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γ-$Cu_2(OH)_3Cl$ as precursor in the preparation of copper (I) and (II) oxides and copper powder

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When γ-$Cu_2(OH)_3Cl$ is decomposed in air or nitrogen flow, different amounts of cuprous oxide are obtained as final product depending on both the heating rate and the ambient atmospheres. However, the temperature of formation of cuprous oxide only appears to depend on the partial pressure of oxygen. When thermal decomposition is carried out under dynamic vacuum in the X-ray high-temperature diffraction chamber, using a tantalum strip as the heating element, copper is obtained as final product at a comparatively low temperature.

1. Introduction

The influence of experimental conditions on the mechanism through which thermal decomposition occurs is well known [1, 2]; as a consequence, the properties of the materials so obtained and the yields of the reactions are deeply modified, this being particularly remarkable if during the decomposition processes some volatile compounds are formed.

On the other hand, when some organometallics or some organic salts (mainly oxalates and formates) are thermally decomposed under suitable conditions, the formation of the metal results [3] and this possibility has been widely explored in order to obtain certain metals, e.g. copper powder among others [4–11]. However, there are quite a few examples in which from the thermal decomposition of inorganic salts, pure copper metal is obtained as the final product [12–14].

Previous studies on thermal decomposition of γ-$Cu_2(OH)_3Cl$ have been carried out by previous authors [15–19] arriving at slightly different results that could be explained on the basis of the different experimental conditions used. We have considered it worthwhile to examine systematically the decomposition reactions of γ-$Cu_2(OH)_3Cl$ in order to correlate the results obtained up to date, as well as to state the influence of the experimental conditions on the mechanisms through which copper hydroxychloride decomposes, bearing in mind the many catalytic applications of the several products formed along the thermolysis reactions; copper (I) and (II) chlorides, oxides and copper powder, and also considering that thermal decomposition of this basic salt is a method that affords a very convenient route for the preparation of the above indicated compounds.

2. Experimental techniques

Paratacamite γ-$Cu_2(OH)_3Cl$ has been prepared as described elsewhere [20]; briefly by incomplete precipitation of 0.2 M solution of $CuCl_2 \cdot 2H_2O$ with 0.4 M NaOH, followed by ageing at 70° C for 30 days. The precipitate was filtered off and washed with alcohol and acetone, and kept on phosphorous pentoxide. The chlorine and copper analyses and the X-ray diffraction diagram [21] showed that the compound was paratacamite.

The thermograms were recorded on a Stanton 781 Simultaneous Thermal Analysis System in still or air flow and in nitrogen flow at several heating rates (2 to $10^\circ\,C\,min^{-1}$). Platinum–rhodium crucibles and Al_2O_3 as reference were used. A Dupont 951 thermobalance joined to a Dupont 990 equipment was occasionally used. The intermediates and final products were identified by X-ray diffraction and infrared spectroscopy. Chlorine evolution, when it occurred, was qualitatively tested by the pink colour developed in a filter paper impregnated with fluorescein and KBr solutions [22].

The X-ray high-temperature diffraction diagrams were obtained on an Anton PAAR HTK 10 attachment mounted on a Philips PW 1310 equipment. The sample was deposited on a platinum sheet placed on a tantalum strip which acts as the heating element. The temperature was measured using a Pt–Pt 13% Rh thermocouple welded on to the centre of the platinum sheet. Vacuum (4.5×10^{-3} mm Hg) was accomplished by a liquid nitrogen trapped rotary pump and it was monitored by a vacuum gauge placed in the chamber cover. Temperature was increased in 10 degree steps and allowed to stabilize; the X-ray diagrams were then scanned or, alternatively, several diagrams were recorded while the temperature was held at some defined values; Cu$K\alpha$, nickel-filtered radiation was used.

3. Results

3.1. Thermal decomposition studies at low heating rate ($2^\circ\,C\,min^{-1}$), air flow and still air environments

Under these conditions, copper (II) hydroxychloride dehydroxylates in one or two consecutive steps, as can be seen respectively in the DTA and TG curves shown in Figs 1a and b. The weight losses and the temperature ranges in which they occur in addition to the temperature of the DTA peaks are shown in Table I.

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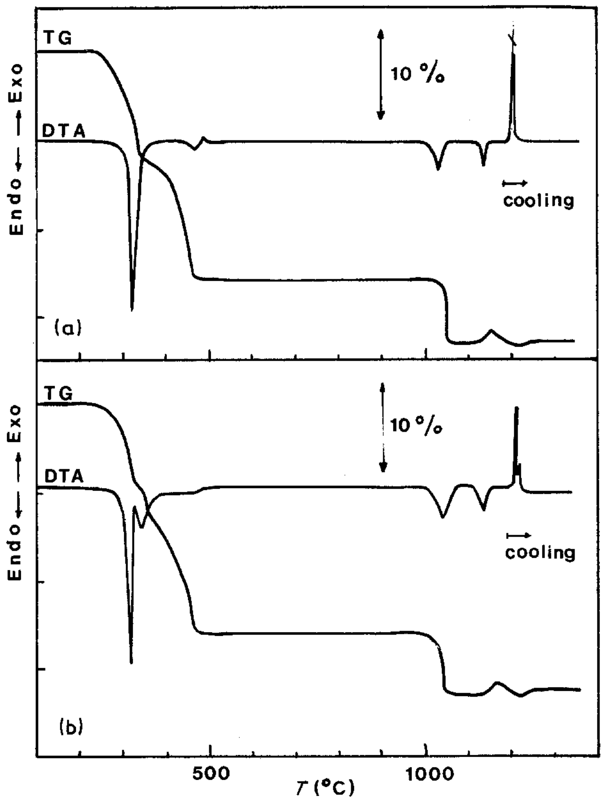

Figure 1 DTA and TG curves of γ-$Cu_2(OH)_3Cl$ obtained at 2° C min^{-1} heating rate in (a) air flow, (b) still air.

It is most probable that copper hydroxychloride Cu(OH)Cl is formed as an intermediate when the initial compound dehydroxylates in still air, but the data provided by the X-ray diffraction and infrared spectroscopy are not conclusive. The X-ray diffraction diagrams obtained on samples heated up to 320° C show the $Cu_2(OH)_3Cl$ and CuO diffraction lines and also two shoulders at angles of 15.90° and 32.61° 2θ; their interplanar spacings are those of the (1 0 0) and (1 2 $\bar{1}$) most intense lines of Cu(OH)Cl [23]. The infrared spectrum shows features of $Cu_2(OH)_3Cl$ and the OH stretching bands are clearly resolved.

Copper (II) oxychloride and oxide are identified on samples heated up to 350° C [23, 24] and chlorine is evolved between this temperature and 456° C; it was tested qualitatively as indicated above; copper oxychloride decomposes and simultaneously oxidizes to cupric oxide.

The experimental weight losses agree with those reported by Ball and Coultard for the thermal decomposition of γ-$Cu_2(OH)_3Cl$. The main differences lie in the decomposition ranges [16].

At low heating rates the formation of cupric oxide is almost quantitative and there is no evolution of any copper halide. This result is in agreement with that obtained by Kiss and Lloyd [19] at low heating rates (3° C min^{-1}), although they did not identify the unstable intermediate $Cu_4Cl_2O_3$, a mixture of Cu_2OCl_2 and CuO, because the X-ray powder diagram was recorded at an inadequate temperature (300° C).

3.2. Thermal decomposition studies at high-heating rate (10° C min^{-1}); air flow or still-air environments

The dehydroxylation reaction occurs, as at low heating rates, in one or two consecutive steps depending on the environmental conditions (see Table II and Figs 2a and b) and in both cases Cu_2OCl_2 and CuO were the compounds identified at 360° C. From this temperature up to 462° C the evolution of chlorine occurs and it is particularly evident when the thermograms are recorded in the 951 Dupont thermobalance in air flow, that because of the strong smell of chlorine, it was qualitatively recognized.

From 460° C up to about 650° C condensation of a yellow product on the colder parts of the quartz tube of the Dupont thermobalance is observed; a yellow film is also formed in the upper cold part of the Stanton equipment. The X-ray diagram of this yellow product showed the most intense lines of anhydrous cupric chloride [25] which rapidly transforms into the dihydrated form [26] on standing in the open air.

When cupric oxychloride is thermally decomposed in air, it transforms into cuprous chloride, cupric oxide and chlorine which can react with some oxide to yield cupric chloride [18]. Accordingly, the following overlapping reactions can be assumed to occur in the temperature range 360 to 465° C.

$$Cu_2OCl_2 \rightarrow CuCl + CuO + \tfrac{1}{2}Cl_2 \qquad (1)$$

$$\tfrac{1}{2}CuO + \tfrac{1}{2}Cl_2 \rightarrow \tfrac{1}{2}CuCl_2 + \tfrac{1}{4}O_2 \qquad (2)$$

$$CuCl \xrightarrow{+\frac{1}{2}O_2} CuO + \tfrac{1}{2}Cl_2 \qquad (3)$$

$$Cu_2OCl_2 \xrightarrow{+\frac{1}{2}O_2} \tfrac{3}{2}CuO + \tfrac{1}{2}CuCl_2 + \tfrac{1}{2}Cl_2 + \tfrac{1}{4}O_2 \qquad (4)$$

The calculated weight loss for the overall Reaction 4 is 12.83%, being the experimental values 11.34% and 13.33% calculated from the data obtained on thermograms recorded in still or air flow, respectively.

The extension and completion of the above reactions will be affected by the environmental conditions and, consequently, some small differences between the experimental and calculated weight losses might be expected.

Later, the cupric chloride thus formed is evolved and cupric oxide is the product isolated up to 1030° C, when it transforms into cuprous oxide which melts at 1140° C with a slight weight gain caused by the picking up of some oxygen [19]. A continuous weight loss of the liquid sample is observed up to the final programmed temperature; this is caused by the evolution of oxygen in the melted sample as well as by the removal of some liquid cuprous oxide.

The experimental and theoretical weight losses calculated according to the proposed reactions are indicated in Table II. In air atmosphere, the temperature of the reaction

$$CuO \rightarrow \tfrac{1}{2}Cu_2O + \tfrac{1}{2}O_2$$

is not affected by the heating rate, as can be seen in Tables I and II, neither is it the temperature at which Cu_2O melts, it being about 100° C lower than the reported melting point [27], but it is in agreement with the data of Kiss and Lloyd [19].

TABLE I Thermal decomposition data of $Cu_2(OH)_3Cl$. Heating rate 2° C min^{-1}

Stages	Still air							Air flow (50 ml min^{-1})						
	Decomposition range: DTA peaks (° C)			TG steps		% found*	% calc.*	Decomposition range: DTA peaks (° C)			TG steps		% found*	% calc.*
	T_i	T_m	T_f	T_i	T_f			T_i	T_m	T_f	T_i	T_f		
I	306	320	322	279	320	8.67	8.42	310	322	337	275	337	12.50	12.64
I bis	322	337	341	320	341	3.83	4.22							
II				341	456	13.52	12.86				341	456	13.85	12.86
III	1025	1037	1042	1027	1040	6.78	7.50	1024	1036	1045	1025	1041	7.99	7.50
IV	1133	1140	1141	1137	1141	1.55†	weight gain	1132	1139	1140	1129	1140	1.5†	weight gain

$$2Cu_2(OH)_3Cl \xrightarrow{I} [2Cu(OH)Cl + 2CuO + 2H_2O\uparrow] \xrightarrow{I\ bis}$$
$$\rightarrow Cu_2OCl_2 + 2CuO + H_2O\uparrow \xrightarrow[+\frac{1}{2}O_2]{II} 4CuO + Cl_2\uparrow \xrightarrow{III}$$
$$\rightarrow 2Cu_2O + O_2\uparrow \xrightarrow{IV} Cu_2O \text{ melts}$$

*Weight losses have been calculated as a percentage of the original sample.

†Weight gain calculated as a percentage of the actual sample weight.

TABLE II Thermal decomposition data of $Cu_2(OH)_3Cl$. Heating rate 10° C min^{-1}.

Stages	Still air							Air flow (50 ml min^{-1})						
	Decomposition range: DTA peaks (° C)			TG steps		% found*	% calc.*	Decomposition range: DTA peaks (° C)			TG steps		% found*	% calc.*
	T_i	T_m	T_f	T_i	T_f			T_i	T_m	T_f	T_i	T_f		
I	279	337	347	279	337	8.19	8.42	279	341	370	281	360	12.37	12.64
I bis	347	356	376	337	362	4.22	4.22							
II	438	460	479	362	462	5.63	6.43	434	457	475	360	466	6.70	6.43
III	622	631	637	462	647	16.08	15.74				466	615	12.88	15.74
IV	1034	1045	1053	1035	1053	6.75	6.55	1032	1045	1052	1033	1052	6.70	6.55
V	1126	1140	1145	1133	1141	1.72	weight gain	1126	1140	1144	1133	1144	1.33	weight gain

$$2Cu_2(OH)_3Cl \xrightarrow{I} Cu_2OCl_2 + 2CuO + 3H_2O\uparrow \xrightarrow[+\frac{1}{2}O_2]{II} \left[\quad\right]$$

$$\rightarrow \tfrac{7}{2}CuO + \tfrac{1}{2}Cl_2\uparrow + \tfrac{1}{4}O_2\uparrow + \tfrac{1}{2}CuCl_2 \xrightarrow{III}$$

$$\rightarrow \tfrac{1}{2}CuCl_2\uparrow + \tfrac{7}{2}CuO \xrightarrow{IV} \tfrac{7}{4}Cu_2O + \tfrac{7}{8}O_2\uparrow \xrightarrow{V} Cu_2O \text{ melts}$$

$$\left[\begin{array}{c} Cu_2OCl_2 \rightarrow CuO + CuCl + \tfrac{1}{2}Cl_2 \\ \tfrac{1}{2}CuO + \tfrac{1}{2}Cl_2 \rightarrow \tfrac{1}{2}CuCl_2 + \tfrac{1}{4}O_2 \\ CuCl \xrightarrow{+\frac{1}{2}O_2} CuO + \tfrac{1}{2}Cl_2 \\ Cu_2OCl_2 \xrightarrow[+\frac{1}{2}O_2]{II} \tfrac{3}{2}CuO + \tfrac{1}{2}CuCl_2 + \tfrac{1}{2}Cl_2 + \tfrac{1}{4}O_2 \end{array}\right]$$

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*Weight losses have been calculated as a percentage of the original sample.

†Weight gain calculated as a percentage of the actual sample weight.

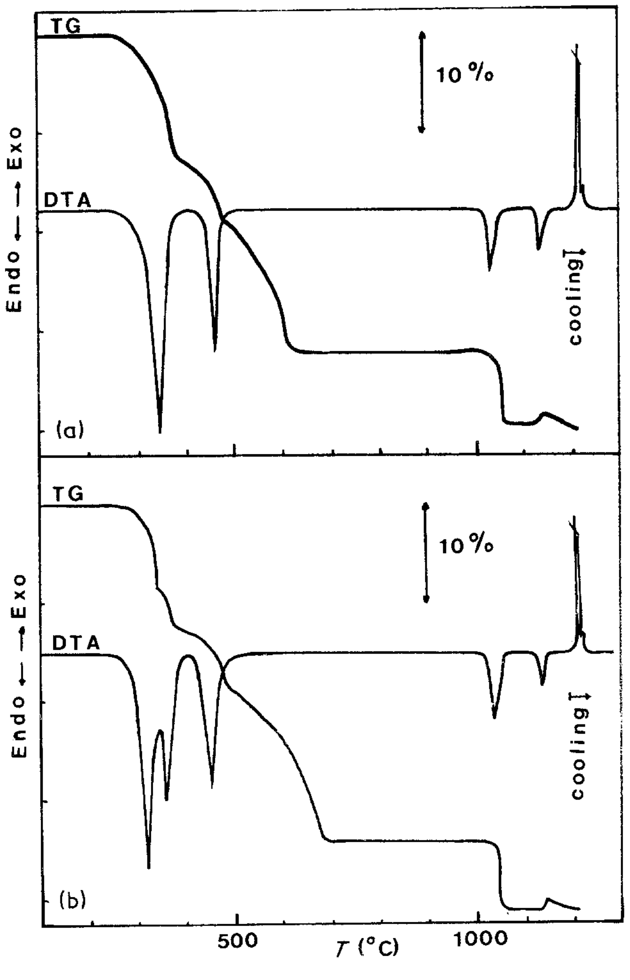

Figure 2 DTA and TG curves of γ-$Cu_2(OH)_3Cl$ obtained at 10° C min^{-1} heating rate in (a) air flow, (b) still air.

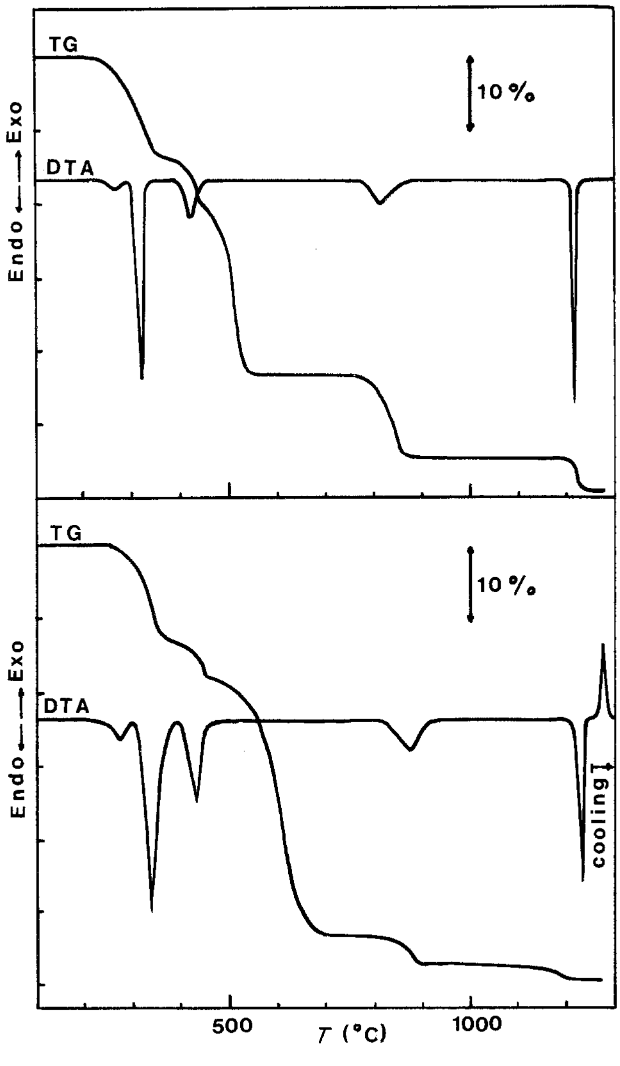

Figure 3 DTA and TG curves of γ-$Cu_2(OH)_3Cl$ obtained in nitrogen flow at (a) 2° C min^{-1}, (b) 10° C min^{-1} heating rates.

3.3. Thermal decomposition studies in nitrogen atmosphere at low and high heating rates (2 and 10° C min^{-1})

The thermograms recorded in nitrogen flow (50 ml min^{-1}) at the heating rates given above, are shown in Figs 3a and b. The main differences between them lie in the usual shift of the initial and final reaction temperatures when the higher heating rate is used, as well as in the experimental weight losses, after dehydroxylation. Consequently, different reaction mechanisms will rule depending on the selected heating rate.

At low heating rate, the intermediate cupric oxychloride identified at 320° C together with cupric oxide, will decompose:

$$Cu_2OCl_2 \rightarrow CuO + CuCl + \tfrac{1}{2}Cl_2$$

Chlorine and cuprous chloride are evolved in two consecutive steps, the latter condenses on the cold parts of the instrument and can be easily identified; cupric oxide is obtained at 530° C.

At 10° C min^{-1}, as the experimental weight loss is considerably higher, chlorination of some cupric oxide must be considered and the proposed reactions are:

$$Cu_2OCl_2 \rightarrow CuO + CuCl + \tfrac{1}{2}Cl_2 \qquad (5)$$

$$\tfrac{1}{2}CuO + \tfrac{1}{4}Cl_2 \rightarrow \tfrac{1}{2}CuCl + \tfrac{1}{4}O_2 \qquad (6)$$

$$Cu_2OCl_2 \rightarrow \tfrac{3}{2}CuCl + \tfrac{1}{2}CuO + \tfrac{1}{4}Cl_2 + \tfrac{1}{4}O_2 \qquad (7)$$

The evolution of chlorine and cuprous chloride has been tested, as has been the formation of cupric oxychloride and oxide as intermediates in the decomposition process, but the evolution of oxygen could not be verified. On the other hand, cupric chloride has not been isolated in any of the decomposition steps when decomposition is carried out in a nitrogen atmosphere.

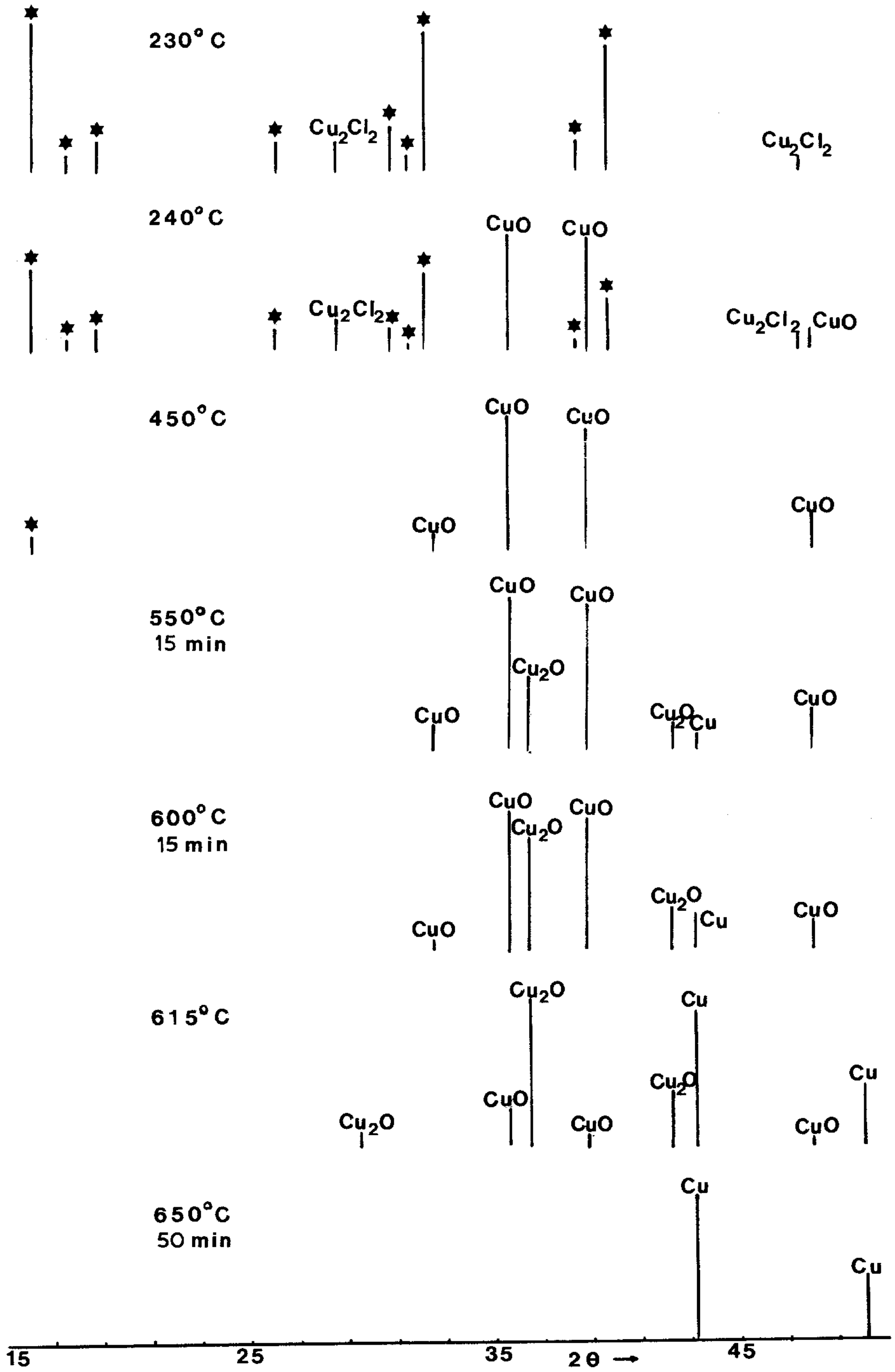

Figure 4 Evolution of γ-$Cu_2(OH)_3Cl$ in the X-ray high-temperature diffraction chamber. *γ-$Cu_2(OH)_3Cl$.

TABLE III Thermal decomposition data of $Cu_2(OH)_3Cl$ in nitrogen flow (50 ml min^{-1})

Stages	Decomposition range: DTA peaks (° C)			TG steps		% found*	% calc.*	Decomposition range: DTA peaks (° C)			TG steps		% found*	% calc.*
	T_i	T_m	T_f	T_i	T_f			T_i	T_m	T_f	T_i	T_f		
Heating rate: 2° C min^{-1}								*Heating rate*: 10° C min^{-1}						
I	242	258	262					255	279	300				
				244	355	12.50	12.64				258	360	12.56	12.64
	302	320	341					300	339	374				
II	392	419	434	335	423	6.78	8.28	399	434	466	360	438	4.92	6.02
III				423	530	27.42	23.2				438	637	35.52	34.78
IV	806	834	839	785	836	5.75	5.62	788	873	884	788	881	4.92	4.70
V	1227	1228	1231	1227	1244	5.19†		1224	1227	1228	1227	1244	6.96†	

$$2Cu_2(OH)_3Cl \xrightarrow{I} Cu_2OCl_2 + 2CuO + 3H_2O\uparrow \rightarrow$$

$$\xrightarrow{II} 3CuO + CuCl + \tfrac{1}{2}Cl_2\uparrow \xrightarrow{III} 3CuO + CuCl\uparrow \rightarrow$$

$$\xrightarrow{IV} \tfrac{3}{2}Cu_2O + \tfrac{3}{4}O_2\uparrow \xrightarrow{V} Cu_2O \text{ melts}$$

$$2Cu_2(OH)_3Cl \xrightarrow{I} Cu_2OCl_2 + 2CuO + 3H_2O \xrightarrow{II} \left[\quad\right] \rightarrow$$

$$\rightarrow \tfrac{5}{2}CuO + \tfrac{3}{2}CuCl + \tfrac{1}{4}Cl_2\uparrow + \tfrac{1}{4}O_2\uparrow \rightarrow$$

$$\xrightarrow{III} \tfrac{5}{2}CuO + \tfrac{3}{2}CuCl\uparrow \xrightarrow{IV}$$

$$\rightarrow \tfrac{5}{4}Cu_2O + \tfrac{5}{8}O_2\uparrow \xrightarrow{V} Cu_2O \text{ melts}$$

$$\left[\begin{array}{c} Cu_2OCl_2 \rightarrow CuO + CuCl + \tfrac{1}{2}Cl_2 \\ \tfrac{1}{2}CuO + \tfrac{1}{4}Cl_2 \rightarrow \tfrac{1}{2}CuCl + \tfrac{1}{4}O_2 \\ Cu_2OCl_2 \rightarrow \tfrac{3}{2}CuCl + \tfrac{1}{2}CuO + \tfrac{1}{4}Cl_2 + \tfrac{1}{4}O_2 \end{array}\right]$$

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*Weight losses have been calculated as a percentage of the original sample.

†Weight gain calculated as a percentage of the actual sample weight.

Cupric oxide transforms into cuprous oxide between 785 and 836° C or 796 and 881° C, depending on the heating rate, and melts in both cases, at 1227° C. In nitrogen flow, melting is not accompanied by any mass increase, but once cuprous chloride is liquid the continuous weight loss observed when the thermograms were obtained in air, also occurs in nitrogen, and it is especially pronounced at the low heating rate.

The most outstanding result obtained when the decomposition is carried out in a nitrogen atmosphere refers to the comparatively low temperature at which cupric oxide transforms into cuprous oxide. On the other hand, this oxide melts at the usually reported temperature (1223° C), that is higher than the values obtained for the melting temperature in air. The slightly different results reported in the literature can be explained in terms of the experimental conditions used by the different authors and in fact, the overlapping of some of the reactions indicated above cannot be rejected. Nevertheless, the obtention of the decomposition products formed during the thermolysis of γ-$Cu_2(OH)_3Cl$ can be considerably improved if the experimental conditions are very carefully chosen.

3.4. X-ray high-temperature diffraction studies

When γ-$Cu_2(OH)_3Cl$ is decomposed under a dynamic vacuum of 4.5×10^{-3} mm Hg in the X-ray high-temperature diffraction chamber, it transforms in the way shown in Fig. 4.

The X-ray diffraction lines of copper oxychloride have never been observed, but those of cuprous chloride are clearly seen in the diagrams recorded between 230 and 350° C. If copper oxychloride is formed, it will rapidly decompose, and cupric oxide is the only product observed at 450° C.

Cuprous oxide begins to appear at about 550° C and from this temperature up to 615° C its characteristic diffraction lines progressively increase; it is the main component of the mixture Cu_2O–CuO–Cu existing at 615° C.

Later the temperature was held at 650° C and several X-ray diagrams were scanned every 5 min; after 50 min the X-ray diagram was that of pure copper [28], which was the final product.

In order to prepare some larger amounts of copper powder, different specimens, placed in a platinum boat, were heated in a furnace under the same vacuum conditions previously used; all the attempts were unsuccesful, the final products were copper (I) or (II) oxides depending on the limit temperatures.

A new experiment was then performed in the high-temperature chamber, but on this occasion a platinum strip was used as the heating element. The evolution of the compound was markedly different. The salt began to decompose at about the same temperature (240° C) and between 480 and 680° C the X-ray diagram was that of cupric oxide. Cuprous oxide was not formed until the 680° C was reached and it was obtained as a pure compound from 780 up to 925° C; copper could never be obtained.

From these experimental data it is inferred that tantalum has a non-passive role in the reaction. The characteristics and properties of the metal and of the oxides formed in the decomposition reactions are being studied.

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