

A Novel Reaction of Metal Oxides with the Mixed Non-aqueous System Dimethyl Sulphoxide–Sulphur Dioxide

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Several metal oxides react with the system dimethyl sulphoxide–sulphur dioxide to give metal disulphates; in contrast with the spontaneous reaction of metals with the system, no evidence is found for the involvement of metal–SO₂[−] ion pairs, and direct conversion of oxide through sulphite is thought to occur.

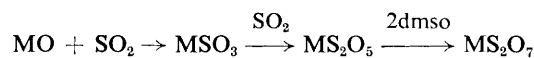
The metal oxides MgO, V₂O₅, CrO₃, MnO₂, CoO, CuO, Cu₂O, and ZnO react readily with the mixed non-aqueous system dimethyl sulphoxide(dmsO)–sulphur dioxide to form metal

disulphates, M_x(S₂O₇)_y·z dmsO. The products were characterised by elemental analysis for metal, sulphur, carbon, and hydrogen, thermogravimetric analysis, and i.r. spectroscopy.

The oxides SnO_2 , PbO_2 , La_2O_3 , and Ag_2O react slowly, or give products whose composition is difficult to determine. The oxides TiO_2 , Cr_2O_3 , Fe_2O_3 , Co_3O_4 , NiO , MoO_3 , and Al_2O_3 do not react at all.

The oxides generally dissolve neither in dimethyl sulphoxide nor in sulphur dioxide separately; the mixed solvent¹ is usually required for dissolution. CrO_3 is the only oxide soluble in dimethyl sulphoxide alone. Reaction of CrO_3 with dmsO-SO_2 leads to the formation of $\text{Cr}_2(\text{S}_2\text{O}_7)_3 \cdot 24\text{dmsO}$, which can be precipitated by addition of diethyl ether. Cr^{VI} in the form of chromate or dichromate can also be reduced in the mixed solvent system to give the same product. This is the first known preparation of a disulphate of chromium, although we have found that chromium can also be converted electrolytically in dmsO-SO_2 into the disulphate. Chromium is the only First Transition Series metal which does not react spontaneously with the mixed solvent system,² and hence this reaction cannot be used for the preparation of the disulphate. Both Cu^{I} oxide and Cu^{II} oxide give rise to the formation of Cu^{II} disulphate in the mixed solvent system. Unlike the process whereby metals react spontaneously with dmsO-SO_2 , the reaction of the system with oxides offers no evidence for the intermediate involvement of ion pairs of the type $[\text{M}^{\text{x}+} \cdot (\text{SO}_2^-)_y]$.² It is likely that, since the metal ion is already strongly bound to oxygen in the oxides, no competition from SO_2^- is experienced, and the initial step is probably direct conversion of oxide into sulphite followed by solvation by sulphur dioxide and oxidation by dmsO to metal disulphate (Scheme 1).

It was shown earlier³ that the sulphites of cobalt and nickel, and more recently⁴ that those of manganese, iron, and copper, react with dmsO-SO_2 to form the disulphates, and the mechanism has been discussed.



Scheme 1

It is not clear at this stage which factors are most important in determining whether or not an oxide reacts with dmsO-SO_2 . It may depend to some extent on the defect structure of the oxide, rather than on the redox parameters of the metal, bearing in mind the clear differentiation observed in the behaviour of CoO and NiO towards dmsO-SO_2 .

Preliminary experiments indicate that other solvent-sulphur dioxide mixed systems react with metal oxides. However, they are less reactive than our system, which is unique in its ability to convert sulphur(IV) into sulphur(VI) in the form of the disulphate ion.

Operations were carried out under dry oxygen-free nitrogen. Dimethyl sulphoxide 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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