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The solid state reaction of $CuCl_2{\cdot}2H_2O$ and 8-hydroxylquinoline

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Abstract

$CuCl_2{\cdot}2H_2O$ reacts with 8-hydroxylquinoline (short as HQ) in two steps if the reactants are mixed in 1 : 2 molar ratio: first, it produces a new intermediate, $Cu(HQ)Cl_2$, and then the intermediate reacts with free 8-hydroxylquinoline and produces CuQCl. However, the same reactants can only give CuQCl or CuQ_2 in the methanol solution. Reasons that lead to those results are discussed. © 1997 Elsevier Science B.V.

Keywords: DSC; Mechanism; Reaction; Solid; XRD

1. Introduction

Unlike reactions among high melting point oxides, solid-state coordination reactions usually take place at much lower temperatures [1,2], so they might be controlled kinetically [3]. Some additional reactions were found, where ligands used were 2,2′-bipyridyl analoges [4,5]. In order to find out whether metathetic reactions can also be controlled kinetically, we have used a new type of ligands that have Brϕnsted acidity.

We have reported that the solid-state reaction of $CuCl_2{\cdot}2H_2O$ and 8-hydroxylquinoline (HQ) in 1 : 1 molar ratio produces a new intermediate [6], $Cu(HQ)Cl_2$. This paper reports their reaction in 1 : 2 molar ratio.

2. Experimental

2.1. Reagents

Analytical grade $CuCl_2{\cdot}2H_2O$ and 8-hydroxylquinoline were obtained from Shanghai Chemicals Factory and used after being ground and passed through 180 mesh sieve.

CuQCl was synthesized according to a literature method [7]. The composition found was C: 44.04, H: 2.57, N: 5.66; Calcd. for $Cu(C_9H_6NO)Cl$ C: 44.35, H: 2.46, N: 5.75.

$[H_2Q]Cl{\cdot}H_2O$ was prepared from a yellow solution of HQ in dilute hydrochloric acid, which was put into a desiccator. The composition found was C: 54.79, H: 5.13, N: 6.80; Calcd. for $(C_9H_8NO)Cl{\cdot}H_2O$ C: 54.15, H: 5.05, N: 7.02.

2.2. Physical measurements

XRD patterns were measured on a Shimadzu XD-3A diffractometer with CuK_α radiation and Be filter; IR on a Nicolet FTIR-170sx with KBr discs and elemental analysis on a 240C microanalyzer. They were used to characterize the products.

TG/DTA measurements were carried out on a TG/DTA meter, which was manufactured by Shanghai Analytical Apparatus Factory, to investigate

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thermal stability of the product under the condition of N_2 atmosphere, gas-flow rate 10 cm^3/min, temperature scan rate 10°C/min, sample weight ca. 10 mg.

DSC curves were measured on a Setaram micro-DSC, using closed cells that had an effective volume of 1 cm^3 Al_2O_3 as reference. The scan rate of temperature was 0.5°C/min, and the temperature range was from 24 to 90°C. They were used to trace reactions.

At 24°C and relative humidity 70% accurately weighed $CuCl_2{\cdot}2H_2O$ and HQ in 1 : 2 molar ratio were carefully mixed in an agate mortar by grinding the reactants as lightly as possible to prevent deep reaction, then rapidly transferred into the calorimeter to measure its DSC curve.

The DSC curve of the reaction between $Cu(HQ)Cl_2$ and HQ in 1 : 1 molar ratio was obtained in a similar way.

2.3. *Reactions under other conditions*

The following experiments were performed to study the pathway of the title reaction: $CuCl_2{\cdot}2H_2O$ and 8-hydroxylquinoline were accurately weighed in 1 : 2 molar ratio and being ground continuously in an agate mortar at room temperature.

The same reaction was also carried out without the mixture being ground. After the starting materials were lightly ground to get the best homogeneity, the mixture was transferred into a covered tube and put into a thermostat at 70°C. XRD pattern of the mixture was measured after 5 h, which showed the reaction had been completed.

3. Results and discussion

3.1. *The characterization of the product*

The product of the reaction between $CuCl_2{\cdot}2H_2O$ and 8-hydroxylquilonine in 1 : 2 molar ratio was dried and analyzed without any further treatment. The composition found is C: 38.14, H: 2.57, N: 4.95, and calcd. for $Cu(C_9H_7NO)_2Cl_2{\cdot}H_2O$ C: 38.57; H: 2.50, N: 5.00. Since its XRD pattern has no diffraction peaks of starting materials, the reaction completes. A series of measurements were carried out to characterize the product. The results are:

Table 1
Important IR bands of the related substances

Reaction product	CuQCl	$[H_2Q]Cl{\cdot}H_2O$	Assignments
3327		3335	ν_{OH} (H_2O)
2800–2500		2800–2500	$\nu_{ammonium}$
1629		1629	ν_{OH} (H_2O)
		1633	ν_{OH} (HQ)
1112	1113		$\nu_{C\text{–}O}$
1097		1097	$\nu_{C\text{–}O}$
316	318		$\nu_{Cu\text{–}O}$
272	275		$\nu_{Cu\text{–}N}$
202	203		$\nu_{Cu\text{–}Cl}$

1. IR spectrum of the product has absorption bands of ammonium ions [8] and other bands of CuQCl and $[H_2Q]Cl{\cdot}H_2O$ (Table 1) [9–11].
2. When the product was washed thoroughly with alcohol and acetone, a yellow filtrate was formed and XRD patterns of the solid remain is identical with that of CuQCl. The main peaks of $[H_2Q]Cl{\cdot}H_2O$ can also be found in the original product (Fig. 1).
3. TG/DTA curves show that the product has a mass loss of more than 30% above 170°C. Since yellow substance was found on the top of sample chamber, and $[H_2Q]Cl{\cdot}H_2O$ sublimes above 170°C, the mass loss is caused by sublimation of $[H_2Q]Cl{\cdot}H_2O$ (Table 2).

Combining with the composition found, we can conclude that the product is a mixture of CuQCl and $[H_2Q]Cl{\cdot}H_2O$ in 1 : 1 molar ratio, and the total reaction of $CuCl_2{\cdot}2H_2O$ and 8-hydroxylquinoline in 1 : 2 molar ratio can be described as:

$$\begin{aligned} & CuCl_2 \cdot 2H_2O + 2HQ \\ & \quad \rightarrow CuQCl + [H_2Q]Cl \cdot H_2O + H_2O \end{aligned} \qquad (1)$$

3.2. *Reaction pathway*

As soon as the reactants were mixed and ground at room temperature, the color of the mixture changed from pale blue to yellow green. XRD shows that it is caused by the superfacial reaction (Fig. 2a). Later, the color changes to brown and white, and the mixture gets aggregated, which occurs because of the release

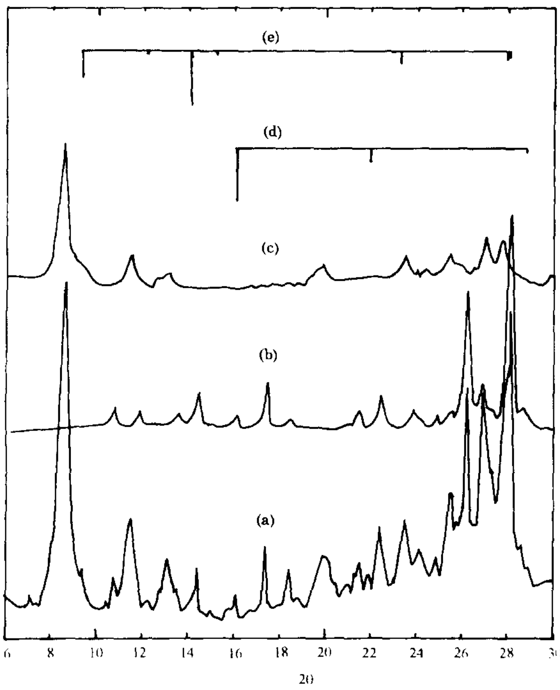

Fig. 1. XRD patterns of (a) reaction product; (b) $[H_2Q]Cl{\cdot}H_2O$; (c) CuQCl; (d) $CuCl_2{\cdot}2H_2O$; (e) HQ.

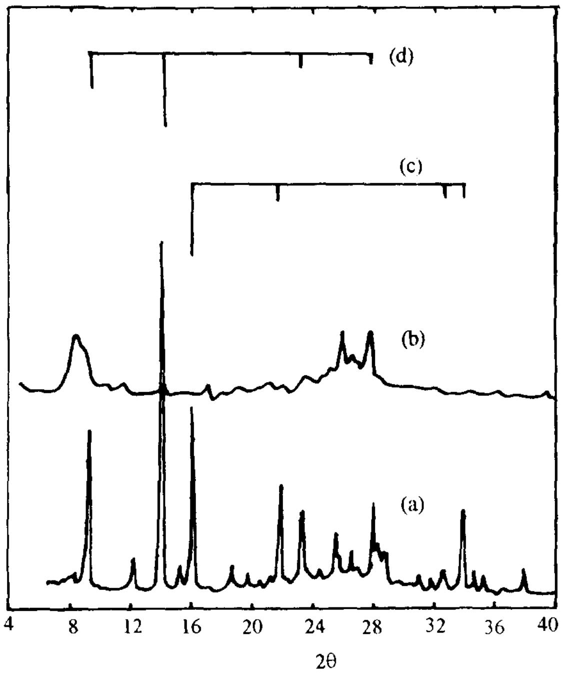

Fig. 2. XRD patterns of the reactant mixture when (a) mixed; (b) reaction finished; (c) $CuCl_2{\cdot}2H_2O$; (d) HQ.

of crystal water crystallisation [4,6]. After the mixture was further ground for several minutes, it stood still. In about 12 h, all the starting materials were exhausted, and new substances formed (Fig. 2b). During the whole process it could be observed that the reaction experienced two periods.

A DSC measurement also shows that the reaction proceeds in two steps. Fig. 3 shows that the DSC curve is composed of a sharp exothermic peak at 40°C, and a group of peaks after 60°C, which has three maximums.

In the previously reported DSC curve of reaction of $CuCl_2{\cdot}2H_2O$ and HQ in 1 : 1 molar ratio, it was found that there are two peaks. The first one is an exothermic peak at 47°C, which is caused by a reaction as following [6]:

$$CuCl_2 \cdot 2H_2O + HQ \rightarrow Cu(HQ)Cl_2 \cdot xH_2O + (2 - x)H_2O \qquad (2)$$

The second one is a wide endothermic peak at 74°C, which is caused by the dehydration of the previous reaction product, $Cu(HQ)Cl_2 \cdot xH_2O$ (Eq. (3)):

$$Cu(HQ)Cl_2 \cdot xH_2O \rightarrow Cu(HQ)Cl_2 + xH_2O \qquad (3)$$

Therefore, in the DSC curve of the reaction in 1 : 2 molar ratio, the first exothermic peak at 40°C

Table 2
TG/DTA Data

Substance(s)	Temperature (°C)	DTA	TG	Explanation
Product	154~200	Endothermic	Mass loss of 27.6%	Sublimation of $[H_2Q]Cl.H_2O$
$[H_2Q]Cl{\cdot}H_2O$	>140	Endothermic	Mass loss of 100%	Sublimation

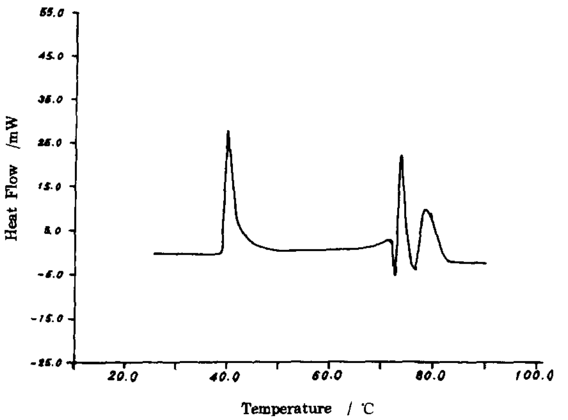

Fig. 3. DSC curve of the reaction between $CuCl_2{\cdot}2H_2O$ and HQ in 1 : 2 molar ratio.

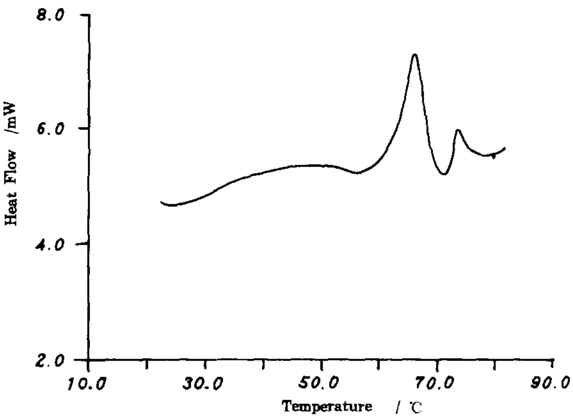

Fig. 4. DSC curve of the reaction between $Cu(HQ)Cl_2$ and HQ in 1 : 1 molar ratio.

must come from the same reaction (2). This is because the peak of reaction in 1 : 2 molar ratio usually lies at a bit lower temperature than that in 1 : 1 molar ratio [4].

The peaks after 60°C may come from following processes: the first, reaction of the previous product, $Cu(HQ)Cl_2 \cdot xH_2O$, with free HQ:

$$Cu(HQ)Cl_2 \cdot xH_2O + HQ \rightarrow CuQCl + [H_2Q]Cl \cdot H_2O \quad (4)$$

This should be an exothermic reaction, since reactions in the condensed state are usually driven by exothermic processes; secondly, endothermic dehydration (Eq. (3)) of the unreacted previous product, $Cu(HQ)Cl_2 \cdot xH_2O$, which is found at 60~78°C in the 1 : 1 reaction; thirdly, free HQ melts at 75°C. The last two processes subsequently cause two endothermic peaks, thus the DSC curve has three maximums.

This is supported by the reaction of $Cu(HQ)Cl_2$ and HQ in 1 : 1 molar ratio. Its DSC curve shows no peaks below 60°C, and only two maximums after 60°C (Fig. 4), because there will be no reaction (3), but the melting of HQ still exists.

The stepwise behavior on activation energy can be understood. There is one unfavorable energy process in reaction (4), that is, one Cl^- must depart from Cu^{2+} ion, so that the activation energy is high, and the reaction takes place much slower, however, reaction (2), which involves only substitution of neutral molecules, will be much faster and can finish before reaction (4) begins.

Reaction of $CuCl_2{\cdot}2H_2O$ and HQ in solutions produces CuQCl and CuQ_2 at different conditions [7], but no $Cu(HQ)Cl_2$ was found. That can be understood from the viewpoint of the mechanism. HQ exist mainly in the form of molecule because its acidity is very weak, so, as the reaction occurs, HQ must be first bidentately coordinated to Cu(II) to form $Cu(HQ)Cl_2$, thus strongly increases the acidity of the HQ. When there is a basic substance, the H^+ will detach easily from HQ.

The condition is easily satisfied when water or alcohol is used as solvent. So if we notice that interaction of Cu(II) and Cl^- is weakened in alcohol, and even broken in water, $Cu(HQ)Cl_2$ is not stable in those solutions. It has been reported that only CuQCl is formed in methanol, and also in water only when high concentration of Cl^- exists [7].

The solid-state reaction does not take that pathway, because there is no such large amount of basic solvent in the solid state. Therefore, $Cu(HQ)Cl_2$ is formed when $CuCl_2{\cdot}2H_2O$ and HQ are mixed in 1 : 1 molar ratio. On the other hand, if there are other free basic substances in the system, or if there is only weak interaction between the anion and the metal ion and the anion is enough basic, the decomposition can occur. This is supported by the above result and the reaction of $CuAc_2{\cdot}H_2O$ and HQ. The latter produces only CuQ_2 in the solid state, no matter whether the reactants are mixed in 1 : 1 or 1 : 2 molar ratio [12].

Acknowledgements

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