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REACTIONS OF COPPER (I, II) SALTS IN A POTASSIUM CHLORIDE MATRIX

A DIFFERENTIAL SCANNING CALORIMETRY STUDY

A. M. WYNNE* AND W. W. WENDLANDT
Department of Chemistry, University of Houston, Houston, Texas 77004 (U.S.A.)
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ABSTRACT

The reactions of CuCl, $CuCl_2$ and $CuSO_4$ in KCl matrices were studied in the temperature range from 25 to 650°C by differential scanning calorimetry (DSC) and thermogravimetry (TG). Eutectic melting of the mixtures was observed as well as the formation of copper(I, II) chloro-complexes. Reduction reactions were also detected at higher temperatures, giving elemental copper and chloro-complexes.

INTRODUCTION

The use of differential scanning calorimetry (DSC) to monitor reactions occurring in or with potassium halide (KCl, KBr, and KI) matrices in disk form has been investigated by Wynne and Wendlandt[1] and by Collins and Wendlandt[2]. The former study was concerned with the deaquation reactions of $BaCl_2 \cdot 2H_2O$ while the latter showed that the disk technique was useful for characterizing certain pharmaceutical products. In both studies, the technique of fabricating the matrix disks was discussed and their usefulness in studying other chemical systems was mentioned. In a continuation of these investigations, the solid-state reactions of several copper(I, II) salts in a potassium chloride matrix are presented. The reactions observed here include eutectic melting, decomposition, and complex formation.

EXPERIMENTAL PART

Sample preparation

The compounds employed were all of reagent grade quality. All were used as obtained from their respective manufacturers except copper(I) chloride, which was prepared by the reduction of copper(II) chloride[3]. The samples were studied as the pure material, pressed in KCl disks as previously described[1], and mixed with KCl but not pressed, designated herein as the free state. All of the samples were heated in open, aluminum sample containers (DuPont) at a heating rate of 10 deg min^{-1} and

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*Permanent address: Chemistry Department, University of Massachusetts, Amherst, Mass. 01002, U.S.A.

in a dynamic nitrogen atmosphere. The disk sample sizes ranged in mass from 1–4 mg diluted with 45–55 mg of KCl while the free state samples contained 20–30 mg of KCl as a diluent.

Apparatus

The instruments used for this study were the DuPont Model 990 differential scanning calorimeter and Model 951 thermogravimetric analyzer.

RESULTS AND DISCUSSION

Copper(I, II) salts

The DSC and TG curves obtained for CuCl are given in Fig. 1. For pure CuCl, endothermic peaks at $\Delta T_{\text{min.}}$ 413 and 425°C, accompanied by a very small peak at $\Delta T_{\text{min.}}$ 435°C, were obtained. The melting point of CuCl is 430°C so, undoubtedly, melting occurred in this temperature range. Between 425 and 535°C, the sample lost 82% of its initial mass. Since conversion to elemental copper would correspond to a mass-loss of only 35.8%, it appears that at least part of the mass loss must have been due to the sublimation of CuCl. The origin of the large endothermic peak at a $\Delta T_{\text{min.}}$ of 550°C is not known. A similar peak was obtained in the decomposition of $CuCl_2$ (Fig. 2) at a point where the TG curve of the latter indicated the conversion of

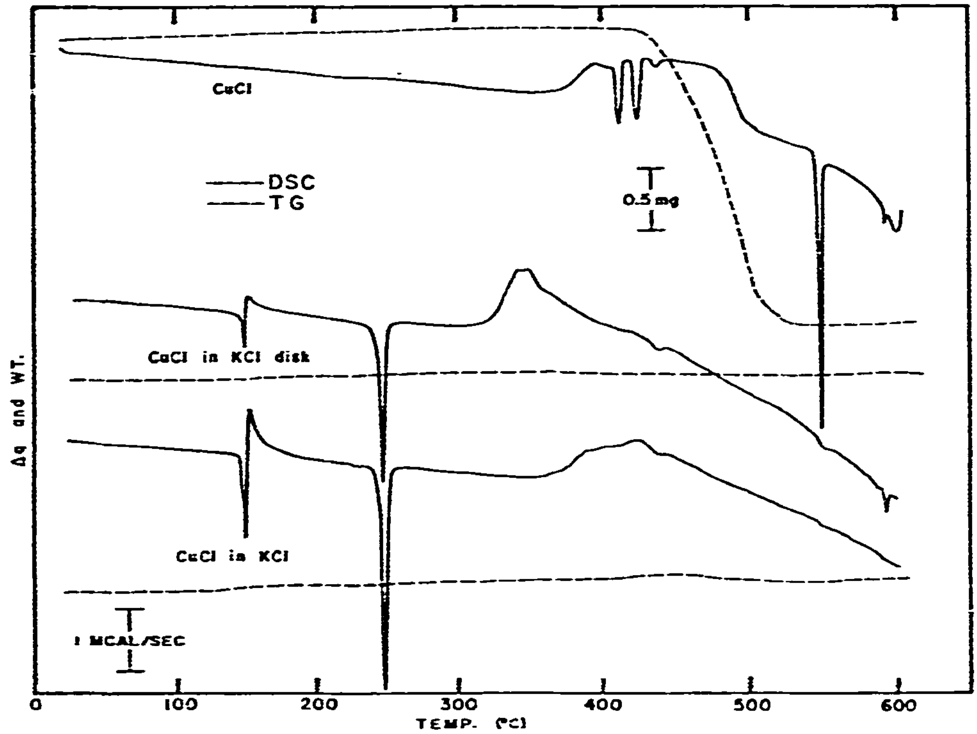

Fig. 1. DSC and TG curves of pure CuCl and CuCl–KCl mixtures.

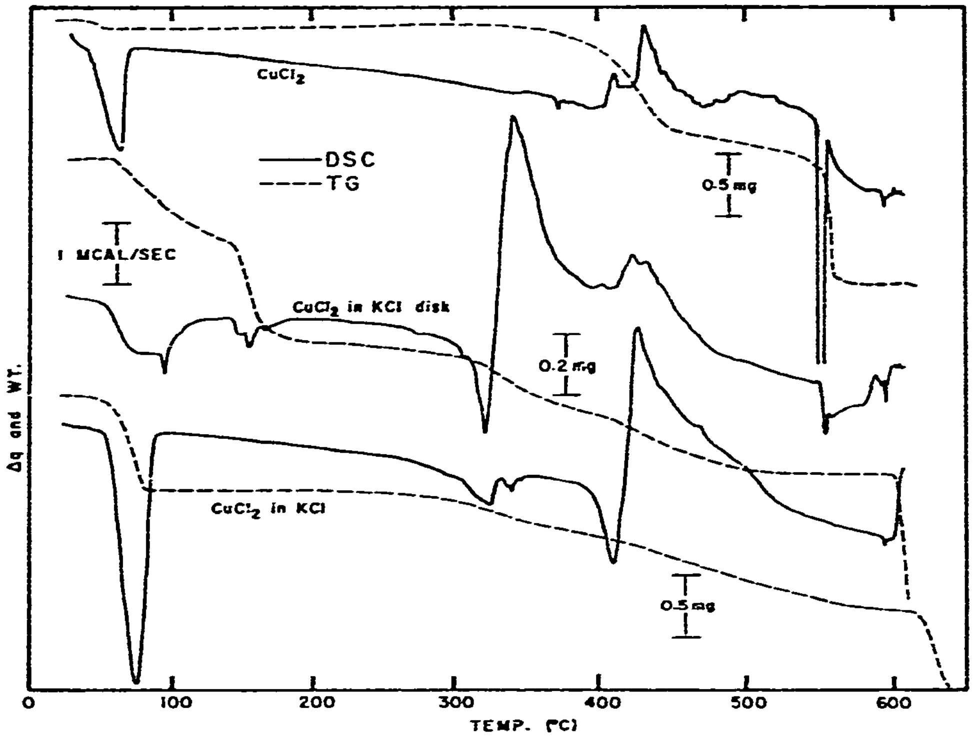

Fig. 2. DSC and TG curves of pure $CuCl_2$ and $CuCl_2$–KCl mixtures.

CuCl to elemental copper. For the CuCl sample, however, the mass-loss was complete prior to the appearance of the peak in question. It is inferred that a phase-change occurred but whether it involved CuCl or copper is not clear.

In the presence of KCl, CuCl showed no mass-loss below 600 °C. A sharp endothermic peak at a $\Delta T_{\mathrm{min.}}$ of 149 °C followed by an exothermic peak at a $\Delta T_{\mathrm{max.}}$ of 155 °C were obtained from both the free state and matrixed samples. This sequence suggests CuCl–KCl eutectic melting followed by the formation of a complex ion, such as $CuCl_2^-$. The fact that the exothermic peak tapers on the high temperature side probably arises from the limited mobility of KCl and CuCl through the intermediate complex layer. An endothermic peak for which $\Delta T_{\mathrm{min.}}$ was 248 °C occurred in both samples. This is believed to indicate simple eutectic melting, probably involving $KCuCl_2$ and KCl, which resulted in increased mobility of CuCl and KCl and, hence, permitted more extensive complex formation. The latter is indicated by broad exothermic peaks at temperatures above 310 °C. The fact that this peak occurred at a lower temperature in the disk than in the free state is consistent with the higher concentration of KCl in the former.

The DSC and TG curves of $CuCl_2$ are illustrated in Fig. 2. In each case, the initial mass-loss or curve-peak was due to the evolution of water. At about 380 °C the pure $CuCl_2$ began a slow, two-step decomposition leading to residual compositions corresponding to CuCl at about 540 °C and elemental copper at 570 °C. In both the free state and matrix disk, an endothermic peak starting at 305 °C and with a $\Delta T_{min.}$ of 324 °C is consistent with the reported $CuCl_2$–KCl eutectic melting temperature of 310 °C[4]. Decomposition in the free state sample started at about 225 °C, however, suggesting enhancement of the process by the presence of excess KCl and, perhaps, a solid-state reaction. The mass-loss attained at 610 °C corresponds to the loss of 0.5 mole of Cl_2 per mole of $CuCl_2$; a rapid, subsequent mass-loss indicates decomposition to elemental copper. The mass-loss in the matrix disk provides evidence of a somewhat more complex situation. If the equivalent of CuCl existed at 530–600 °C, the decomposition of $CuCl_2$, along with the evolution of a small amount of water, started at 60 °C. Endothermic peaks at 140–160 °C, a range in which CuCl–KCl eutectic melting occurs, as has already been noted, support such an inference. It was shown in earlier studies[5] that water-loss from the matrix disk is slow and, at the heating rate used, may extend over a range of 50 to 100 °C. As a result, there is distinct possibility that the decomposition reaction up to 175 °C or so may actually have occurred in aqueous solution. Following melting of the $CuCl_2$–KCl eutectic, a highly exothermic transition ($\Delta T_{max.}$ 342 °C) took place in the disk. This is thought to manifest the formation of the complex, $KCuCl_3$, which has been shown to exist at temperatures above 310 °C[4]. On the other hand, a mass-loss in the matrix disk became somewhat more rapid than in the free state at this temperature and this could be interpreted in terms of enhancement of the decomposition rate by the formation of

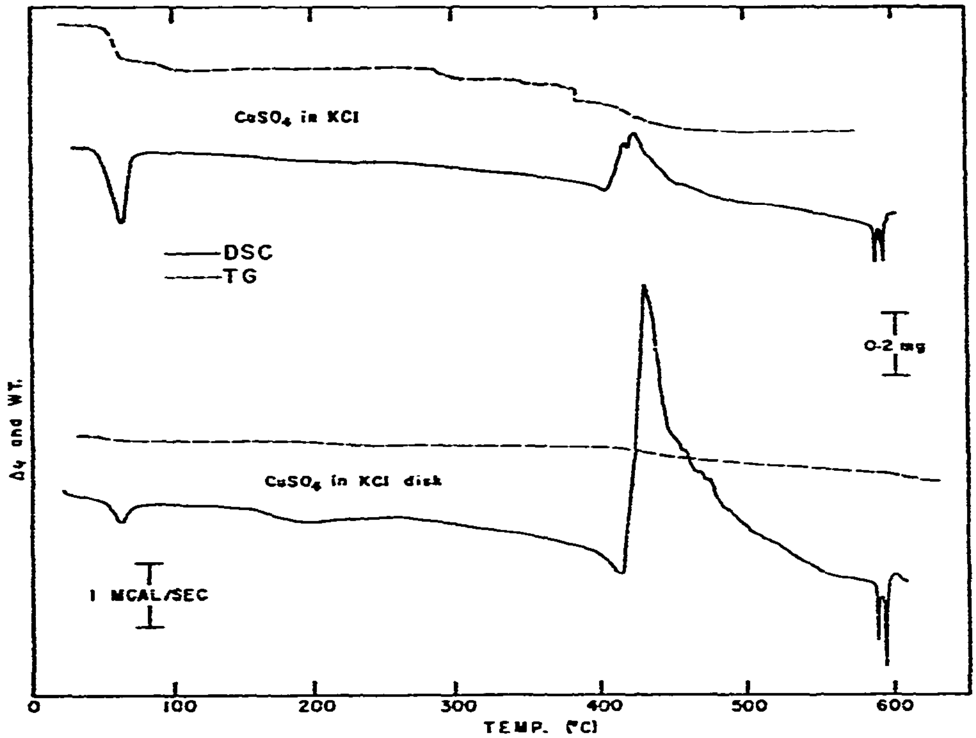

Fig. 3. DSC and TG curves of $CuSO_4$–KCl mixtures.

a copper(I) chloro-complex. It is possible that a mixture of complexes was present at this point. An endotherm at a $\Delta T_{\text{min.}}$ of 410°C for the free state sample indicates melting, which is followed by the exothermic information of additional complex. Evidence for the latter transition was obtained from the disk sample as well. In all probability, the compound observed at 600°C is a copper(I) chloro-complex rather than CuCl. This would at least partially explain the higher final decomposition temperature for the disk and free state samples than that for pure $CuCl_2$.

The DSC and TG curves for $CuSO_4$ in KCl are shown in Fig. 3. Small amounts of water initially present were evolved by 100°C, followed by a slow decomposition reaction, which began at 285°C, leading to the loss of the equivalent of 0.5 mole of Cl_2 per mole of $CuSO_4$ at 480°C. In the matrix disk, mass-loss started at a higher temperature and a stable form was not attained, reflecting the decreased diffusability of the evolved gaseous products in the latter medium. The absence of endothermic melting peaks in the 305–319°C temperature range indicates that $CuCl_2$ was not formed and it is felt that the endothermic peak at a $\Delta T_{\text{min.}}$ of 410°C represents $CuSO_4$–KCl eutectic melting. The exothermic peak which follows probably arises from the formation of copper(II) chloro-complexes and, as expected, is of a greater magnitude in the disk with its higher concentration of KCl.

In the case of the $CuSO_4 \cdot 5H_2O$–KCl matrix disks, as shown in Fig. 4, preparation of the pressed disk caused the formation of a yellow-colored compound

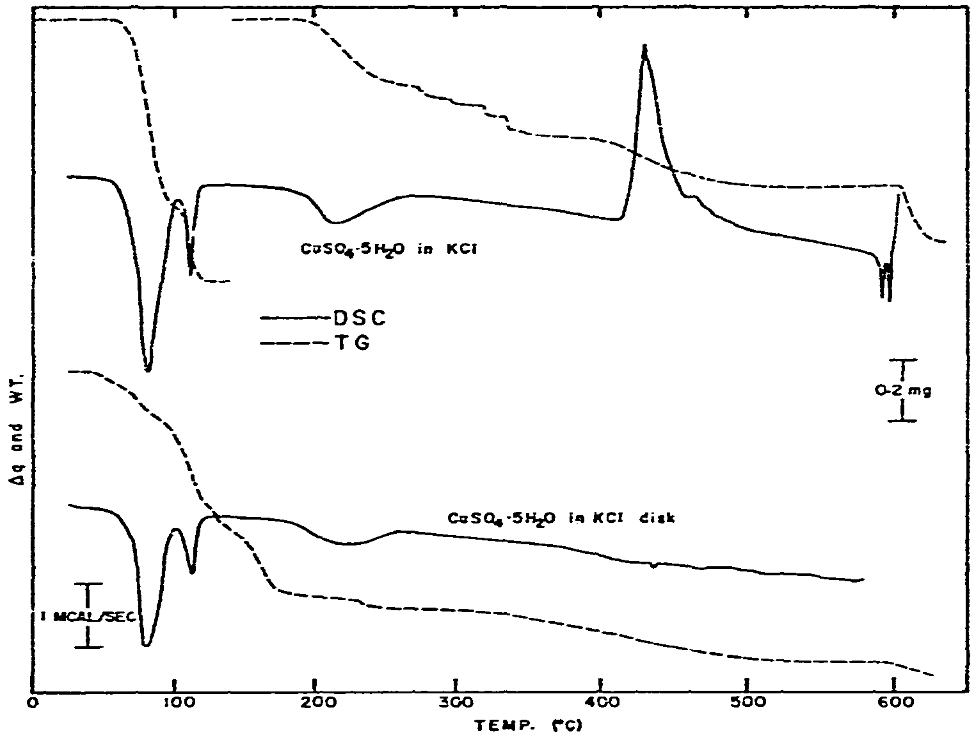

Fig. 4. DSC and TG curves of $CuSO_4 \cdot 5H_2O$–KCl mixtures.

indicating extensive interaction before the heating cycle was begun. There was little suggestion of any chemical reaction after the deaquation reactions were complete. In the free state, decomposition started at about 195°C. Again, the mass-loss corresponds to the evolution of 0.5 mole of Cl_2 per mole of anhydrous $CuSO_4$. A DSC curve peak at a $\Delta T_{max.}$ of 431 °C very strongly resembles one noted in the anhydrous $CuSO_4$–KCl matrix disk. It appears that water present during the early portion of the run caused at least partial dissolution of the sample. The residue which remained after the evolution of water was probably quite compact, similar to that in the pressed matrix disk.

ACKNOWLEDGMENT

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