February, 1975] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(2), 469—471 (1975) 469

Reaction of Cupric Ion Fixed on the Ion Exchange Resin with Acetylacetone

Takashi Okamura, Kunio Ohzeki, and Tomihito Kambara
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received November 19, 1974)

It was found that the cupric ions fixed on the resin are removed by acetylacetone(Hacac) to form bisacetylacetonatocopper(II), Cu(acac)$_2$. By the addition of a small amount of pyridine–water mixture to the copper(II) form resin in acetylacetone milieu, the cupric ions are quantitatively removed from the resin in the form of pyridine adduct, and the pyridinium ions are adsorbed on to the resin in place of the cupric ions. The reaction was successfully applied to the synthesis of Cu(acac)$_2$.

Recently, the conversion of a metal ion fixed on the ion exchanger to a chelate compound based on the ion exchange reaction in organic medium[1,2] has been studied. Higgins[1] developed the new preparation method of cesium lanthanoids hexafluoroacetylacetonates by treating the rare earth ion fixed on Dowex 50 with 0.4 mol/l of cesium hexafluoroacetylacetonate in 50% ethanol.

The authors[2] have reported the quantitative removal of iron(III) ions fixed on Amberlyst 15 by Hacac with the aid of the addition of a small amount of pyridine-water mixture. In this work, the reaction of the cupric ions fixed on Amberlyst 15 resin with Hacac is investigated and the conditions of the quantitative removal of the cupric ions are discussed. The reaction of Cu(II)-form resin with Hacac is shown by

$$(RSO_3)_2Cu + 2\,Hacac = 2\,RSO_3H + Cu(acac)_2 \qquad (1)$$

where R denotes the resin matrix.

Experimental

Apparatus and Reagents. A Hitachi 356 two-wavelength double beam spectrophotometer with 10-mm cells was used for the absorption measurement. A Hitachi 508 atomic absorption spectrophotometer was used for the copper absorption measurement at 324.8 nm in air-acetylene flame. Acetylacetone and pyridine, both of analytical grade (Wako Pure Chemical Inc.), were used without further purification.

Preparation of Copper(II)-Form Resin. The resin used is the sulfonic acid cation exchanger, Amberlyst 15, with a macroreticular structure. The commercially available Amberlyst 15 is crushed and sieved to a fraction of 60—80 mesh. The resin was converted to Cu(II)-form by treatment with 0.1 mol/l solution of cupric nitrate. The Cu(II)-form resin was washed with water, dried at 110 °C and then stored in a desiccator over phosphorus pentoxide.

Determination of Cupric Ions on the Resin. The cupric ions on the dried Cu(II)-form resin were eluted by 2 mol/l hydrochloric acid solution and determined by EDTA titration. It was found that 3.90±0.13 meq of cupric ions were adsorbed onto 1 g of the dried Cu(II)-form resin.

Water Associated with Cu(II)-form Amberlyst Resin. It was pointed out that the water plays an important role in the reaction of β-diketone with metal ion fixed on the resin,[2] and so it is necessary to determine the water content in the oven-dried cupric form resin. The air-dried H-form resin is weighed in a glass filter and dried at 110 °C in oven until a constant weight, and then the resin is converted into cupric form and washed with deionized water, and the resulting resin is dried at 110 °C until a constant weight. Cupric ions fixed on the resin are eluted by 2 mol/l hydrochloric acid and determined by EDTA titration. The data obtained are summarized in Table 1. The ratio of exchange capacity of cupric ion to proton was 1.03. When the H-form resin is converted to Cu(II)-form, the increase in weight is expected, but as is shown in Table 1, the weight increase is larger than that of copper determined by titration. It may be safe to say that the difference is caused by water coordinated to the copper ion on the resin. Consequently, it is supposed that one molecule of water is coordinated to a copper(II) ion on the resin, such as $(RSO_3)_2Cu\cdot H_2O$.

Reaction of Cu(II)-Form Resin with Hacac. A portion of 3 ml of Hacac was poured onto the 40 mg of dried Cu(II)-form resin in a test tube and shaked by hand for 10 min. at room temperature (around 22 °C). After the filtration, the resin was washed with ethyl alcohol and water. The cupric ions remaining on the resin were eluted by 2 mol/l hydrochloric acid solution, and determined by atomic absorption spectrophotometry.

Results and Discussion

Effect of Pyridine. The reaction of Cu(acac)$_2$ with pyridine(py) has been investigated and the adduct formation of Cu(acac)$_2$·py has been reported.[3] Upon addition of pyridine to Hacac in contact with Cu(II)-form resins, the color of the solution turned from pale blue to green, indicating the formation of Cu(acac)$_2$·py.

Table 1. Water associated with Cu(II)-form resin

Weight of H-form resin, taken (g)	Weight of resin converted into Cu-form, found (g)	Increase in weight (g)	Cu on resin, found by titration (mmol)	Weight increase calculated[a] (g)	Coordinated water estimated[b] (mmol)	Mole ratio H_2O/Cu
0.8146	0.9667	0.1521	1.83	0.1145	2.09	1.14
0.7366	0.8740	0.1374	1.71	0.1066	1.71	1.00
0.7273	0.8634	0.1361	1.74	0.1089	1.51	0.87

a) Provided that the non-hydrated cupric ion is adsorbed on the resin. b) If two mmol hydrogen ions on the resin are replaced by one mmol copper(II) ion, the increase in resin weight should be (63.54−1.008×2) mg, provided that no water molecule is coordinated to the cupric ion on the resin.

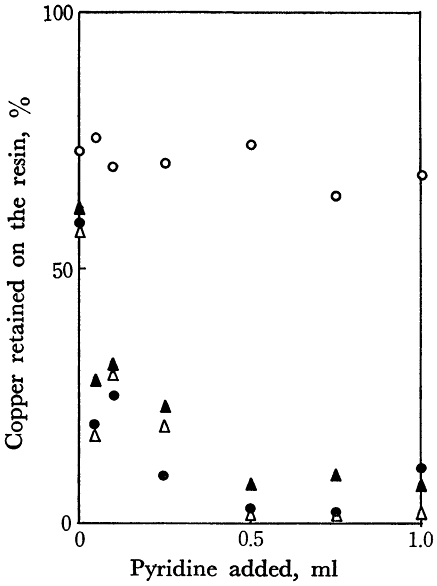

Fig. 1. Effect of pyridine and water.
The pyridine and water were added to 3 ml of Hacac in contact with 40 mg of Cu(II)-form resin. Water added, μl, 0(○), 10(▲), 25(●), 50(△).

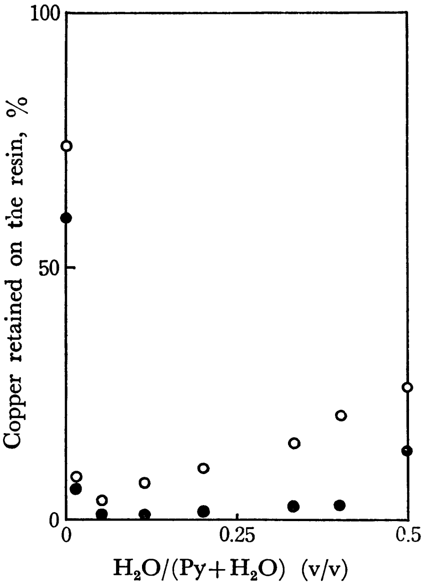

Fig. 2. Effect of the pyridine-water mixture with various ratios on the removal of the copper(II) from 40 mg of the Cu(II)-form resin with 3 ml of Hacac. The pyridine-water mixture added, 0.5 ml (○), 1 ml (●).

Nevertheless, the amount of the copper removed from the resin is hardly affected by the addition of pyridine to Hacac as shown in Fig. 1.

Effect of Pyridine and Water. The separate addition of pyridine or water does not effect remarkably, but the coexistence of them in Hacac is found highly effective for adduct formation, as shown in Fig. 2. More than 99% of copper ions are removed from the resin by addition of *ca.* 30 : 1 pyridine–water mixture to the extent of one-third of the volume of Hacac employed.

The dissociation of the Hacac is accelerated in the presence of pyridine–water mixture as shown by equations (2) and (3).

$$\text{py} + H_2O = \text{pyH}^+ + OH^- \qquad (2)$$

$$\text{Hacac} + OH^- = \text{acac}^- + H_2O \qquad (3)$$

Acetylacetonate anion withdraws the copper ion from the resin and pyridinium ion is adsorbed on the resin instead of monoaqua cupric ion and the resulting $Cu(acac)_2$ coordinates the excess pyridine to form $Cu(acac)_2 \cdot py$. The total reaction can be written as follows.

$$(RSO_3)_2Cu + 2\,\text{Hacac} + 3\,\text{py} \xrightarrow{H_2O} Cu(acac)_2 \cdot py + 2\,RSO_3Hpy \qquad (4)$$

The air-dried Cu(II)-form resin, one gram of which contains 3.64±0.16 meq copper, has an appropriate amount of water, namely, around 10% by weight. Thus, there may occur the reaction shown by equation (4) even without addition of water. The various amounts of pyridine are added to 10 ml of Hacac containing 40 mg of air-dried Cu(II)-form resin. After the reaction, the resin is separated by filtration. The absorbance measurement of the filtrate at 655 nm *vs.* Hacac clearly reveals that the amount of copper liberated from the resin increases with increasing amount of pyridine added, as shown in Fig. 3.

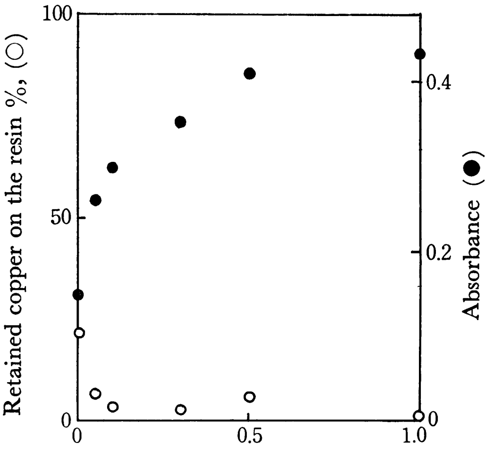

Fig. 3. Effect of pyridine on the air-dried resin.
The absorbance mesurement of the filtrate (●), and copper retained on the resin (○).

Application to the Synthesis of Chelate Compound. Treat 500 mg of air-dried Cu(II)-form resin with 10 ml of Hacac and add 3 ml of pyridine. After the reaction, separate the resin by filtration and wash it with Hacac containing appropriate amount of pyridine until the filtrate shows no color of $Cu(acac)_2 \cdot py$. Boil off the excess Hacac and pyridine by bubbling the nitrogen gas into the filtrate at 130 °C. In the course of this procedure, the adduct $Cu(acac)_2 \cdot py$ is decomposed to $Cu(acac)_2$, which is confirmed by color change of the chelate compound. The crude $Cu(acac)_2$ is purified by sublimation at 175 °C under 1 mmHg. One obtains 0.209 g of $Cu(acac)_2$ in 85% yield. The result of elementary analysis was: Found: C, 45.84; H, 5.35%. Calcd for $Cu(acac)_2$: C, 45.89; H, 5.39%.

We wish to thank the Ministry of Education for financial support granted to this research.

References

1) C. E. Higgins, *J. Inorg. Nucl. Chem.*, **35**, 1941 (1973).
2) K. Ohzeki, M. Ikeuchi, and T. Kambara, This Bulletin, **48**, 67 (1975).
3) W. R. May and M. M. Jones, *J. Inorg. Nucl. Chem.*, **25**, 507 (1963).