A Novel Reduction of Oxides of Copper in the Mixed Non-aqueous System Dimethyl Formamide–Sulphur Dioxide

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Copper(I) oxide and copper(II) oxide react with the system dimethyl formamide–sulphur dioxide to yield copper metal; conversion of oxide into a copper(I) sulphur oxyanion compound is thought to occur, followed by disproportionation to copper(0).

The metal oxides Cu_2O and CuO react at room temperature with the mixed non-aqueous system dimethyl formamide (dmf)–sulphur dioxide to form copper metal. Initially, the oxides dissolve to form an orange solution, but copper precipitates after the solution has been allowed to stand for three days. In this way, extremely pure metal is obtained. This is the first reported reduction of Cu_2O and CuO to metal with SO_2, and is of special importance in that it is a low-temperature process. The orange intermediate is probably a sulphur oxyanion compound of copper(I) and the reaction may involve conversion of oxide directly into sulphite, followed by solvation by sulphur dioxide and disproportionation of copper(I) to copper(0) and copper(II), the latter being further transformable into copper(I) sulphite (Scheme 1).

$$\begin{tikzcd}
Cu_2O + SO_2 \arrow[r, "dmf"] & Cu_2SO_3 \arrow[r, "SO_2"] & Cu_2S_2O_5 \arrow[r] & Cu + CuSO_3 \arrow[ll, bend left, "SO_2"] \\
(CuO) & & &
\end{tikzcd}$$

Scheme 1

Copper(I) is known to be stabilised by some non-aqueous solvents,[1] although copper(I) is unstable in water. In dmf–SO_2, copper(0) is produced, most likely by disproportionation of copper(I). The orange intermediate is air-sensitive, quickly becoming green, suggesting oxidation of copper(I) to copper(II); these green solutions again become orange if air is excluded, presumably as a result of reduction of copper(II) by SO_2. In the absence of an oxidiser, such as dimethyl sulphoxide (dmso) in the mixed system dmso–SO_2,[2] the orange intermediate is likely to contain an anion of sulphur(IV), such as disulphite. Similar orange colours have been observed for solutions of copper(I) disulphite[3] in non-aqueous media.

The reaction proceeds at any concentration of SO_2, but is most rapid at high SO_2 concentration.

Cu_2O and CuO also dissolve in 1:1 dmf–H_2O, which has been saturated with SO_2, to form red solutions from which Chevreul's salt, $CuSO_3 \cdot Cu_2SO_3 \cdot 2H_2O$,[4] crystallises.

No reaction was observed between CuS and dmf–SO_2. The solvent dmf–SO_2 also reacts with the oxides MgO, V_2O_5, CrO_3, MnO_2, CoO, ZnO, SnO_2, PbO_2, La_2O_3, and Ag_2O, and generally shows the same selective behaviour towards oxides as dmso–SO_2,[5] but the products are of an indeterminate nature, containing sulphur(IV); sulphite has been detected amongst the reaction products.

The oxides generally dissolve neither in dimethyl formamide nor in sulphur dioxide separately, the mixed solvent being necessary for dissolution. CrO_3 is the only oxide soluble in dimethyl formamide alone. No evidence was obtained for the intermediate involvement of $SO_2^{\cdot -}$, in contrast with the reaction between metals and dmf–SO_2.[6]

The mixed solvent system acetonitrile–sulphur dioxide only reacts with the oxides of copper(I) and copper(II), and not with any of the other oxides which have been treated with dmf–SO_2 or dmso–SO_2.[5]

Operations were carried out under dry oxygen-free nitrogen. Dimethylformamide was dried over 4A molecular sieve, deoxygenated, and redistilled under reduced pressure. Sulphur dioxide was dried by passage over phosphorus(V) oxide and through concentrated sulphuric acid.

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