

THERMOCHEMICAL PROPERTIES OF THE COPPER(II) HYDROXYCHLORIDES*

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ABSTRACT

CuOHCl and the three polymorphs of $\text{Cu}_2(\text{OH})_3\text{Cl}$ (botallackite, atacamite, and paratacamite) have been studied by means of thermogravimetry, differential scanning calorimetry, infrared spectroscopy, and X-ray powder diffraction. The OH stretching frequencies show a progressive increase in the strength of hydrogen-bonding in the order botallackite < atacamite < paratacamite. This correlates with the order of thermal stabilities, as evidenced by the decomposition temperatures and peak areas in the thermograms. Each of the copper hydroxychlorides passes through an intermediate phase having the stoichiometry Cu_2OCl_2 before being completely converted to CuO. Sealed tube experiments show that botallackite and atacamite are readily thermally converted to paratacamite, but that the latter can be kept at 500°C for hours without any detectable effects if the products of reaction, *viz.*, H_2O and Cl_2 are not permitted to escape. The relative enthalpies of the thermal decomposition reactions of the hydroxychlorides and the intermediate Cu_2OCl_2 can be deduced from the DSC curves.

INTRODUCTION

The properties of the copper(II) hydroxychlorides have been the subject of considerable interest, especially in recent years. This interest stems in part from the fact that the cupric hydroxychlorides have been identified as products of the corrosion of copper metal and alloys. Furthermore, they are of fundamental interest because of the stepwise and apparently variable modes of decomposition which exist. The basic cupric chloride system consists of four compounds, three of which, botallackite, atacamite, and paratacamite, are naturally occurring and polymorphous, having the composition $\text{Cu}_2(\text{OH})_3\text{Cl}$. The fourth compound, CuOHCl, does not occur as a mineral.

In spite of considerable interest in the thermal decomposition of these compounds, there is little hard data on their relative stabilities and the phase relationships

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which exist among them. The heats of decomposition of the basic cupric chlorides were measured by Ramamurthy and Secco¹, who reported values of 8.07 kcal/mole for the heat of decomposition of CuOHCl , and 21.79, 21.98, and 22.72 kcal/mole for botallackite, atacamite and paratacamite respectively. However their observed thermogravimetric analyses show poor agreement with calculated weight losses based upon their proposed decomposition reactions. Furthermore, they report data for a fourth species of $\text{Cu}_2(\text{OH})_3\text{Cl}$ (referred to as *beta* $\text{Cu}_2(\text{OH})_3\text{Cl}$) which was previously found to be only a mixture of atacamite and paratacamite². The present study undertakes to investigate this system by X-ray powder diffraction and infrared techniques, as well as differential scanning calorimetry.

It has been shown that order-disorder transitions in crystalline substances are accompanied by characteristic changes of their infrared absorption spectra which stem from the changes taking place in the fields polarizing the ions of the crystal lattice^{3,4}. In the case of compounds containing the hydroxyl group, specific relationships between the frequency of absorption and the strength of hydrogen bonding of the type $\text{O}-\text{H}\cdots\text{O}$ are now well established⁵⁻⁷. Hence the IR spectra of the cupric hydroxychlorides may be expected to provide insights into the relative magnitudes and disymmetries of the force fields acting on the lattice constituents. It has been observed that in the case of crystals containing polyatomic anions, such as the inorganic sulfates, the thermal stability decreases with increasing polarizing power of the associated cation⁸. It is of interest to determine whether similar correlations exist for crystals containing partially hydrolyzed transition metal cations, such as the hydroxycopper(II) ions. Comparison of the IR absorption frequencies with relative thermal stabilities deduced from DSC curves should provide us with data germane to this question.

EXPERIMENTAL

All of the compounds used in this study were synthetically prepared by following established procedures⁹. All chemicals used were of reagent grade. Brief descriptions of these procedures are given below.

CuOHCl — Greenish-yellow crystals of pure CuOHCl were prepared by heating 0.1 g $\text{CuO} + 1.0$ g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ for 45 h in a sealed tube at 270°C. After heating, the mixture was filtered and washed with warm ethanol to remove the excess $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. The CuOHCl was kept in a desiccator to prevent interaction with moisture, which causes it to be converted to $\text{Cu}_2(\text{OH})_3\text{Cl}$ ^{10,11}.

Botallackite — A powder consisting of pure botallackite was prepared by allowing synthetic brochantite (copper hydroxysulfate) to stand in contact with unstirred, saturated NaCl solution at 25°C for 48 h. The precipitate was then filtered through a glass Gooch crucible, washed with distilled water and air-dried².

Paratacamite — A powder consisting of fine particles (ca. 0.1–1 micron in linear dimensions) of pure paratacamite was prepared by suspending copper foil (99.99% pure, 0.25 mm thick) in 0.020 *F* CuCl_2 solution which was mechanically

stirred at room temperature for 48 h. The resulting precipitate was filtered through a glass Gooch crucible, washed with distilled water and air-dried. A similar procedure has been reported by Feitknecht and Maget¹¹.

Atacamite — A powder composed of pure atacamite (particle size ca. 0.1–1 micron in linear dimensions) was prepared most conveniently as follows. One gram of finely divided CaCO_3 (*e.g.*, precipitated chalk) was added to 1000 ml of 0.1 *F* CuCl_2 and the mixture was stirred for 2–4 h. At the end of this period, the CaCO_3 had completely dissolved, and about 3.6 g of atacamite powder could be filtered from the solution. Pure atacamite has also been reported to form as a surface deposit on magnesite or calcite spar crystals which have been kept immersed in dilute CuCl_2 for extended periods¹².

Analyses of compounds

The identity and purity of all compounds used were confirmed by the X-ray diffraction patterns for CuOHCl ¹¹, botallackite¹³, paratacamite¹⁴, and atacamite^{9,15}.

Differential scanning calorimetry

The thermograms were recorded with a Perkin–Elmer model DSC-1B differential scanning calorimeter. A 3–9 mg sample was placed in an aluminum cup, with or without a crimped on cover, as desired, and the temperature was increased from 25° to 500°C at a programmed rate of 20°/min. Thermogravimetric data were obtained by heating larger samples (100–500 mg) in porcelain crucibles in an oven at temperatures corresponding to the observed endotherms.

All intermediate and final products of the thermal decomposition of CuOHCl and $\text{Cu}_2(\text{OH})_3\text{Cl}$ were analyzed by X-ray diffraction and standard wet quantitative analysis.

Infra-red analysis

The infrared spectra were recorded by means of a Beckman IR 18 grating spectrophotometer, in the range 600 to 4000 cm^{-1} at a scanning rate of 60 $\text{cm}^{-1}/\text{min}$. The samples were prepared by the KBr disc technique unless otherwise stated. The sample concentration was 0.5% relative to the KBr. The validity of the KBr spectra was verified by comparison with Nujol mulls of the same samples.

RESULTS

Thermogravimetric analysis

The results of the TGA runs are presented in Table I. The proposed reactions for each compound are those which best fit the observed weight loss and are based on X-ray and quantitative analyses of the intermediate and final products of the thermal decomposition.

CuOHCl — This compound decomposes thermally via a two-step process; *viz.*, dehydration, followed by loss of halogen

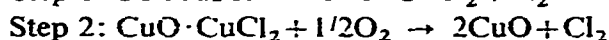
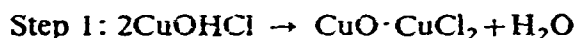


TABLE I

THE THERMAL DECOMPOSITION OF THE COPPER HYDROXYCHLORIDES: THERMAL GRAVIMETRY

Compound	Step ^a number	Temperature ^b range (°C)		Percentage of total wt. lost ^c	
				Observed	Calculated
CuOHCl	1	263;	279	7.8	7.8
	2	431;	457	24.1	23.7
Botallackite	1	251;	281	12.8	12.6
	2	413;	437	12.9	12.9
Atacamite	1	265;	301	12.8	12.6
	2	399;	442	12.8	12.9
Paratacamite	1	254;	295	12.8	12.6
	2	407;	443	12.9	12.9

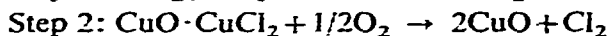
^aThe first step corresponds to dehydration, the second to loss of halogen and the formation of CuO.

^bFor each step is given the temperature of the start followed by that of the maximum of the endotherm.

^cThe observed weight losses were obtained by heating the samples at 260°C for 2 h (for Step 1), and at 500°C for 1 h (for Step 2).

Quantitative analysis of the intermediate product of the thermal decomposition, for copper and chloride, showed excellent agreement with the theoretical percentages of copper and chloride according to the formula $\text{CuO} \cdot \text{CuCl}_2$ (found: 59.4% Cu, 33.1% Cl; theoretical: 59.4% Cu, 33.1% Cl). The X-ray diffraction pattern for this product is identical to that reported by Glasner and Mayer¹⁶ who prepared it by the thermal hydrolysis of anhydrous CuCl_2 . The observed weight losses for each stage of the decomposition are in good agreement with theoretical values based on the above equations. These results are not in agreement with the work of Ramamurthy and Secco¹, who have reported that only a mixture of $\text{CuO} + \text{CuCl}_2$ results from the first stage of the decomposition.

$\text{Cu}_2(\text{OH})_3\text{Cl}$ — All three polymorphic forms of this compound were found to decompose in two consecutive, discrete stages: dehydration, followed by loss of halogen. The following decomposition scheme fully accounts for the percentage weight losses, X-ray diffraction patterns, and stoichiometry.



Quantitative analysis performed on the intermediate products ($\text{CuO} \cdot \text{CuCl}_2 + 2\text{CuO}$) gave an average of 68.1% Cu and 19.0% Cl and a balance of 12.9% O, indicating a molar ratio of $\text{Cu}:\text{Cl} = 2:1$. There are three conceivable intermediates which might give these quantitative results and obey the observed weight losses indicated by the above equations. These are $\text{CuCl}_2 \cdot 3\text{CuO}$ (as reported by Ball and Coultard¹⁷), the mixture $3\text{CuO} + \text{CuCl}_2$ (as reported by Ramamurthy and Secco¹), and the mixture $2\text{CuO} + \text{CuO} \cdot \text{CuCl}_2$. Our X-ray diffraction results clearly establish the presence of both free CuO and the compound $\text{CuO} \cdot \text{CuCl}_2$. There were no diffraction lines which could not be assigned unambiguously to the two species cited.

The intermediate and final products of decomposition were the same for all three modifications of the compound $\text{Cu}_2(\text{OH})_3\text{Cl}$.

Differential Scanning Calorimetry

In the DSC procedure, the sample and reference temperatures are continuously maintained at equal values by control of the power input to the heaters. The DSC record presents the rate of energy absorption as a function of linearly increasing sample temperature. Consequently, on a linear time base recorder, a peak area represents the total enthalpy of the associated transition.

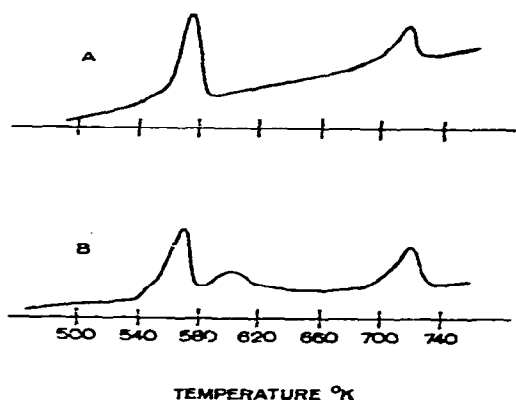


Fig. 1. The differential thermograms of: A, atacamite powder unheated and B, atacamite powder heated with some water in a sealed tube at 150°C for 159 h. Both atacamite specimens were prepared by the same method, namely, reaction of calcite in cupric chloride solution.

Fig. 1 shows thermograms for two specimens of atacamite which differ only in crystalline size and perfection. The finely divided sample (curve A) shows two pronounced endotherms, corresponding to the two stages of decomposition discussed in the preceding section. The sample consisting of larger, more perfect crystals produced by thermal annealing (curve B) shows an additional endotherm following the first one. The total area under these two peaks is greater than that under the single first-stage peak of the finely divided sample. However, for both specimens the thermogravimetric data show the percentage weight losses, and the same dehydration products.

It is, thus, clear that the annealed specimen of atacamite yields a double endotherm for a single dehydration reaction. This double endotherm is due to the two types of crystals present, one less perfect than the other. The less perfect crystals possess strain energy and therefore require less additional energy for decomposition. The more perfect crystals require a greater amount of energy to induce the same reaction. Thus as the proportion of the more perfect crystals increases (due to longer annealing times or higher temperatures) the total energy required for the decomposition increases and the area of the second peak increases at the expense of the first peak. Similar effects of particle size or crystal perfection on the differential thermogram have been reported for organic compounds, such as fats and waxes^{18,19}.

Paratacamite samples differing with respect to particle size and degree of thermal annealing behave in the same fashion as atacamite, as shown by the thermograms of Fig.2. There are only two endothermic stages of decomposition, but the first stage

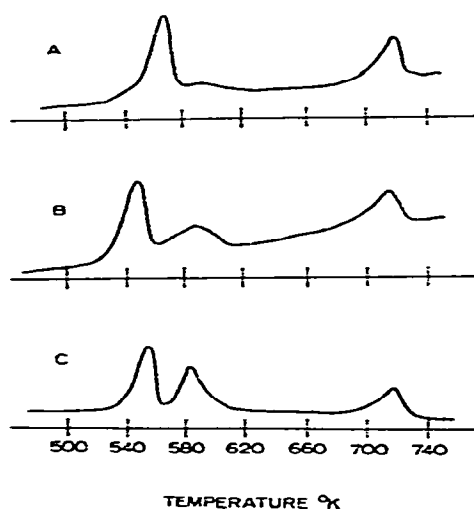


Fig. 2. The differential thermograms showing the influence of thermal history of the specimen: A, the oxidation of copper metal in cupric chloride solution at room temperature; B, the reaction of sodium hydroxide and cupric chloride, evaporated to dryness at 90°C for 3 h; C, a mixture of atacamite and paratacamite heated in a sealed tube in the presence of water, 150°C, 159 h, 100% conversion to paratacamite.

TABLE II
DSC PEAK AREAS FOR ATACAMITE AND PARATACAMITE

Specimen	Weight (mg)	Peak temp. (°C)		Peak area (arbitrary thermal units per mg)			
		Start	Max	Peak 1	Peak 2	Peak 1+2	Peak 3
Atacamite (A)	8.10	265	301	1.07			
		407	442				0.46
Atacamite (B)	9.40	265	296	0.84			
		307	325		0.35	1.19	
		402	446				0.52
Paratacamite (A)	9.40	254	294	1.03			
		307	319		0.13	1.16	
		407	443				0.44
Paratacamite (B)	12.30	252	278	0.78			
		293	312		0.43	1.21	
		400	440				0.40
Paratacamite (C)	9.40	255	282	0.73			
		292	308		0.67	1.40	
		397	441				0.52

evidences itself either as a single endotherm if the specimen consists of very finely divided particles, or a pair of endotherms, the total area of which is greater than that of the single peak, when the particle size has been increased by annealing.

The quantitative results obtained with the specimens depicted in Figs. 1 and 2 are shown in Table II.

In both stages of the decomposition of the copper(II) hydroxychlorides, gaseous products are released. In addition, the second stage involves reaction of an intermediate with atmospheric oxygen. It was observed that the thermogram was sensitive to the method of sample preparation, primarily in the final peak, since good access of air to the particles in the sample cup is necessary if that stage of the reaction is to go to completion rapidly enough to give a good endotherm that can be accurately distinguished from the baseline. Fig. 3, curves B and C, show the effect on the

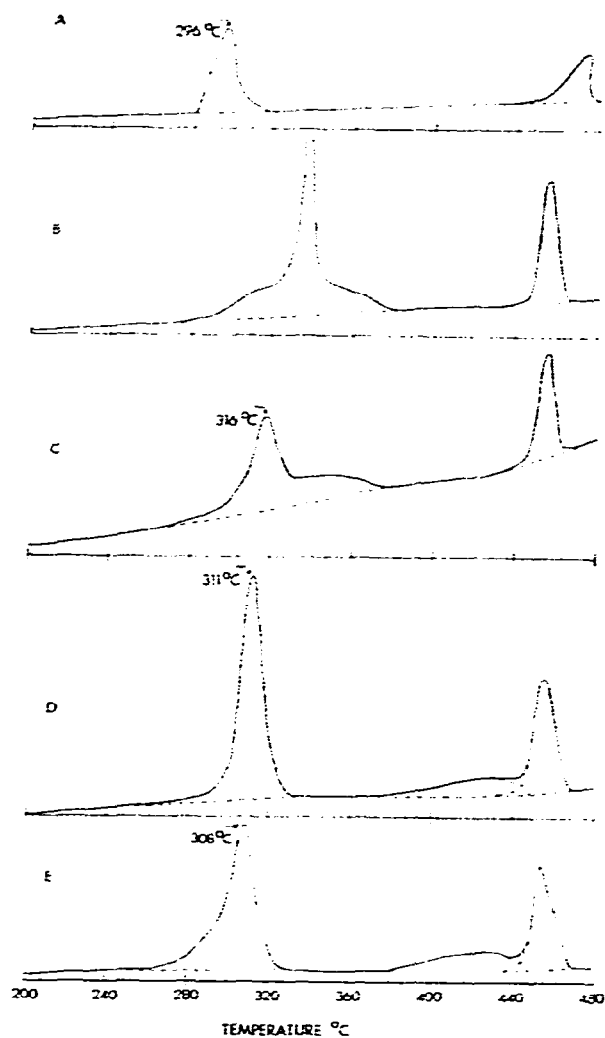


Fig. 3. The differential thermograms of: A, CuOHCl ; B, paratacamite, cover crimped in; C, paratacamite, uncrimped cover; D, atacamite; E, botallackite.

thermogram of placing the sample in an aluminum cup with a tightly crimped-on cover, as compared to a cup whose cover is only resting lightly on the sample.

Therefore, in order to assess the relative enthalpies of reaction of the copper(II) hydroxychlorides, the standard conditions employed were: (a) specimens of very fine particle size, and (b) sample cups with uncrimped covers resting lightly on the powder.

The data obtained in this way are depicted in Fig. 3, and the areas of the respective endotherms, calibrated by reference to indium as the standard, are given in Table III. In the thermograms run as indicated, without crimping on the holder cups, a new endotherm appears just prior to, and overlapping with, the second stage of the decomposition process. This appears to involve a sintering phenomenon occurring among the particles of the product which was generated by the first stage of the decomposition. This is confirmed by the fact that when the final endotherm is corrected for the overlap, its area is the same, within experimental error, for all three polymorphs.

TABLE III
ENTHALPIES OF REACTION FROM DSC THERMOGRAMS

Specimen	Weight (mg)	$\Delta H(\text{cal/g})$		
		Dehydration	Sintering	Oxidation
Paratacamite	3.610	142.5		51.0
Paratacamite	2.820	139.2		55.6
Atacamite	3.690	133.5	31.0	58.0
Botallackite	3.535	119.5	35.0	54.0

Infrared analysis

The infrared absorption spectra yielded the wave numbers of the band maxima which are shown in Table IV, and the corresponding spectra are reproduced in Fig. 4.

The spectra for copper compounds containing the hydroxyl group are usually complex due to the low symmetry of the distorted octahedral coordination about copper. The observed spectra do, however, show two common regions of absorption: $3000\text{--}3600\text{ cm}^{-1}$ and $600\text{--}1000\text{ cm}^{-1}$ representing respectively, the stretching vibration frequencies and the planar deformation frequencies of the hydroxyl group.

The compound CuOHCl exhibits a single peak at 3375 cm^{-1} due to OH stretching, whereas each of the three forms of $\text{Cu}_2(\text{OH})_3\text{Cl}$ exhibits three closely spaced peaks in this region. The polymorphs botallackite, atacamite, and paratacamite are easily distinguishable by their respective IR spectra, especially in the region of the planar deformation frequencies.

Thermal interconversion

For additional insight into the relative stabilities of the basic cupric chlorides, their behaviors at elevated temperatures were studied. In this method 0.7500 g specimens of pure hydroxychloride were sealed in glass tubes (length = 10 cm,

TABLE IV

THE OBSERVED INFRARED ABSORPTION BANDS OF THE CUPRIC HYDROXYCHLORIDES

$Cu_2(OH)_3Cl$			
<i>Botallackite</i>	<i>Atacamite</i>	<i>Paratacamite</i>	<i>CuOHCl</i>
3500 cm^{-1}	3425 cm^{-1}	3420 cm^{-1}	3375 cm^{-1}
3410	3340	3330	900
3395	3320	3280	866 w
870	985	987	853
857	952	926	806
820	920	915 w	
785	900	900 w	
703	870 w	865	
	852	830	
	823 w		

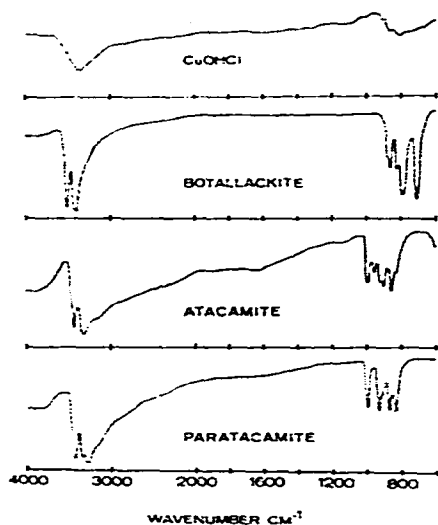
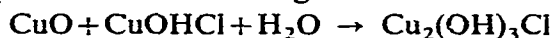


Fig. 4. The infrared spectra of the cupric hydroxychlorides.

width = 1 cm, I.D.) and heated in an oven at various times and temperatures. Volatile decomposition products were thus prevented from escaping, and the samples could be heated as high as 500°C without complete decomposition. The products were then cooled, ground, and submitted to X-ray analysis.

The compound $CuOHCl$ is quite unstable with respect to $Cu_2(OH)_3Cl$, being quickly converted to it in the presence of moisture even at room temperature²⁰. We have found that paratacamite is the only modification formed under these conditions. Furthermore in the preparation of $CuOHCl$, an excess of $CuCl_2 \cdot 2H_2O$ must be used in relation to CuO or else the $CuOHCl$ formed reacts with any unconverted CuO to give paratacamite according to:



Stoichiometric amounts of the above starting materials were heated in a sealed tube at 250°C for 20 h to verify the correctness of the above equation.

The botallackite modification of $\text{Cu}_2(\text{OH})_3\text{Cl}$ is unstable with respect to atacamite and paratacamite. For example, in the preparation of botallackite, synthetic basic copper sulfate is allowed to stand in saturated NaCl for 48 h, during which time the sulfate ions are topochemically replaced by chloride ions to form botallackite. We have observed that the absence of stirring is critical for the replacement, and that the product will be paratacamite if stirring is employed. Botallackite also converts to pure paratacamite when heated in a sealed tube; 100% conversion being obtained after heating moist botallackite at 80°C for 20 h.

Oswald and Feitknecht² have observed that atacamite transforms to paratacamite when heated in a sealed tube at 200°C for 48–72 h; hence paratacamite is the more stable modification at least at 200°C. These workers concluded from the presumption that the formation of atacamite appears above all to be promoted by a very limited reaction velocity (slow hydrolysis of dilute CuCl_2 containing urea for one year, or magnesite crystals suspended in CuCl_2 for several months), and the frequent occurrence of atacamite in nature, that atacamite is more stable than paratacamite at room temperature, and that the situation becomes reversed at some temperature below 200°C.

It has been shown⁹, however, that a limited reaction velocity is not essential to the formation of atacamite, since it can be prepared conveniently and rapidly by reaction of finely divided CaCO_3 with dilute CuCl_2 . Furthermore, we have found no temperature at which paratacamite thermally converts to atacamite at temperatures from 200°C down to room temperature, whether the paratacamite is dry, in water, or in the presence of aqueous CuCl_2 solutions of various concentrations. Atacamite heated in the dry state in a sealed tube readily converts to paratacamite at temperatures ranging from 500° down to 170°C. When a small amount of water and some seeds of paratacamite are added to the starting atacamite, this conversion temperature can be reduced to around 120°C. No atacamite–paratacamite interconversion was found to take place at lower temperatures, even with heating times up to 840 h. These results are summarized in Table V. The influence of a small amount of added water on the rate of conversion of atacamite to paratacamite is shown by the results at 170°C; one gram of dried atacamite heated for 110 h showed only an 18% conversion to paratacamite, while in the presence of several drops of water 100% conversion was obtained in the course of 90 h. A 50:50 atacamite–paratacamite mixture heated at 150°C for only 63 h showed 100% conversion, the presence of paratacamite quite clearly increasing the rate of conversion.

DISCUSSION

For the interpretation of phase formation and transformation studies it is essential to know the relative stabilities of the several phases involved. An objective of the present work is to establish the order of thermodynamic stabilities for the

TABLE V

THE THERMAL INTERCONVERSION OF THE CUPRIC TRIHYDROXYCHLORIDES IN A SEALED TUBE

Starting material	Temperature (°C)	Time (h)	Percent conversion	Conditions
Botallackite	80	20	100 ^a	H ₂ O
Paratacamite	500	7	0 ^b	dry
	280	192	0	dry
	80	840	0	H ₂ O
Atacamite	280	14	100 ^a	dry
	170	110	18	dry
	150	200	0	dry
	170	9	21	H ₂ O
	170	30	40	H ₂ O
	170	90	100	H ₂ O
	80	840	0	H ₂ O
Atacamite- paratacamite (50:50)	150	63	100 ^a	H ₂ O
	120	282	50	H ₂ O

^aPercent conversion to paratacamite. ^bPercent conversion to atacamite.

polymorphs of copper(II) trihydroxychloride, the kinetics and mechanism of formation of which have been the subject of several investigations^{1,2,9,11}.

Three independent lines of evidence support the conclusion that at ordinary pressures the most stable polymorph is paratacamite, that atacamite is slightly less stable, and that botallackite is very much less stable.

(1) Both botallackite and atacamite, when heated in sealed tubes, convert completely to paratacamite. For botallackite, this thermal conversion can be produced at as low a temperature as 80°C; for atacamite at 120°C. Paratacamite does not transform into either of the other two polymorphs under any conditions of heating and seeding.

(2) The enthalpies of dehydration of the polymorphs are: paratacamite 141.0, atacamite 133.5, botallackite 119.5 cal/g; the average deviation in the measurements is ± 2 cal/g. In the case of substances of a given chemical type which decompose to yield common gaseous products, differences in stability are due to ΔH^0 , since ΔS^0 values arise primarily from the formation of the gaseous product. Therefore, in the present case, ΔS^0 is the same for all three polymorphs, and the measured enthalpies of reaction are valid measures of the thermodynamic stabilities of the respective polymorphs.

(3) The crystal structures of the three forms of $\text{Cu}_2(\text{OH})_3\text{Cl}$ are complex, and there are four or more different environments about the OH groups in each case, as indicated in Table VI. Hence, there is considerable splitting in the hydrogen-stretch region of the IR spectrum. Nevertheless, it is clear that the trend of the frequencies of the OH stretches taken as a group is: paratacamite < atacamite < botallackite. From the well established relations between hydrogen stretch frequencies and $\text{O-H}\cdots\text{O}$

TABLE VI

STRUCTURE CONSTANTS FOR THE CUPRIC HYDROXYCHLORIDES

Compound	Symmetry	Lattice dimensions	Distances from Cu in the Octahedron (A)		Ref.
			Near	Far	
CuOHCl	Monoclinic	$a=5.555$ $b=6.671$ $c=6.127$ $\beta=114^{\circ}53'$	3 OH 2.01 1 Cl 2.30	2 Cl 2.71	23
Botallackite	Monoclinic	$a=5.73$ $b=6.12$ $c=5.63$ $\beta=93^{\circ}45'$	2 OH 1.86 2 OH 1.95 4 OH 1.97	2 Cl 2.76 1 Cl 2.86 1 OH 2.37	24
Atacamite	Orthorhombic	$a=6.01$ $b=9.13$ $c=6.84$	2 OH 2.04 2 OH 2.00 2 OH 1.94 2 OH 2.07	2 Cl 2.76 1 OH 2.36 1 Cl 2.75	25
Paratacamite	Rhombohedral	$a=9.17$ $\alpha=96^{\circ}28'$	4 OH 4 OH	2 OH 2 Cl	26

bond length^{5,7,21,22}, it follows that the strength of the hydrogen-bonding in the solid phase is greatest for paratacamite and least for botallackite. Stronger hydrogen-bonding in these closely related structures would be associated with greater free energy of formation of the phase, and hence greater stability.

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