A Potent Solvent for Dissolution of Metallic Copper

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Metallic copper was found to dissolve in a mixture of ammonia and carbon tetrachloride under extremely mild conditions. The solubilized copper was determined to be in the form of an ammine complex of copper(II) chloride, $[Cu(NH_3)_m]Cl_2{\cdot}nH_2O$.

Mineral acids such as sulfuric acid, hydrochloric acid and nitric acid have traditionally been used to dissolve metals. In fact, they are still recognized as one of the most powerful and practical reagents for dissolving inorganic compounds, as well as metals. In contrast, only a few attempts have been made to dissolve metals in organic solvents. A recent report described the effectiveness of aprotic solvents such as dimethyl sulfoxide (DMSO) in dissolving metals.[1–3] Shortly thereafter it was shown that a variety of metals (e.g., Fe, Ni, Cu, Zn, Pd, Ag and Au) can be dissolved in a system consisting of a combination of a common organic solvent with an elemental halogen and a long-chain quaternary ammonium halide.[4] Perhaps more striking is the fact that a solvent system containing Cl_2, Me_2NHCl and MeCN dissolves Au faster than *aqua regia*.[5]

It is widely known that copper readily dissolves in nitric acid and sulfuric acid in the presence of oxygen. Copper is also soluble in ammonium hydroxide, ammonium carbonate, or potassium cyanide in the presence of O_2. The redox potential of the Cu(I) and Cu(II) oxidation states are indicated by the following data: $Cu^0 + Cu^{2+} \rightleftharpoons 2Cu^+$, $E^0 = -0.37\,V$.[6] The relative stabilities of the Cu(I) and Cu(II) ions in solution depend very strongly on the nature of the anions or other ligands present and varies considerably with the nature of the solvent. As part of our investigations on the chemistry of Cu(I) we have been preparing copper(I) complexes by the interaction of Cu(II) compounds with Cu^0. In the course of these investigations we made the striking observation that metallic copper can be dissolved in a solution of ammonia in the presence of carbon tetrachloride.

Bearing in mind the results of early studies that halogen and/or halogenated compounds play an important role in dissolving metals in organic solvents, we attempted to extend our preliminary observations to investigate in more detail the ability of solutions of ammonia mixed with halocarbons to dissolve metals.

Thus, we first examined the efficiency of solutions of ammonia mixed with several different halogenated compounds in dissolving metallic copper. To this end, 2.5 g (40 mmol) of copper powder was suspended in 50 mL of ammonia solution with stirring at 30 °C. To this suspension 20 mmol of halogenated compound was added. After 3 h of reaction a dark-blue solution was obtained. Upon filtering the unreacted solid, the content of copper in the supernatant was determined by EDTA titration.

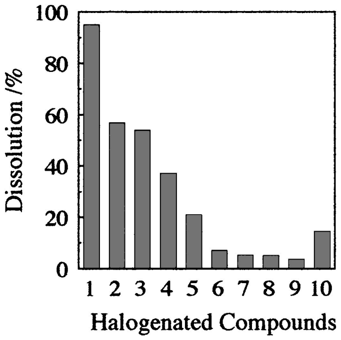

Figure 1. Dissolution of copper in ammonia solution containing various halogentaed compound. Reaction conditions: Cu, 40 mmol; halogenated compound, 20 mmol; NH_4OH, 50 mL; 30 °C, 3 h. (**1**, CCl_4; **2**, $CHCl_3$; **3**, $CHBr_2CHBr_2$; **4**, CH_2Br_2; **5**, CH_3CCl_3; **6**, $CHCl_2CHCl_2$; **7**, $CH_2ClCHCl_2$; **8**, CCl_2CCl_2; **9**, CH_2ClCH_2Cl; **10**, NH_4OH).

As shown in Figure 1, among the 9 halogentaed compounds used in this study, the solution of ammonia containing CCl_4 exhibits the highest ability to dissolve metallic copper, although other combined ammoniacal solution (i.e., NH_4OH–$CHCl_3$ and NH_4OH-$Br_2CHCHBr_2$) showed moderate dissolution power toward Cu^0.

We then concentrated our efforts to investigate some of the details of the dissolution reaction of Cu^0 in the solvent system consisting of NH_4OH–CCl_4. Figure 2 illustrates the efficiency of CCl_4 on the dissolution of metallic copper. The dissolution of Cu^0 in the NH_4OH–CCl_4 system reached an almost quantitative yield within 1 h, whereas that in the system without CCl_4 was less than 10% at the same time. Furthermore, it is noteworthy that the dissolution of Cu^0 in NH_4OH–CCl_4 proceeds 150 times faster than that in NH_4OH alone, if the initial slopes of each curve in Figure 2 are taken as a measure of the relative rate constants.

In order to elucidate the stoichiometry of this reaction, the effect of the mole ratio of Cu^0/CCl_4 on the dissolution of Cu^0 was examined. It is apparent from Figure 3 that the reaction pro-

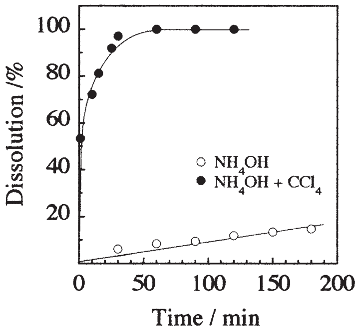

Figure 2. Effect of addition of CCl_4 on the dissolution of copper in ammonia solution at 30 °C; Cu, 80 mmol; CCl_4, 40 mmol; NH_4OH, 100 mL.

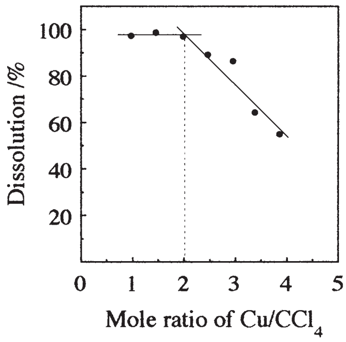

Figure 3. Variation of the dissolution of copper with the mole ratio of Cu/CCl_4; CCl_4, 20 mmol; NH_4OH, 50 mL; 30 °C, 3 h.

ceeds with a stoichiometry of Cu^0:$CCl_4 = 2:1$. In an attempt to understand the reaction mechanism, the reaction products and volatile components were analyzed. The former were analyzed by concentrating the resultant ammoniacal solution mixture, and examining the solid by titration,[7] IR and TG-DTA.[8] Based on these analyses, the product was determined to be an amine complex of copper(II) chloride, $[Cu(NH_3)_m]Cl_2 \cdot nH_2O$. The volatile component, which was trapped during the reaction, was identified to be CH_2Cl_2 by ^{1}H-NMR.[9]

On the study of dissolution of metallic copper in a dimethyl sulfoxide (DMSO)–CCl_4 system,[2] Tezuka, et. al. proposed the generation of a dichlorocarbene intermediate via an interaction between Cu^0 and CCl_4. Since we found CH_2Cl_2 in our NH_4OH–CCl_4 system, it seems reasonable to assume that a dichlorocarbene could also be formed in our reaction system. Thus, the following over-all reaction might be proposed, although the reaction mechanism is not clear at this time and attempts to confirm the generation of CO failed.

$$2Cu^0 + CCl_4 + 2nNH_4OH \longrightarrow 2[Cu(NH_3)_n]Cl_2 + 2nH_2O + (CO)$$

The dissolution ability of the NH_4OH–CCl_4 system for typical metals such as Zn, Ag, Sn, Pb, and Fe was also examined with conditions similar to those used to dissolve Cu. The solvent system was able to dissolve Zn but the efficiency was ca. 60%, relative to Cu. The dissolution of both Ag and Sn were less than 0.5%. However, it was found that Pb and Fe were not dissolved in NH_4OH–CCl_4 solvent. Although the reason why there is a difference in the dissolution of metals by NH_4OH–CCl_4 system is not clear at the present time, ease of the decomposition of CCl_4 as well as the formation of dichlorocarbene by metals, and that of the ammine complex formation might play an important role.

In summary, it has been found that some halogenated compounds can be decomposed by metallic copper in NH_4OH. Furthermore, it was found that a unique solvent system consisting of a mixture of NH_4OH and CCl_4 can quantitatively dissolve metallic copper at ambient temperature. Since the solvent system has an excellent efficiency and a good selectivity toward metallic copper, this method might be applicable as a promising process for selective leaching of metallic copper from waste printed wiring boards. Indeed, in additional experiments, it was found that the dissolution ability of NH_4OH–CCl_4 system in the leaching of copper from waste printed circuits at ambient temperature is almost comparable to that in mineral acid such as HNO_3, when the concentration of acid is the same as that of NH_4OH.

Further studies to reveal detail mechanism of the dissolution of metallic copper in NH_4OH–CCl_4 system are now in progress.

References and Notes

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6 F. A. Cotton and G. Wilkinson, in "Advanced Inorganic Chemistry," 5th ed., John Wiley & Sons, New York (1988), p. 757.
7 Since the composition of residue was varied with drying conditions, the final solution was concentrated and dried in vacuo at 100 °C. The contents of copper ion and chloride ion were determined by EDTA titration and Volhard method, respectively. Found: Cu, 33.6; Cl, 37.2%.
8 The final solution was concentrated and dried gently at ambient temperature. IR(KBr)/cm^{-1}: 3492 for νOH; 3314 for $\nu_{as}NH_3$; 3184 for $\nu_s(NH_3)$. Observed and calculated weight loss percentage in parenthesis, and possible assignment of eliminant, assuming that the residue is $[Cu(NH_3)_4]Cl_2 \cdot 4H_2O$: 17.4 (18.9)% at ca. 240 °C for $3H_2O$; 20.3 (22.9)% at 240–270 °C for ($3H_2O + NH_3$); 15.9 (16.4)% at 390–480 °C for $3NH_3$.
9 ^{1}H-NMR(400 MHz, $CDCl_3$, TMS): δ 5.30 (s).