Direct Reaction of Metals with the Mixed Non-aqueous System Dimethyl Sulphoxide–Sulphur Dioxide

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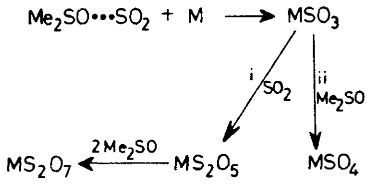
Summary The metals (M = Mg, Sr, Ba, V, Mn, Fe, Co, Ni, Cu, Zn, Al, In, Pb, and Yb) are dissolved by mixed non-aqueous solvent system dimethyl sulphoxide–sulphur dioxide to form the pyrosulphates of M = Mg, V, Mn, Fe, Co, Ni, Cu, Zn, Al, In, and Yb, and the sulphates of M = Sr, Ba, and Pb, and the metals Na, Be, Ca, Ce, Pr, Eu, Dy, Ga, Tl, Sn, Sb, Bi, I, and Cd also dissolve, but the products have not yet been characterized; phase studies indicate the existence of a 1 : 1 adduct of dimethyl sulphoxide and sulphur dioxide, which is considered responsible for the solution of metals in the system.

MANY metals, both transition and non-transition (M = Mg, V, Mn, Fe, Co, Ni, Cu, Zn, Al, In, and Yb) dissolve in the mixed non-aqueous solvent dimethyl sulphoxide-sulphur dioxide to form crystalline metal pyrosulphates, $M_x(S_2O_7)_y.zMe_2SO$. Other metals (M = Sr, Ba, and Pb) dissolve in the mixed solvent but yield only metal sulphate. The products were characterized by elemental analysis for metal, sulphur, carbon, and hydrogen, thermogravimetric analysis, and i.r. spectroscopy. The elements Na, Be, Ca, Ce, Pr, Eu, Dy, Ga, Tl, Sn, Sb, Bi, I, and Cd also dissolve in the mixed solvent, but the products await characterization. Thermogravimetric analysis carried out on the dimethyl sulphoxide-solvated pyrosulphates showed that in some cases (where M = Ni, Co, and Cu) the unsolvated pyrosulphate and in most cases (where M = Mg, Mn, Co, Ni, Cu, and Zn), the unsolvated sulphate was formed.

Reaction of many metals with the mixed solvent is complete within 48 h. However, Be, Sr, Ba, Ce, Pr, Eu, Dy, V, Ga, In, Tl, Sb, and Bi react more slowly. The state of division of the metal has a marked effect on the rate of reaction, and some metals, notably Sr, Ba, and Pb, become passive with a coating of insoluble sulphate.

Metals dissolve in neither dimethyl sulphoxide nor sulphur dioxide separately, and the mixed solvent is required for dissolution of metal to occur and for the oxidation of sulphur(IV) to sulphur(VI). The process, in which dimethyl sulphide is liberated, appears to involve, as a first stage, conversion of metal into metal sulphite, followed by either (i) solvation by sulphur dioxide and oxidation by dimethyl sulphoxide to metal pyrosulphate or (ii) oxidation by dimethyl sulphoxide to metal sulphate. Such processes have already been shown to occur for the anhydrous sulphites of cobalt and nickel[1] when these are treated with dimethyl sulphoxide and sulphur dioxide in solvents such as acetone and ethanol. We have recently found this process to occur with the sulphites of iron and copper.



Scheme

Phase studies indicate the existence of a discrete **1 : 1** adduct (m.p. −38 °C) of dimethyl sulphoxide and sulphur dioxide. It is this species which is considered necessary for the dissolution of metals (Scheme).

Operations were carried out under dry oxygen-free nitrogen. Dimethyl sulphoxide was dried over 4A molecular sieves and redistilled under reduced pressure. Sulphur dioxide was dried by passage through concentrated sulphuric acid.

(*Received*, 10*th May* 1976; *Com.* 522.)

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[1] R. Maylor, J. B. Gill, and D. C. Goodall, *J.C.S. Dalton*, 1973, 534.