Dissolution of Copper Metal in a Dimethyl Sulphoxide–Carbon Tetrachloride Mixture

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Copper metal is found to dissolve in a dimethyl sulphoxide–carbon tetrachloride mixture under extremely mild conditions with the formation of copper(II) chloride bis(dimethyl sulphoxide), $CuCl_2(DMSO)_2$.

Copper is traditionally known as a coinage metal together with silver and gold because of its resistance to corrosion under ordinary atmospheric conditions.[1] We report here an unusual reaction of copper metal in a neutral, non-corrosive organic solution consisting of common chemical compounds, namely dimethyl sulphoxide (DMSO) and carbon tetrachloride (or other halocarbon compounds), during which copper metal is dissolved under extremely mild conditions.

Copper powder† (10 mmol) was suspended in 20 ml of DMSO‡ with stirring at ambient temperature (20—22 °C), then carbon tetrachloride§ (10 mmol) was added. After an induction period (15—30 min), an exothermic reaction took place resulting in a clear, homogeneous, emerald-green solution. With the addition of either a drop of hydrochloric acid or a small amount of copper(I) chloride during the induction period, the exothermic reaction started immediately. Addition of a small amount of copper(II) chloride also reduced the induction period. DMSO must be present for the dissolution reaction to occur and could not be effectively replaced by methanol, tetrahydrofuran, benzene, chloroform, acetonitrile, or pyridine. Diphenyldichloromethane, di- or tri-chloroacetic acid esters, and organic bromides such as carbon tetrabromide were found to be effective substitutes for carbon tetrachloride. It is interesting to note that no metal other than copper was found to dissolve in the DMSO–carbon tetrachloride mixture (Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Ag, Au, and Pt were tested).

The DMSO–carbon tetrachloride mixture was able to react with and dissolve copper metal in other than powder form. A 2.5 × 2.5 cm copper laminated plate¶ (supplied for the production of printed circuit boards) was placed in a 100 ml beaker containing DMSO (40 ml) and carbon tetrachloride (10 ml) whilst stirring. The copper metal was found to dissolve in the mixture, the reaction time being temperature dependent, *e.g.* 560 min at 50 °C, 20 min at 70 °C, and 4.0 min at 90 °C.

To elucidate the mechanism of this unique process, the

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† From Nakarai Chemical Co., 325 mesh, minimum purity 98%.

‡ From Nakarai Chemical Co., minimum purity 99.0%, maximum water content 0.2%.

§ From Nakarai Chemical Co., Minimum purity 99.0%.

¶ Matsushita Denko copper laminated plate, R1700, copper sheet thickness 35 μm on epoxy–glass plate (total thickness 1.0 mm)

$$\begin{array}{lcl} \mathrm{Cu + 2DMSO + CCl_4} & \rightarrow & \mathrm{CuCl_2(DMSO)_2 + :CCl_2} \\ \mathrm{:CCl_2 + DMSO} & \rightarrow & \mathrm{Me_2S + COCl_2} \\ \mathrm{COCl_2 + Cu + 2DMSO} & \rightarrow & \mathrm{CuCl_2(DMSO)_2 + (CO)} \end{array}$$

Scheme 1

reaction mixture containing the copper powder system was separated into volatile and residual solid components by evacuation. The residual solid was assigned the structure, copper(II) chloride bis(dimethyl sulphoxide), based on comparison of its i.r. and u.v. spectra with those of an authentic sample prepared separately.[2] The volatile mixture was analysed by g.l.c. and ^{1}H n.m.r. spectroscopy. Consumption of carbon tetrachloride accompanied by the formation of dimethyl sulphide was observed. The molar quantity of the consumed carbon tetrachloride equalled that of the dimethyl sulphide formed.

Generation of dichlorocarbene from carbon tetrachloride as shown in Scheme 1 best accounts for these observations. The dichlorocarbene intermediate generated in the presence of DMSO is thought to undergo instantaneous oxidation by DMSO to produce dimethyl sulphide and phosgene, as dichlorocarbene generated by the usual procedure, namely the base treatment of chloroform or trichloroacetate,[3] also reacted with DMSO to yield dimethyl sulphide. The phosgene presumably formed in the system is believed to be consumed by direct reaction with copper metal in DMSO, since the independent reaction of phosgene with copper powder suspended in DMSO was found to proceed readily to give $\mathrm{CuCl_2(DMSO)_2}$. An alternative reaction pathway, namely a Kornblum type oxidation[4] of carbon tetrachloride by DMSO in the presence of copper metal, might be possible. However, the formation of carbene coupling products, namely maleate and fumarate esters, in the reaction of copper–DMSO–dichloroacetic acid esters, again favours the proposed involvement of the carbene species in the carbon tetrachloride system. The observation that the addition of hydrochloric acid, CuCl, or $\mathrm{CuCl_2}$, promotes the copper dissolution reaction, strongly suggests the involvement of CuCl and/or $\mathrm{CuCl_2}$ as the self-catalytic intermediate species necessary for the present reaction to proceed smoothly. The unusually strong tendency of copper metal to form the dimethyl sulphoxide complex is presumably another driving force of this unique reaction.

Received, 12th May 1987; Com. 641

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