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THE SOLUTION OF METALS IN DIMETHYL SULPHOXIDE AND OTHER NON-AQUEOUS SOLVENTS CONTAINING SULPHUR DIOXIDE

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ABSTRACT

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The metals (Mg, Al, In, Sn, Ti, V, Mn, Fe, Co, Ni, Cu, Zn and Cd) react with the mixed non-aqueous system dimethylsulphoxide(dmso)—sulphur dioxide to form metal disulphates as final products. Sr, Ba and Pb react with the same system to form metal sulphates. Other metals (Li, Na, Be, Ca, Ga, Tl, Sb, Bi; Ce, Pr, Eu, Dy, U) dissolve in the mixed solvent, but it has not been possible to characterize the final products, although intermediate dithionite formation was observed. Evidence indicates the existence of a 1 : 1 adduct of dmso and SO_2, which is considered responsible for the reaction of metals with the system. A likely mechanism for the oxidative process is discussed. The existence of the $[SO_2]^-$ radical ion, and of ion-pairs containing a metal ion and $[SO_2]^-$ has been demonstrated for solutions of metals in various solvents containing sulphur dioxide. The reactivity of metals in such solvents containing sulphur dioxide has been related to dielectric constant and donor number of the solvent. Several oxides also react with the mixed solvents. $[SO_2]^-$ can be generated by electrolysis in the mixed solvents.

INTRODUCTION

Recent work on the properties of sulphur dioxide in dimethyl sulphoxide and other non-aqueous solvents (Harrison et al., 1978, 1979) has indicated the potential of such a medium as a leaching agent for metals and oxides. In certain circumstances excellent selectivity is observed and, provided metals can be recovered from solution in such a way that the organic solvent can be recycled without high losses, the system offers practical possibilities for the recovery of values from complex ores, and intermediates or secondary materials containing mixtures of metals. Further work is currently in progress on such aspects and the present paper represents an attempt to indicate the chemical behaviour of the system and the various solvents that show promising reactions with metals and oxides.

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EXPERIMENTAL

Compounds were obtained by adding finely-divided metal to freshly distilled solvent, and the mixture was saturated with sulphur dioxide. The solutions were filtered from excess metal, and the metal sulphur—oxyanion compounds obtained either by the addition of ether to the filtrate, or by allowing the compound to crystallize.

Solutions for spectroscopic studies were obtained by placing a small amount of a metal into a sample of stock solution of sulphur dioxide in the required solvent. The colours were allowed to form, and the solution was quickly decanted into a quartz glass cell, which was then stoppered. The reference cell contained the stock solution of sulphur dioxide in the solvent being investigated.

Spectra were recorded on a Pye Unicam SP8000 spectrophotometer. Infrared spectra were recorded on a Perkin—Elmer 457 grating spectrophotometer as Nujol mulls. Raman spectra were obtained using a Coherent Radiation model 52 tunable argon-ion laser, operating at 488 nm.

Thermogravimetric curves were obtained using a Stanton thermobalance. Metals were determined gravimetrically. C, H and S were determined by Mr. A. Hedley of this department.

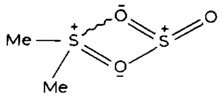
RESULTS AND DISCUSSION

The metals (Mg, Al, In, Sn; Ti, V, Mn, Fe, Co, Ni, Cu, Zn and Cd) dissolve in the mixed non-aqueous system dimethylsulphoxide(dmso)—sulphur dioxide, from which the metal disulphates, $M_x(S_2O_7)_y \cdot z\text{dmso}$, finally crystallize, or may be precipitated on addition of an inert solvent such as ether. The metals (Sr, Ba and Pb) dissolve to form the metal sulphates. The metals (Li, Na, Be, Ca, Ga, Tl, Sb, Bi; Ce, Pr, Eu, Dy, U) dissolve in the mixed solvent, but no pure final products have yet been isolated, although intermediate dithionite formation was observed. The metals dissolve neither in dmso nor in SO_2 separately. The mixed solvent is required for dissolution of metal to occur, and for oxidation of sulphur(IV) to sulphur(VI). Some metals react completely with the mixed solvent within a few hours, others more slowly, and the state of division of the metal has a marked effect on the rate of solution. The mixed solvent appeared completely inert towards chromium. Some metals, particularly Sr, Ba and Pb, became passive with a coating of insoluble sulphate.

The thermal decomposition of the solvated metal disulphates was studied up to 1000°C. In general, heating causes an initial loss of solvent to form unsolvated disulphate, followed by loss of SO_3 to form sulphate, and finally, oxide:

$$\begin{tikzcd} M_x(S_2O_7)_y \cdot z\text{dmso} \arrow[r] & M_x(S_2O_7)_y \arrow[r] & M_x(SO_4)_y + ySO_3 \arrow[d] \\ & & M_xO_y + ySO_3 \end{tikzcd}$$

It is not absolutely clear what is involved in the oxidation of metal to metal disulphate. Dimethyl sulphide is one of the reaction products, and this suggests that dmso is acting as an oxidising species, but it is not clear whether all the oxygen for the oxidation arises from dmso. Phase studies indicate the existence of a discrete 1:1 adduct (m.p. −38°C) of dmso and SO_2, and this is supported by Raman spectroscopic studies, which indicate an adduct of the form:

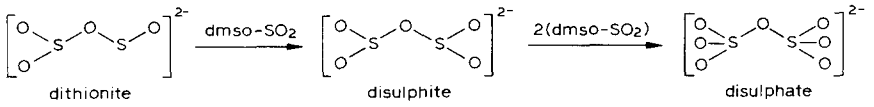


Although metals are generally converted by dmso—SO_2 into metal disulphate, in the case of the more reactive metals (Li, Na, Mg, Sn, Zn and Cd), formation of metal dithionite was observed, as it was with several other solvents containing sulphur dioxide. This is considered to arise as a result of dimerisation of the $[SO_2]^-$ radical ion, formed when the metal reacts with sulphur dioxide (eqns. (1) and (2)). Formation of the $[SO_2]^-$ ion had been observed when sodium dissolves in dmso—SO_2 (Byler and Shriver, 1976).

$$M + xSO_2 \rightarrow M^{x+} + x[SO_2]^- \tag{1}$$

$$2[SO_2]^- \rightleftharpoons [S_2O_4]^{2-} \tag{2}$$

The metal dithionites are oxidised to metal disulphates by the mixed solvent dmso—SO_2. Rinker and Lynn (1969) observed the formation of a very reactive form of dithionite, which was considered to be the form containing an S—O—S link, $[SO_2.SO_2]^{2-}$. Although in the solid state dithionites have the S—S link, $[O_2S.SO_2]^{2-}$, the form with the S—O—S link may well be the reactive intermediate in the oxidative process. Such an intermediate is especially attractive in that it can be oxidised by dmso-SO_2 to disulphate without the need for any bond rearrangements, and a transitionary disulphite having an S—O—S link may form, as is considered to be the case when transition metal sulphites are converted to disulphates (Maylor et al., 1973):



Rinker (1959) had observed the formation of the $[SO_2]^-$ ion in aqueous solutions of sodium dithionite. It arises as a brown species absorbing at 395 nm, and is paramagnetic (esr *g*-value = 2.007). We have been able to show that when, for example, magnesium dissolves in dmso—SO_2, a series of colour changes occurs. We observe, as the reaction progresses, the formation of the brown $[SO_2]^-$ ion, and a blue species absorbing in the region 550—590 nm. The same blue colour is observed when sodium dithionite is dissolved in dmso. Rinker and Lynn (1968) also noticed the formation of a blue species when sodium amalgam reacts with the mixed solvent dimethylformamide—SO_2, as well as the formation of $[SO_2]^-$. We have shown that the $[SO_2]^-$ ion can be observed in many solvents. It is generated in two ways: (i) by dissociation of the dithionite ion in solution, and (ii) by reduction of SO_2 in solution by a metal. We investigated the reactions of several metals with SO_2 in a wide range of solvents (Table 1).

TABLE 1

Reactivity of metals with solvents containing sulphur dioxide

Solvent	Metal	Reaction
Dimethyl sulphoxide	Li, Na, Mg, Ca, Fe, Zn	positive
Dimethyl acetamide		+
Dimethyl formamide		+
Formamide		+
Ethanol		+
Water		+
Trimethyl phosphate		+
Tris(dimethylamino)phosphine oxide		+
Tetrahydrothiophen 1,1-dioxide		negative
Nitrobenzene		–
Nitromethane		–
Ethyl acetate		–
Acetonitrile		–
Diethyl ether		–
Dioxan		–
Tetrahydrofuran		–
Pyridine		–
Acetone		–

The position of the maximum intensity of the blue species in the visible region of the spectrum was shown to depend on the metal ion present, and this can best be explained by considering the formation of some kind of contact ion-pair, $[M^{x+}\cdot SO_2^-]$: e.g.

$[Fe^{2+}\cdot SO_2^-]$	$[Mg^{2+}\cdot SO_2^-]$	$[Li^+\cdot SO_2^-]$	$[Na^+\cdot SO_2^-]$
550 nm	560—565 nm	585 nm	585—590 nm

The stability and nature of the ion-pair varies according to the metal ion. Ion-pairs containing lithium or sodium seem to be the most stable. The order of stability observed is as follows:

$$[Li^+ \cdot SO_2^-] \simeq [Na^+ \cdot SO_2^-] > [Mg^{2+} \cdot SO_2^-] > [Fe^{2+} \cdot SO_2^-] > [Zn^{2+} \cdot SO_2^-]$$

It was observed that, in order for a reaction between a metal and SO_2 to occur in a solvent, the solvent must have both a high donor number (>20), as defined by Gutmann (1968), and a high dielectric constant (>20). The dielectric constant gives an approximate guide as to whether a reaction will occur. Thus a solvent of high dielectric constant will favour the reaction:

$$M + x\,SO_2 \rightarrow M^{x+} + x\,[SO_2]^-$$

Reaction occurs at the metal surface (the coloured species always arise at the metal surface), and the rate-controlling step is that of diffusion of metal ions from the metal surface. A solvent of high donor number will favour solvation of metal ions, and prevent the recombination:

$$M^{x+} + x\,[SO_2]^- \rightarrow M + x\,SO_2$$

The $[SO_2]^-$ ion can be generated in solution in the absence of metal. Solutions of SO_2 in dimethylformamide, dimethylsulphoxide, dimethylacetamide, and formamide were electrolysed using carbon electrodes. In each case, the brown $[SO_2]^-$ ion alone was formed in solution.

It has also been observed that many oxides dissolved in the mixed solvent systems, notably acidic oxides such as MnO_2, CrO_3, Al_2O_3.

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