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Stepwise Reaction of $CuCl_2 \cdot 2H_2O$ with 2,2′-Bipyridyl in the Solid State

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A consecutive reaction between two solids, $CuCl_2 \cdot 2H_2O$ and 2,2′-bipyridyl, in a 1 : 2 molar ratio proceeds in two steps: $CuCl_2 \cdot 2H_2O$ first converts to $Cu(bipy)Cl_2$, then $Cu(bipy)Cl_2$ turns into $Cu(bipy)_2Cl_2 \cdot 2H_2O$. This is because the second step of the reaction is much slower than the first. The heat of the two reactions has been measured. © 1995 Academic Press, Inc.

INTRODUCTION

Consecutive reactions are very important in coordination chemistry, and have been extensively studied in solutions. Since there are often equilibria in homogeneous reactions, preparation of the intermediates is difficult (1). Recently, we have found that it is easy to prepare the intermediates through solid state reactions at room temperature or at slightly elevated temperatures (2). If we note that interaction of reactants must follow the diffusion of reactant(s) through the intermediate product layer, one question arises: why does the diffusing material not react with the intermediate first?

To our knowledge, there have been a few examples thus far reported in which the intermediates were detected by Mössbauer spetroscopy (3) and DSC (4), but no further work was done. The present paper reports the solid state reaction of $CuCl_2 \cdot 2H_2O$ with 2,2′-bipyridyl, for which the intermediate was detected by XRD. The DSC curves were also obtained for reactions from different initial molar ratios of reactants, and accordingly, the question is answered.

EXPERIMENTAL

Reagents

Analytical grade $CuCl_2 \cdot 2H_2O$ and 2,2′-bipyridyl were purchased from Shanghai Chemicals Factory, and were used after being ground and passed through a 180 mesh sieve.

$Cu(bipy)Cl_2$ and anhydrous $CuCl_2$ were prepared according to literature methods (5, 6).

Apparatus

XRD patterns were measured on a Shimadzu XD-3A diffractometer with Cu$K\alpha$ radiation and a Be filter; DSC was measured on a France Setaram micro-DSC, with Al_2O_3 as reference; UV diffuse reflectance spectra were measured on a Shimadzu UV-240; IR spectra were measured on a Nicolet FTIR-170sx with KBr discs; and elemental analysis was performed on a 240C microanalyzer.

Methods

Four reactions, $CuCl_2 \cdot 2H_2O$ with 2,2′-bipyridyl in a 1 : 1 or 1 : 2 molar ratio, $Cu(bipy)Cl_2$ with 2,2′-bipyridyl in a 1 : 1 molar ratio, and anhydrous $CuCl_2$ with 2,2′-bipyridyl in a 1 : 1 molar ratio, were carried out in an open system probed by XRD (except the last reaction), and in a calorimeter to measure their DSC curves. Typical methods are as follows:

Reactions in open systems. Accurately weighed reactants were mixed and ground in an agate mortar at room temperature, and the XRD patterns of the reaction mixture were measured at different times to probe the reaction mixture. The results are shown in Figs. 1 and 2. After the reactions were completed, the products were washed with anhydrous alcohol and ether, and then analyzed. The XRD patterns of the products were the same before and after washing.

DSC measurements. At room temperature the accurately weighed reactants were carefully mixed in an agate mortar by being ground as lightly as possible to prevent deep reaction, then rapidly transferred to a cell of the calorimeter. Al_2O_3 of approximately the same specific heat was introduced into another cell as a reference. Both cells are the same, are closed, and have an effective vol-

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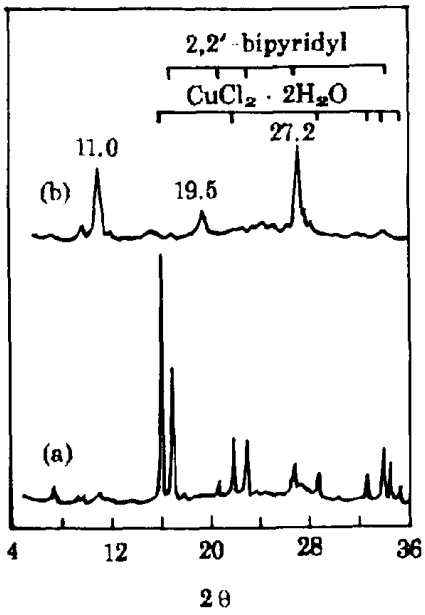

FIG. 1. XRD patterns of the reaction of $CuCl_2 \cdot 2H_2O$ and bipy in a 1 : 1 molar ratio (a) after the reactants are mixed, (b) after the mixture becomes aggregated (Peak positions of starting materials are given in the stick diagram, and those of $Cu(bipy)Cl_2$ are given with a 2θ value).

ume of 1 cm^3. The temperature scanning rates were constant, and the temperature ranged from room temperature to 100°C.

RESULTS AND DISCUSSION

The Characterization of the Products

The products were characterized by elemental analysis, UV diffuse reflectance spectra, and IR. The product of the reaction in a 1 : 1 molar ratio is $Cu(bipy)Cl_2$. The composition found is C 41.20 H 2.70 N 9.36, calculated C 41.24 H 2.75 N 9.62. Its XRD pattern is the same as the reported value (7), and the reaction product in a 1 : 2 molar ratio is $Cu(bipy)_2Cl_2 \cdot 2H_2O$. The composition found is C 49.84 H 3.80 N 10.70, calculated C 49.69 H 4.14 N 10.70.

It is found that the visible absorption of $Cu(bipy)Cl_2$ (712 nm) lies at a higher frequency than that of $Cu(bipy)_2Cl_2 \cdot 2H_2O$ (812 nm). This phenomenon was also observed when Faye (8) studied the system of copper salts and *o*-phenanthroline. Faye pointed out that this can be explained if $Cu(phen)Cl_2$ adopts an octahedral structure, and $Cu(phen)_2X_2$ adopts a trigonal bipyramidal structure. The latter assumption was supported by the single crystal structure (9, 10). Since 2,2′-bipyridyl and *o*-phenanthroline have similar properties, we think the bipyridyl analogues of the complexes have similar structures.

Reaction Pathway

In the 1 : 1 reaction, it is found that the blue color of $CuCl_2 \cdot 2H_2O$ immediately turns greenish on mixing with 2,2′-bipyridyl; however, the XRD pattern measured at this time shows that it is only a superposition of the reactants (Fig. 1a), so the color change can only be caused by surface reaction. The color does not change until the mixture becomes aggregated. During this time the color rapidly turns green, and does not change any more. Its XRD pattern is shown in Fig. 1b. Obviously, the diffraction peaks of the starting materials disappear and new ones appear instead. They are peaks of $Cu(bipy)Cl_2$ (7).

The same phenomena can also be found in the 1 : 2 reaction at the first stage of the reaction as in the above 1 : 1 reaction. Figure 2a shows the XRD pattern after the reaction mixture becomes aggregated; it can be determined that the peaks of $Cu(bipy)Cl_2$ appear, and those of $CuCl_2 \cdot 2H_2O$ disappear. The color of the mixture will turn from green to blue once more. Figure 2b shows the XRD pattern of the reaction mixture after the reaction is completed; there are no diffraction peaks of starting materials or $Cu(bipy)Cl_2$, therefore, a new substance is formed.

The reaction of $Cu(bipy)Cl_2$ and bipy proceeds much more slowly than the above two reactions. Although the color of the mixture changes in minutes, its XRD pattern shows that no product is produced. After about only 4 days, the reaction is completed.

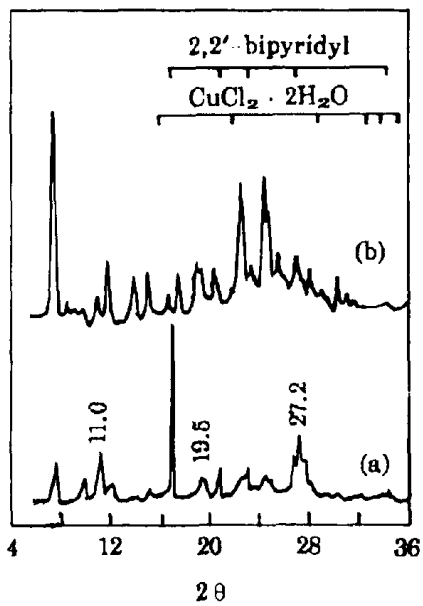

FIG. 2. XRD patterns of the reaction of $CuCl_2 \cdot 2H_2O$ and bipy in a 1 : 2 molar ratio (a) after the mixture becomes aggregated (b) after the reaction is finished (Peak positions of starting materials are given in the stick diagram, and those of $Cu(bipy)Cl_2$ are given with a 2θ value).

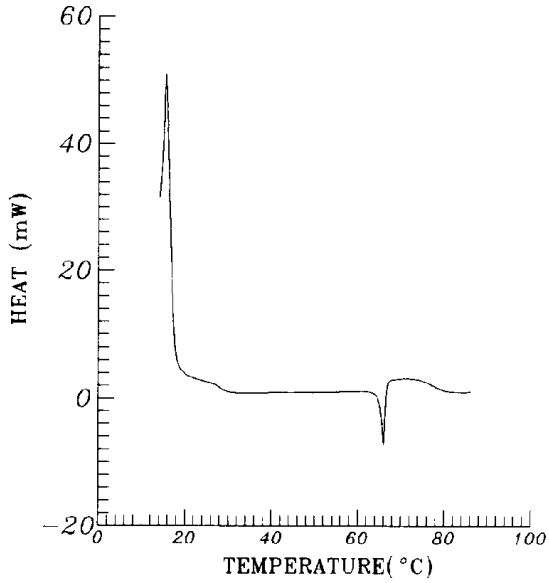

FIG. 3. DSC curve of the reaction of $CuCl_2 \cdot 2H_2O$ and bipy in a 1 : 2 molar ratio. Scan rate: 0.3°C/min; room temperature, 13°C.

Consequently, the 1 : 1 reaction between two solid reactants is:

$$CuCl_2 \cdot 2H_2O\,(s) + \text{bipy}\,(s) \rightarrow Cu(\text{bipy})Cl_2\,(s) + 2H_2O\,(l). \quad (1)$$

For the 1 : 2 reaction, the occurrence of the same phenomena at the first stage and the formation of $Cu(bipy)Cl_2$ during the reaction course show that it includes reaction (1). A further reaction (2) must be included so that the final product can be formed:

$$Cu(\text{bipy})Cl_2\,(s) + \text{bipy}\,(s) + 2H_2O\,(l \text{ or } g) \rightarrow Cu(\text{bipy})_2Cl_2 \cdot 2H_2O\,(s). \quad (2)$$

This is also in accordance with general knowledge on the consecutive reactions.

DSC curves were measured to further study the reactions. In the system with a 1 : 2 molar ratio, the reaction contains two thermal processes (Fig. 3): at 16°C the first exothermal process occurs, with a peak area (in molar heat of reaction, the same hereafter) of 62 ± 1 kJ/mole; and after 64°C a small endothermal process occurs, with a peak area of −4.6 ± 0.1 kJ/mole, followed immediately by a small exothermal process. The total peak area is 4.8 ± 0.1 kJ/mole, and the product is $Cu(bipy)_2Cl_2 \cdot 2H_2O$. This means there is a two-step reaction, since the first exothermal process may be caused by reaction (1), and the other by reaction (2), which in turn is composed of two processes: the endothermal melting of bipy

$$\text{bipy}\,(s) \rightarrow \text{bipy}\,(l), \quad (3)$$

and the exothermal reaction of $Cu(bipy)Cl_2$ and molten bipy

$$Cu(\text{bipy})Cl_2\,(s) + \text{bipy}\,(l) + 2H_2O\,(l) \rightarrow Cu(\text{bipy})_2Cl_2 \cdot 2H_2O\,(s). \quad (4)$$

The reasons are (a) from a thermodynamic point of view, spontaneous reactions not involving gas are generally exothermic; thus reactions (1), (2), and (4) must be exothermic; (b) the endothermal melting process of pure bipy takes place at 72.5°C, which is in accordance with the endothermal peak temperature 66°C. The melting heat of bipy is 19.80 kJ/mole, so reaction (4) takes place before all the bipy melts.

The DSC of the 1 : 1 molar ratio reaction was also measured to verify the above inference, since there will be only one exothermic peak at the similar place if it is right. The experiment does show that there is only one exothermal peak at 26°C, with a peak area of 62 ± 1 kJ/mole, and that there is no thermal effect after 60°C (Fig. 4). This can only mean that the 1 : 1 molar ratio reaction is completed with no bipy left when the exothermal process ends, and because both the first peak of the 1 : 2 molar ratio reaction and the only peak of the 1 : 1 molar ratio reaction are of equal peak area, they are both caused by reaction (1). Therefore, the 1 : 2 reaction is composed of reactions (1) and (2). This supports the above conclusion.

The conclusion is further proved by the measurements of DSC curves for another two experiments: the reaction of $Cu(bipy)Cl_2$ and bipy in a 1 : 1 molar ratio (Fig. 5, curve

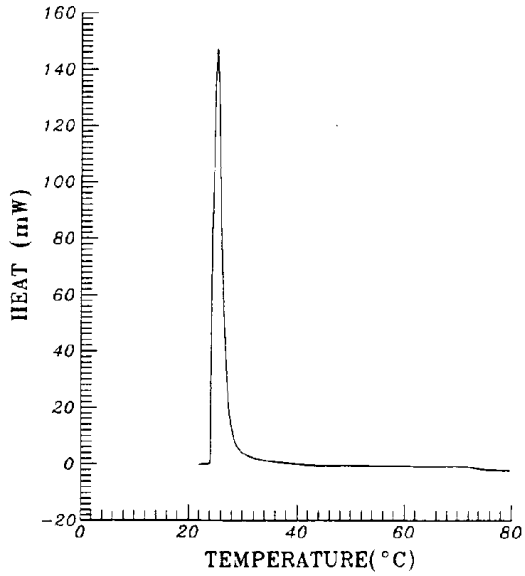

FIG. 4. DSC curve of the reaction of $CuCl_2 \cdot 2H_2O$ and bipy in 1 : 1 molar ratio. Scan rate: 0.3°C/min; room temperature, 13°C.

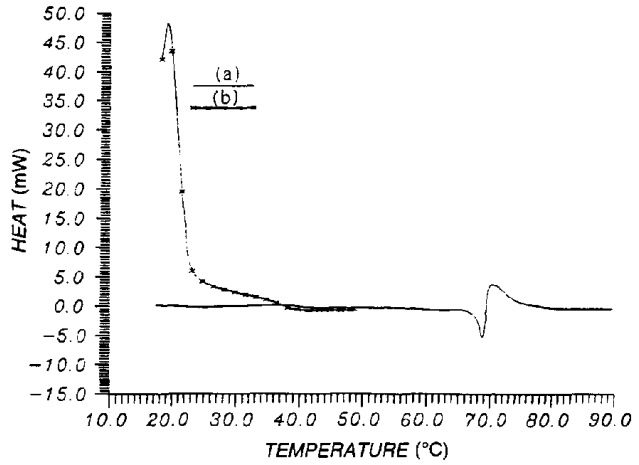

FIG. 5. DSC curves of the reactions of (a) $Cu(bipy)Cl_2$ and bipy in a 1 : 1 molar ratio; (b) $CuCl_2 \cdot 2H_2O$ and bipy in a 1 : 2 molar ratio stopped after the first peak ended. Scan rate: 0.5°C/min; room temperature, 10°C.

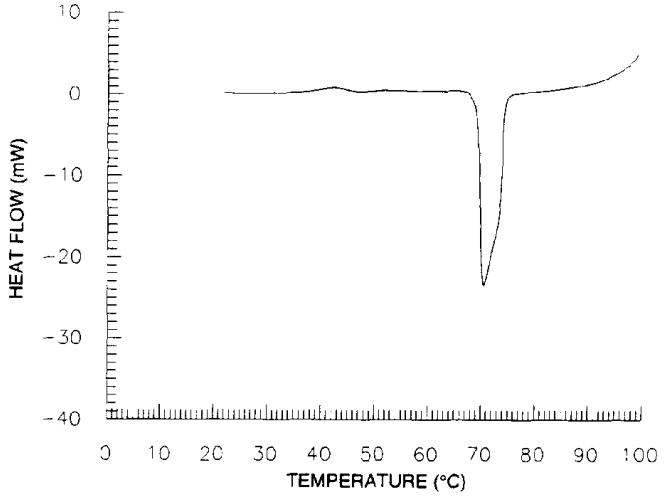

FIG. 7. DSC curve of reaction between $CuCl_2$ and bipy. Scan rate: 0.3°C/min; room temperature: 20°C.

a) and the reaction of $CuCl_2 \cdot 2H_2O$ and bipy in a 1 : 2 molar ratio with a range of scanning temperatures controlled to make only the first peak appear (Fig. 5, curve b). It is found that the first experiment gives only the second part of the 1 : 2 molar ratio reaction; the XRD pattern of the product shows that a new substance is formed and no starting materials are left, and the products of the second experiment give the same XRD pattern as Fig. 2a.

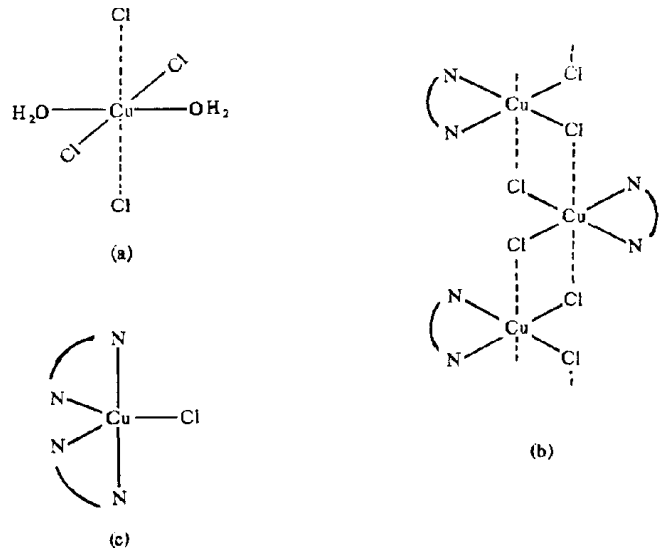

FIG. 6. (a) Crystal structure of $CuCl_2 \cdot 2H_2O$[13] (b) Supposed structure of $Cu(bipy)Cl_2$ (8) (c) Crystal structure of $Cu(bipy)_2Cl_2$-type (10) (N stands for 2,2′-bipyridyl).

Factors That Affect the Rate of Reaction and DSC Curves

It can be found on the DSC curves that the peaks of reaction (1) appear at 16 and 26°C for the 1 : 2 and 1 : 1 reactions, respectively. According to nonisothermal reaction theory (11), the position of the reaction peak is determined by both the reaction rate and the temperature scanning rate for the peak position of reaction (1) in the 1 : 1 and 1 : 2 reactions, this means that there is a difference in reaction rate. Since the same reaction and the same temperature scanning rate are involved, the difference can only come from the difference in the molar ratio of the reactants. As we know that the rate of solid state reaction is related to the number ratio of reactant grains (12), it is easy to understand that the rate of reaction (2) in a 1 : 2 molar ratio is faster than that in a 1 : 1 molar ratio. Consequently, the peak of reaction (1) appears earlier in a 1 : 2 reaction than in a 1 : 1 reaction.

The large gap between the two processes in the DSC of a 1 : 2 reaction (Fig. 3) means that the two processes are very different in their reaction rates (11). This may be due to different reaction paths and to the different structures of reactants and products. Figure 6 shows the structures of the important compounds. Obviously, there are small changes from (a) to (b), which involve the weakly linked waters being substituted for bipyridyls; and the linear chain of —Cu—(Cl_2)— of $CuCl_2 \cdot 2H_2O$ is twisted to fit the coordination requirement of bipyridyl. However, great changes are made on going from (b) to (c): the polymer structure of (b) is destroyed, and one Cl^- is excluded from the inner coordination sphere to form separated ion pairs. Consequently, reaction (2) has a higher activation energy than reaction (1).

Second, the reaction (1) may be an autocatalytic reaction. This is because copper chloride hydrate can dissolve in the water produced by reaction (1). Since we know that the difficulty in the solid state reaction is the diffusion of reactants, the soluted and solvated $\{CuCl_2\}_n$ will help the diffusion, and thus increase the reaction rate. This is supported both by the reactions detected by XRD in an open system and by DSC experiments. On the DSC curve of the 1 : 1 reaction, there is a straight line before a very sharp peak (Fig. 4), which shows that, after a long induction period, the reaction starts, rapidly speeds up, and then is completed. In the open system detected by XRD, there is also a period during which the reaction goes on at the surface and is rapidly completed, with the results that the mixture is aggregated and the color changes rapidly, which are vital evidence for the water catalytic reaction.

This is also supported by a further reaction of anhydrous $CuCl_2$ and bipy: the DSC curve of the reaction (Fig. 7) shows that there is no reaction before bipy melts, which means that the reaction rate is very slow without water.

Therefore, it can be concluded that, for these two reasons the last process begins only when the first process is complete, thus making possible all the phenomena we have observed.

ACKNOWLEDGMENT

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REFERENCES

1. E. Konig, *Coord. Chem. Rev.* **3,** 471 (1968).
2. Changxiong Li, Lixu Lei, and Xinquan Xin, *Chin. Sci. Bull.* **39,** 394 (1994).
3. P. Gutlich and K. M. Hasselbach, *Angew. Chem. Int. Ed. Engl.* **8,** 600 (1969).
4. P. S. Bassi, G. S. Chopra, and K. Kaur, *Indian J. Chem. A* **29,** 454 (1990).
5. R. E. Wilde, T. K. K. Srinivasan, and S. N. Ghosh, *J. Inorg. Nucl. Chem.* **35,** 1017 (1973).
6. T. Moeller, Ed., "Inorganic Syntheses," Chinese ed., translated by Panwen Shen, Vol. 5, p. 135, McGraw–Hill, New York, 1963.
7. JCPDS, "Powder Diffraction File," 19-1613.
8. G. H. Faye, *Can. J. Chem.* **44,** 2165 (1966).
9. B. J. Hathaway, I. M. Procter, R. C. Slade, and A. A. G. Tomlinson, *J. Chem. Soc. A,* 2219 (1969).
10. B. J. Hathaway and A. Murphy, *Acta Crystallogr. Sect. B* **36,** 295 (1980), and references therein.
11. E. Koch, Non-Isothermal Reaction Analysis, Chap. 3 and 4, p. 90, Academic Press, San Diego, 1977.
12. Yu-Jun Hao, Tatsuo Tanaka, *Can. J. Chem. Eng.* **66,** 761 (1988).
13. Ase Enger, *Acta Chem. Scand.* **24,** 3510 (1970).