Reactions in Mixed Non-aqueous Systems containing Sulphur Dioxide. Part 6.† The Reaction of Metal Oxides with Dimethyl Sulphoxide–Sulphur Dioxide

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The metal oxides MgO, V_2O_5, CrO_3, MnO_2, CoO, CuO, Cu_2O, and ZnO react with dimethyl sulphoxide–sulphur dioxide to form the metal disulphates $M_x(S_2O_7)_y \cdot z$dmso. The oxides SnO_2, PbO_2, La_2O_3, and Ag_2O give products of indeterminate composition, and TiO_2, Cr_2O_3, Fe_2O_3, Co_3O_4, NiO, MoO_3, and Al_2O_3 do not react with the mixed-solvent system. The mechanism of conversion of oxide into disulphate is discussed.

The mixed-solvent system dimethyl sulphoxide(dmso)–sulphur dioxide has been shown to react spontaneously with many metals,[1,2] often displaying a high degree of selective attack, as exemplified by the ready reaction with manganese and iron, but total lack of reactivity towards chromium. The reactivity of this solvent system towards metals has been attributed to the formation of the sulphoxylate radical ion, $SO_2^{\bullet -}$, and to intermediate sulphur oxy-anion species which contain highly reactive S–O–S linkages in which sulphur(IV) can be oxidised to sulphur(VI) to yield ultimate products containing disulphate.

In this paper we describe how several metal oxides react with dmso–SO_2, which also shows a high degree of selectivity in its behaviour with oxides.

Results and Discussion

A recent communication[3] reported the reaction of metal oxides with the mixed non-aqueous system dimethyl sulphoxide (dmso)–sulphur dioxide. The oxides MgO, V_2O_5, CrO_3, MnO_2, CoO, CuO, Cu_2O, and ZnO react readily to form the crystalline metal disulphates, $M_x(S_2O_7)_y \cdot z$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 yielded impure products, and TiO_2, Cr_2O_3, Fe_2O_3, Co_3O_4, NiO, MoO_3, and Al_2O_3 were completely inactive towards the solvent system. All the oxides were used as finely divided powders, and they generally dissolve neither in dimethyl sulphoxide nor in sulphur dioxide separately; the mixed solvent[1] is usually required for dissolution of oxide to occur and for the oxidation of sulphur(IV) to sulphur(VI).

The solvated disulphates of the metals Mg, V, Mn, Co, Cu, and Zn were prepared previously and fully characterised.[1,2] Chromium(VI) oxide, CrO_3, is the only oxide soluble in dimethyl sulphoxide alone. It reacts with dmso–SO_2 to form $Cr_2(S_2O_7)_3 \cdot 24$dmso, a hygroscopic crystalline solid. Infrared data are recorded in the Table. A thermogram was unobtainable, since the compound underwent rather violent decrepitation on heating. Chromium(VI) in the form of chromate or dichromate can also be reduced by the mixed-solvent system to yield the same product. This is the first known preparation of a disulphate of chromium, although we have since shown that chromium metal can be converted electrolytically in dmso–SO_2 into the disulphate, which arises in a crystalline form containing a greater number of solvent molecules[4] than is observed in the case of its formation from CrO_3 in dmso–SO_2. Chromium is the only metal of the First Transition Series which does not react spontaneously with the mixed-solvent system[2] and thus such a reaction may not be used for the preparation of the disulphate.

Table. Infrared bands (cm^{-1}) of $[Cr_2(dmso)_{24}][S_2O_7]_3$

	Assignment
575m 590m	$[S_2O_7]^{2-}$
690 (sh) 940 (sh)	dmso
1 000s 1 030s 1 155s	$[S_2O_7]^{2-}$
1 230s 1 320w	dmso

Both copper(I) oxide and copper(II) oxide give rise to the formation of copper(II) disulphate in the mixed-solvent system. It is interesting to observe that both oxidation of copper and of sulphur are taking place in the mixed solvent. In aqueous media containing SO_2, reduction of copper(II) to copper(I) would normally occur, as would reduction of chromium(VI) to chromium(III). It is therefore important to note the very different redox characteristics which SO_2 exhibits in the system dmso–SO_2, namely oxidising with respect to copper but reducing with respect to chromium. This behaviour may be in part a consequence of the adduct formation which takes place between dmso and SO_2, but it may also depend on the mechanism of conversion of oxide into disulphate. It is not known, for example, whether the intermediate sulphur oxy-anion species, which are thought to contain S–O–S linkages, stabilise one oxidation state of a metal or another. It is known that dmso acts as an oxidiser in dmso–SO_2,[1] but in the case of the reaction of CrO_3 with dmso–SO_2 it is not known whether chromium(VI) plays any part in the oxidation of sulphur(IV) to sulphur(VI). It does appear that no conversion of SO_2 into sulphate occurs, and that the SO_2 is involved entirely in the formation of disulphate. This precludes the redox reaction between chromium(VI) and SO_2 which takes place in aqueous solution.

Unlike the process in which metals react with dmso–SO_2, no evidence was acquired to indicate that the reaction of the system with oxides involves the intermediate formation of $SO_2^{\bullet -}$, or of ion pairs of the type $M^{x+} \cdot ySO_2^{\bullet -}$.[2] The metal ion is strongly bound to oxygen in the oxides, and it is unlikely that the much weaker donor $SO_2^{\bullet -}$ would displace the oxide oxygen. The initial reaction step probably involves direct conversion of oxide into sulphite, followed by solvation by SO_2 to disulphite, and oxidation of the latter by dmso to metal disulphate [equation (1)].

$$MO + SO_2 \longrightarrow MSO_3 \xrightarrow{SO_2} MS_2O_5 \xrightarrow{2\text{dmso}} MS_2O_7 \quad (1)$$

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† Part 5, N. K. Graham, J. B. Gill and D. C. Goodall, *Aust. J. Chem.*, 1983, **36**, 1991.

We have already shown that the sulphites of manganese, iron, cobalt, nickel, and copper[5,6] react with dmso–SO_2 to form the disulphates, and the mechanism has been discussed. An essential requirement for this conversion is that the intermediate sulphite should be highly covalent, in order to act as a precursor for the formation of S–O–S bonds in which the sulphur(IV) atoms can subsequently be oxidised by dmso. The presence of highly covalent oxide is therefore very favourable for the formation of covalent sulphite. It is not yet clear which factors are important in determining the reactivity of an oxide. There may be some dependence on the defect structure. The redox parameters of the metal may or may not be decisive. The remarkably strong differentiation observed in the behaviour of CoO and NiO towards dmso–SO_2 suggests the redox factor is not very important, but in the case of CrO_3 and Cr_2O_3, and of CoO and Co_3O_4, it seems that the redox factor could be of some significance.

Experimental

All operations were carried out under dry oxygen-free nitrogen. Dimethyl sulphoxide was dried by stirring it over activated alumina for 24 h, followed by storage over 4A molecular sieve and repeated fractional crystallisation. Sulphur dioxide was dried by passage over phosphorus(V) oxide and through concentrated sulphuric acid.

Preparations.—The salts $[Mg(dmso)_6][S_2O_7]$, $[V_2(dmso)_{12}][S_2O_7]_3$, $[Mn(dmso)_6][S_2O_7]$, $[Co(dmso)_6][S_2O_7]$, $[Cu(dmso)_6][S_2O_7]$, and $[Zn(dmso)_6][S_2O_7]$ were prepared by adding finely divided metal oxide to dimethyl sulphoxide saturated with sulphur dioxide. In each case, the mixture was kept in a closed container for 1—2 d. The solution was filtered, and the product obtained either by spontaneous crystallisation or by the addition of diethyl ether to the filtrate. The product was filtered off, washed with diethyl ether, and pumped for 12 h. Analyses, i.r. spectra, and thermograms corresponded to those found for the same compounds prepared by spontaneous dissolution of metal in the binary solvent.[1,2]

$[Cr_2(dmso)_{24}][S_2O_7]_3$. Chromium(VI) oxide was added to dimethyl sulphoxide–diethyl ether (1:1), and the mixture was saturated with sulphur dioxide. A green crystalline solid precipitated, which was recrystallised from dimethyl sulphoxide–diethyl ether (1:1). The product was filtered off, washed with diethyl ether, and pumped for 12 h (Found: C, 22.05; H, 6.1; Cr, 4.1; S, 37.4. Calc. for $C_{48}H_{144}Cr_2O_{45}S_{30}$: C, 22.9; H, 5.8; Cr, 4.15; S, 38.3%).

Physical Measurements.—Infrared spectra were recorded for Nujol mulls on a Pye Unicam SP2000 spectrophotometer. Thermograms were obtained using a Stanton thermobalance. Carbon, hydrogen, sulphur, and metals were determined by Mr. A. Hedley of this department.

Acknowledgements

Generous financial support (to B. J.) is acknowledged from RTZ Services Ltd. and the S.E.R.C.

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Received 17*th April* 1984; *Paper* 4/633