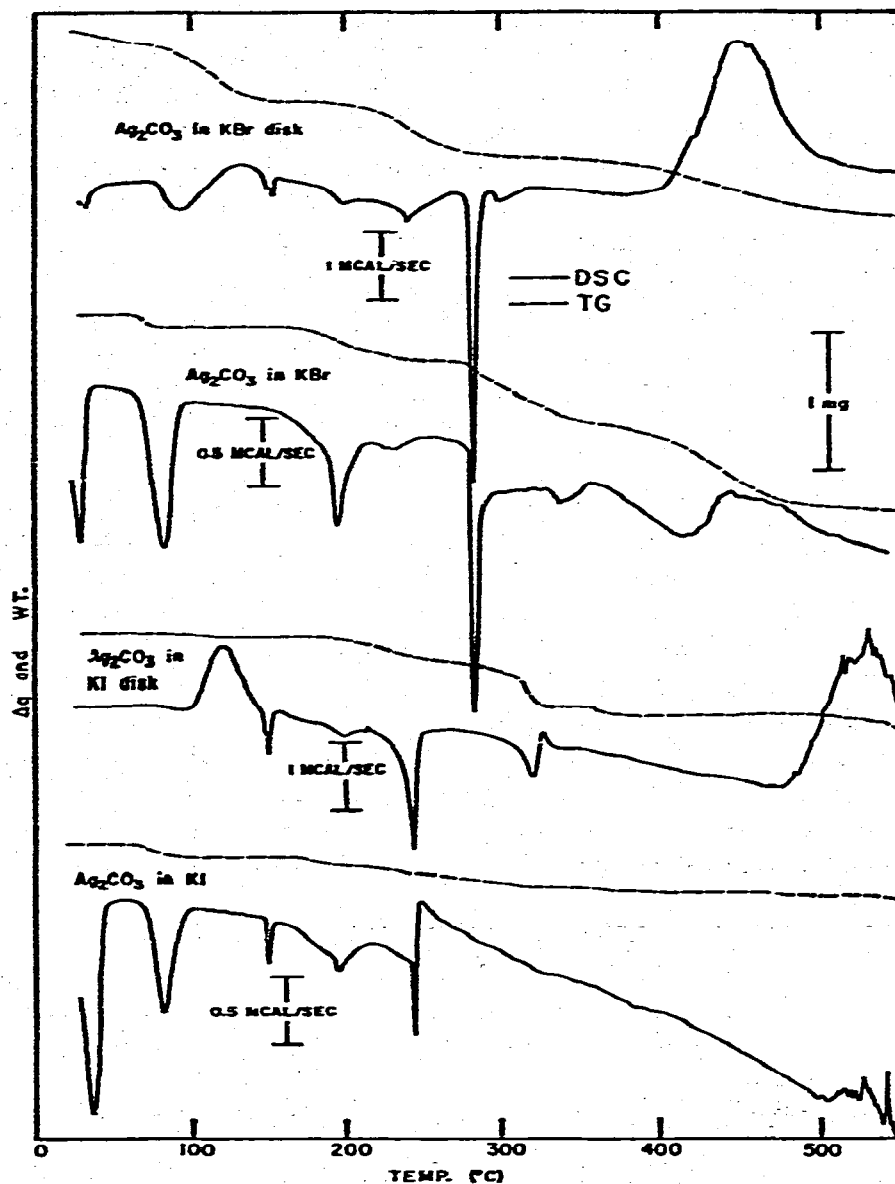


Fig. 7. DSC and TG curves of Ag_2CO_3 -KBr mixtures and of Ag_2CO_3 -KI mixtures.

Ag_2CO_3 with AgBr -KBr eutectic melting at 283°C . Initial decomposition of the Ag_2CO_3 was again observed at 197°C in the free state sample and at a lower temperature in the disk. The endotherms at temperatures below 100°C probably arose from the loss of water. In the disk, a broad exothermic peak with a ΔT_{max} of

about 450°C is believed to denote the formation of a silver bromo complex. No such reaction occurred in the free state sample.

The DSC and TG curves of Ag_2CO_3 in KI are also shown in Fig. 7. The endothermic peaks at temperatures below 100°C are attributed to the loss of water. The disparities between KI and either KBr or KCl as a matrix medium noted in this system are even more pronounced than those noted for Ag_2SO_4 . Endothermic peaks for which the ΔT_{min} is 245°C indicate AgI-KI eutectic melting, and, hence, the presence of AgI at that temperature. Endothermic peaks for which the ΔT_{min} is 150°C correspond quite closely to the 147°C value associated with the $\beta \rightleftharpoons \alpha$ transition of AgI¹². It is known that the AgI-KI system is fairly complex, involving compounds such as K_2AgI_3 and KAg_4I_5 ¹² and there is no reason to believe that its complexity is attenuated here. The overall decrease in mass was substantially less than that which would be observed if one mole of CO_2 per mole of Ag_2CO_3 were evolved. This indicates that the system includes CO^{2-} even at high temperatures. Clearly, a detailed interpretation of this system will require additional study.

ACKNOWLEDGMENT

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