

## IR and XRD Study of the Tribochemical Reactions of Copper Sulfate with Alkali Halides

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Tribochemical reactions of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{CuSO}_4$  during milling with KCl, KBr, and KI have been studied by IR and XRD techniques. The reactions are rather similar for the hydrated and anhydrous salts, but proceed faster with the former. With KCl, the reaction leads directly to  $\text{CuK}_2\text{SO}_4\text{Cl}_2$  also known as the mineral chlorothionite. With KBr, the mixed salts  $\text{CuK}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  and  $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  are first obtained which transform to a new compound upon further milling, that we postulate as  $\text{CuK}_2\text{SO}_4\text{Br}_2$ . With KI, there is a fast reaction to a mixture of  $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\gamma\text{-CuI}$ , and  $\text{I}_2$ , later proceeding to  $\text{K}_2\text{SO}_4$ ,  $\gamma\text{-CuI}$ , and  $\text{I}_2$ . © 1993 Academic Press, Inc.

### Introduction

When the KBr disk technique is used to obtain IR spectra of solids, reactions between the analyte and KBr can take place during milling and pressing (1). Such is the case for hydrated and anhydrous copper sulfate whose spectra in Nujol (2) are different from those in KBr (1, 3). Meloche and Kalbus (1) noted that during milling of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  with KBr, the powder turned brown and the related IR spectra changed with further milling. These artifacts have importance in studying patinas (4).

In order to understand these tribochemical reactions we have studied the milling of hydrated and anhydrous copper sulfate with KCl, KBr, and KI. The changes have been monitored by IR and XRD techniques.

### Experimental

All applied reagents were analytical-grade commercial products. Anhydrous  $\text{CuSO}_4$

was obtained by heating the pentahydrate to 180°C for 24 hr in air.

The tribochemical reactions were carried out with weighted samples with molar ratios 1:1 and 1:2  $\text{CuSO}_4$ -alkali halide. The weighted reactants were ground in an agate mortar or in a "wobble bug" type stainless steel ball vibrator for periods of several minutes to one hour.

The solid reaction mixtures were analyzed "as prepared," except for the KI mixtures that were treated with  $\text{CCl}_4$  to extract free  $\text{I}_2$ .

Infrared (IR) spectra were obtained from Nujol mulls between KBr and NaCl windows and from KBr and KCl pressed disks. Spectra were run in a Pye Unicam PU-9880 Fourier transform spectrometer.

X-ray diffraction (XRD) patterns of the solid mixtures and standards were measured with a HZG4 Carl Zeiss powder diffractometer using  $\text{CuK}\alpha$  radiation.

### Results and Discussion

#### (a) IR spectra of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CuSO}_4$ in Nujol

Slightly ground samples of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{CuSO}_4$  without any additions were run

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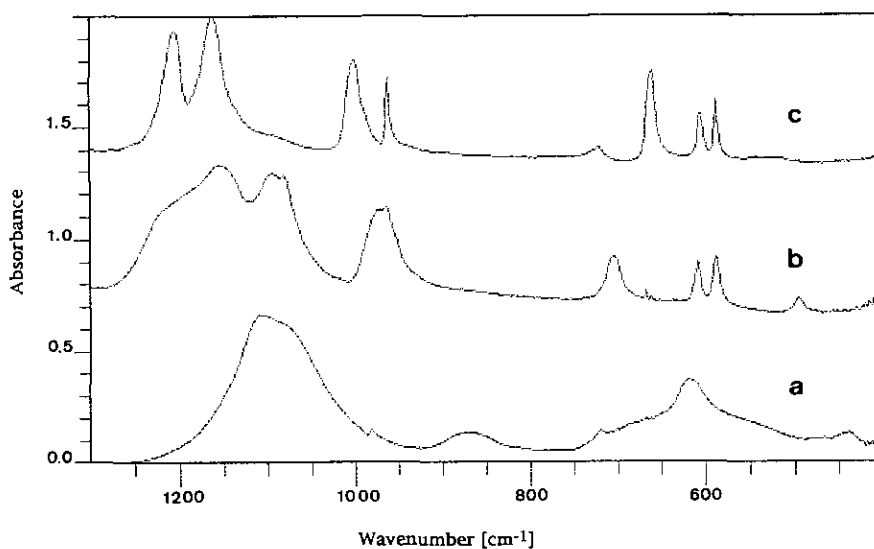


FIG. 1. IR spectra of (a)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in Nujol, (b)  $\text{CuSO}_4$  in Nujol, (c)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in KCl disk (Pattern I). Spectra were shifted vertically for clarity.

in Nujol between KBr and NaCl windows. The spectra reported in Fig. 1 are identical with those found in the Aldrich Library Series (2). However, when the Nujol mull of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  between KBr windows is rotated with force, a tribochemical reaction takes place with the window material leading to a new spectral pattern, designed below as Pattern II (see Table I). No evidence for a similar tribochemical reaction is obtained with NaCl windows.

*(b) Reactions of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{CuSO}_4$  with KCl*

The reaction of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  with KCl at a molar ratio 1 : 2 takes place rapidly upon

grinding. The mixture turns into a green paste which dries during further milling. The anhydrous  $\text{CuSO}_4$  reaction is similar except that a green powder is produced instead of a paste. The spectrum of this green compound is called Pattern I (see Table I).

The XRD patterns of both the dry and the pasty sample are identical and closely resemble the diffractogram reported for  $\text{CuK}_2\text{SO}_4\text{Cl}_2$  (5), a volcanic mineral called "chlorothionite," which was detected for the first time in the volcanic exhalations of the 1906 Vesuvius eruption (6). We have tried to prepare it from solutions of  $\text{CuSO}_4$  and KCl but the crystalline product so obtained corresponds to the salt  $\text{CuK}_2(\text{SO}_4)_2$ .

TABLE I  
IR BAND LOCATION [ $\text{cm}^{-1}$ ] FOR THE SULFATE ION IN THE DIFFERENT REACTION SYSTEMS

System	Type of pattern	$\nu_1$	$\nu_3$	$\nu_4$
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + 2\text{KCl}$	I	963, 1001	1162, 1207	588, 607, 662
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + 2\text{KBr}$	I	961, 996	1156, 1197	584, 602, 659
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + 2\text{KBr}$	II	982	1097, 1148	618
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{KI}$	II	983	1088, 1145	618
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + 2\text{KI}$	$\text{K}_2\text{SO}_4$	983	1115	619

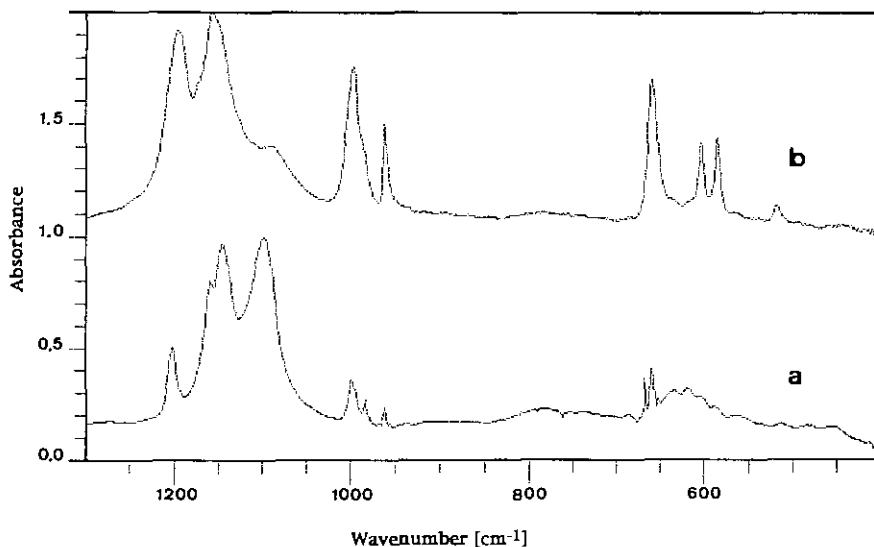


FIG. 2. IR spectra of: (a)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + 2\text{KBr}$  (not too milled, Pattern II), (b)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + 2\text{KBr}$  (very milled, Pattern I). Spectra were shifted vertically for clarity.

$6\text{H}_2\text{O}$ . It is well known that during grinding of solid crystals, high temperatures are generated at the colliding edges, leading to hot plasma spots, which could produce the chlorothionite.

When  $\text{K}_2\text{SO}_4$  and  $\text{CuCl}_2 \cdot \text{H}_2\text{O}$  are mixed and milled, similar IR spectrum and XRD pattern are obtained as was noted for the reaction of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  with  $\text{KCl}$ . Chlorothionite is therefore a stable species in the tribochemical reactions in these systems. We have also obtained this compound from crystalline  $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  milled with  $\text{KCl}$ .

*(c) Reactions of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{CuSO}_4$  with  $\text{KBr}$*

Milling of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  with  $\text{KBr}$  produces a browning of the mixture but no  $\text{Br}_2$  odor is detected. The IR spectrum is shown in Fig. 2 and we labeled it as Pattern II (see Table I). With further milling or exposure to light, the IR spectrum changes to Pattern I (see Table I) as can be observed in Fig. 2. The XRD pattern corresponding to Pattern II coincides with the one reported for  $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (5). However, the XRD

pattern corresponding to Pattern I can not be found in the literature. It is similar to that of  $\text{CuK}_2\text{SO}_4\text{Cl}_2$ , but with interplanar distances slightly larger (see Table II). The IR frequencies are also slightly lower in the case of  $\text{KBr}$  than in the case of  $\text{KCl}$  (see Table I). These results indicate that the compound obtained on prolonged milling of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  with  $\text{KBr}$  is the bromine analogue of chlorothionite,  $\text{CuK}_2\text{SO}_4\text{Br}_2$ .

When anhydrous  $\text{CuSO}_4$  is milled with  $\text{KBr}$ , the reaction is slower than with the pentahydrate, but the IR spectra are similar to Pattern II. XRD patterns indicate the additional presence of  $\text{CuK}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ , indicating that the tribochemical process absorbed moisture from the atmosphere, which is high in our conditions.

*(d) Reactions of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{CuSO}_4$  with  $\text{KI}$*

When  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{KI}$  are mixed, there is a fast reaction with the formation of  $\text{I}_2$ . The free iodine can be removed by washing the powder with  $\text{CCl}_4$ . With anhydrous  $\text{CuSO}_4$  the reaction is much slower, but proceeds upon milling.

TABLE II  
XRD DATA OF  $\text{CuK}_2\text{SO}_4\text{Cl}_2$  AND ITS BROMINE ANALOGUE RESULTING  
FROM THE TRIBOCHEMICAL REACTION:  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + 2\text{KBr}$

$\text{CuK}_2\text{SO}_4\text{Cl}_2$				$\text{CuK}_2\text{SO}_4\text{Br}_2$	
Ref. [5]		This paper		This paper	
$d$ [Å]	$I/I_0$	$d$ [Å]	$I/I_0$	$d$ [Å]	$I/I_0$
3.04	100	3.04	100	3.12	100
2.19	70	2.19	66	2.20	41
2.85	35	2.85	34	2.88	31
6.98	9	6.92	11	8.11	24

When a mixture of the anhydrous salt and KI at a molar ratio 1:1 is milled slightly, the IR spectrum corresponds to Pattern II (see Fig. 3, Table I), indicating formation of the double potassium-copper salt  $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , which is confirmed by XRD.  $\gamma\text{-CuI}$  and free  $\text{I}_2$  are also formed. However, with more KI to match the 1:2 molar ratio, the reaction proceeds to the formation of  $\text{K}_2\text{SO}_4$ ,  $\gamma\text{-CuI}$ , and  $\text{I}_2$ , for the anhydrous and hydrated salts (see Fig. 3, Table I).

If crystalline  $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  is milled

with KI, the reaction leads to  $\gamma\text{-CuI}$ ,  $\text{K}_2\text{SO}_4$ , and free  $\text{I}_2$ .

#### (e) Spectra—Structure Correlation

We have used IR spectroscopy to monitor the tribochemical changes occurring when  $\text{CuSO}_4$  is milled with potassium halides. However, the actual identification of the products of the reactions has been accomplished by XRD of the powdered samples in unequivocal form. We will now discuss

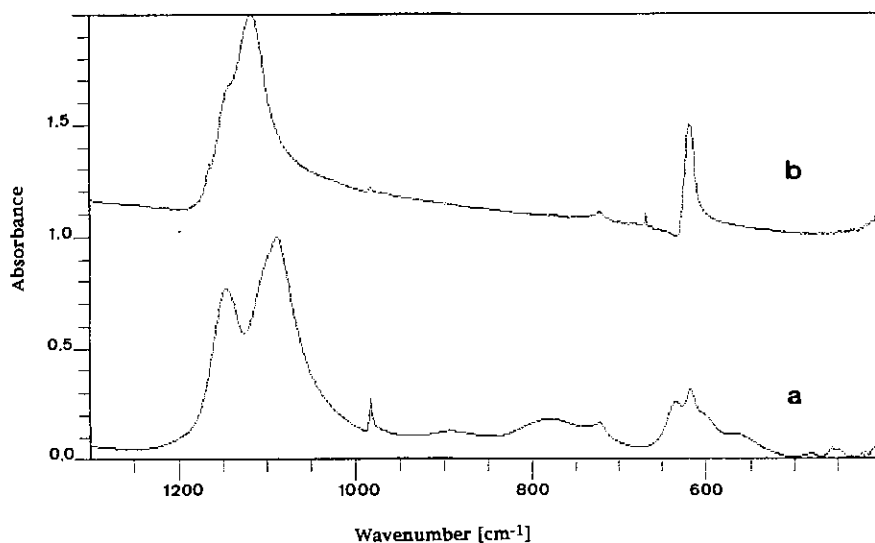


FIG. 3. IR spectra of: (a)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{KI}$ , (b)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + 2\text{KI}$ . Spectra were shifted vertically for clarity.

the IR spectra considering the structure of the Cu-containing compounds.

In  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , the  $(\text{SO}_4^{2-})$  anion has a nearly perfect tetradral configuration. The high symmetry is confirmed by the very low intensity of the IR-forbidden totally symmetric S–O stretching mode  $\nu_1$  at  $982\text{ cm}^{-1}$ . The asymmetric stretching mode  $\nu_3$  is a broad intense band with a maximum at  $1105\text{ cm}^{-1}$  and a shoulder at  $1080\text{ cm}^{-1}$ . The splitting of the degeneracy of  $\nu_3$  is due to hydrogen bonding of the  $(\text{SO}_4^{2-})$  anion to one  $\text{H}_2\text{O}$  molecule. This interaction is also responsible for the low frequency of  $\nu_3$ . A similar situation applies also to the hydrated mixed salts  $\text{CuK}_2(\text{SO}_4)_2 \cdot n\text{H}_2\text{O}$  ( $n = 2, 6$ ).

Another piece of evidence of the nearly perfect tetrahedral symmetry is the nonresolved splitting of the asymmetric degenerated bending mode  $\nu_4$ , a broad band at  $620\text{ cm}^{-1}$ .

This situation is very different with chlorothionite and the analogous Br phase. The normally forbidden band  $\nu_1$  is observed as a medium intensity doublet at  $963$  and  $1001\text{ cm}^{-1}$  for both Cl and Br derivatives. This is due to the pseudo-tetrahedral symmetry of the  $(\text{SO}_4^{2-})$  group which has two of its O atoms coordinated to a  $\text{Cu}^{2+}$  cation and the other two O atoms to a  $\text{K}^+$  cation. The S–O distances are very different,  $1.51$  and  $1.46\text{ Å}$ , respectively (6). This low symmetry is also responsible for the splitting of  $\nu_3$  ( $1161$ – $1207\text{ cm}^{-1}$  for the Cl and  $1156$ – $1197\text{ cm}^{-1}$  for the Br derivative). The high frequency of  $\nu_3$  is due to the lack of hydrogen bonding of the  $(\text{SO}_4^{2-})$  since the compounds are anhydrous. The Cl atoms are too far away from the O atoms to have a noticeable effect on the  $(\text{SO}_4^{2-})$  frequencies (6).

The degenerated bending  $\nu_4$  is totally separated into three bands at  $558$ ,  $607$ , and  $662\text{ cm}^{-1}$  for the Cl compound, and at  $584$ ,  $603$ , and  $659\text{ cm}^{-1}$  for the Br derivative confirming again the low symmetry of the  $(\text{SO}_4^{2-})$  anion.

## Conclusions

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and its anhydrous form react with potassium halides when milled. For KCl, the product obtained is the mineral chlorothionite. With KBr, initial milling produces  $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CuK}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ . With further milling the quadruple salt  $\text{CuK}_2\text{SO}_4\text{Br}_2$  is obtained. No reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  or Cu is detected.

With KI, the above-mentioned double salts,  $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CuK}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ , are intermediates that react with excess KI to form  $\text{K}_2\text{SO}_4$ , CuI ( $\gamma$  phase), and free  $\text{I}_2$ .

The reactions of the pentahydrate are faster than of the anhydrous form.

Moisture is absorbed from the atmosphere during the tribochemical reactions of the anhydrous salt.

## References

1. V. W. MELOCHE AND G. E. KALBUS, *J. Inorg. Chem.* **6**, 104, (1958).
2. Aldrich Library FT-IR Series. (I. Charles J. Pouchet, Eds.).
3. J. R. FERRARO AND A. WALKER, *J. Chem. Phys.* **42**, 1278, (1965).
4. M. MATTEINI, A. MOLES, AND O. LALLI, "Proc. ICOMM 7th Triannual Meeting," p. 2218. Copenhagen (1984).
5. Powder Diffraction File, Joint Committee on Powder Diffraction Standards, NBS, USA (1989).
6. C. GIACOVAZZO, *Z. Kristallogr.* **144**, 226, (1976).