Reactions in Mixed Non-aqueous Solution containing Sulphur Dioxide. Part 9.† Mechanisms of Dissolution of Metals, Oxides, and Sulphites

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A new mechanistic pathway which explains the dissolution of metals into binary mixtures of SO_2 and dimethyl sulphoxide (dmso) is presented. The adduct, dmso$\cdot$2SO_2, which is a component of these mixtures contains the S–O–S linkage necessary to the formation of $[S_2O_7]^{2-}$. The process must proceed through free-radical electron transfer and a series of O-atom transfer steps. The reactions of metal oxides and sulphites with dmso–SO_2 also conform to the mechanistic scheme proposed.

Reactions of metal sulphites,[1] metal oxides,[2,3] and metals (by both spontaneous[4,5] and electrolytic[6,7] dissolution) with binary solvent mixtures containing SO_2 in dimethyl sulphoxide (dmso) and other dipolar aprotic solvents have been extensively investigated in our laboratories and reviewed by one of us.[8]

When metals and their oxides react with SO_2 in dmso the product is normally the disulphate salt of the metal, but with other co-solvents, sulphites, disulphites, dithionites, or metals are obtained. Dimethyl sulphoxide oxidises sulphur from sulphur(III) or sulphur(IV) to sulphur(VI); partially oxidised products like $2.5Zn(S_2O_4)\cdot Zn(dmso)_6(S_2O_7)$ have also been isolated.[9] It also acts as an O-atom transfer agent by providing the additional oxygen atoms needed in $[S_2O_7]^{2-}$; within this process dmso is reduced to dimethyl sulphide (dms).

Addition of the acceptor solvent SO_2 to donor solvents such as dmso, dimethylformamide (dmf), dimethylacetamide (dma), or hexamethylphosphoramide (hmpa) leads to the release of considerable enthalpy of mixing, signifying adduct formation. Recent Raman[10] and phase studies[11] have provided further evidence for, and the stoicheiometries of, adducts between SO_2 and dmso, and dmf.

None of the metals (or their oxides) which react spontaneously with these binary solvent mixtures reacts directly with either pure liquid SO_2 or the pure cosolvent, at ambient or sub-ambient temperatures. They only do so if SO_2 is present with a cosolvent of high donicity and high dielectric constant.[4,7] Electrolytic dissolution can be promoted with many other cosolvents if the metal concerned is used as a sacrificial anode. Thus we are led to the conclusion that the active intermediate(s) must be either adducts of SO_2 with the co-solvent, or species obtained by reduction of the adducts.

The chemical processes we have reported can be categorised into the following set of general reactions. Care must be exercised to exclude water from these systems because $[S_2O_7]^{2-}$ is readily hydrolysed to $[HSO_4]^-$.

$$\mathrm{M + SO_2\text{–}dmso \longrightarrow M(S_2O_7) + dms} \qquad (i)$$

$$\mathrm{M + SO_2\text{–}dmf\ (or\ dma,\ hmpa,}\ etc.) \longrightarrow \mathrm{M(S_2O_4)} \qquad (ii)$$

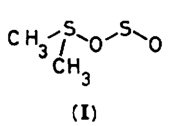
$$\mathrm{MO + SO_2\text{–}dmso \longrightarrow M(S_2O_7) + dms} \qquad (iii)$$

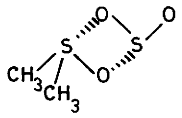
$$\mathrm{M(SO_3) + SO_2\text{–}dmso \longrightarrow M(S_2O_7) + dms} \qquad (iv)$$

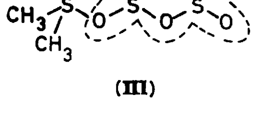
Our earlier attempt to describe a mechanistic pathway[4,5] for the dissolution of metals into binary mixtures containing SO_2 was inadequate through paucity of experimental information. In consequence our original proposals should be regarded as well considered speculations; the best explanations which could be presented at the time. They were based on the sound experimental evidence that the solvated sulphoxylate radical ion, $[SO_2]^{\cdot -}$, participates in the metal dissolution process. It is now confirmed, from spectroscopic,[12,13] voltammetric,[14,15] and e.s.r.[9] studies, that this species is produced in the first step of metal dissolution (both spontaneous and electrolytic): $M + xSO_2 \longrightarrow x[SO_2]^{\cdot -}$ (solvated) + M^{x+}.

It is the generation of solvated $[SO_2]^{\cdot -}$ which causes the colours observed during metal dissolution in dmso–SO_2 mixtures. For instance, in the dissolution process of Mg metal the solution passes through a succession of colours: first brown, then blue-black, finally fading through green to colourless or pale yellow. Depending upon the total SO_2 concentration, and/or the dielectric constant of the solvent mixture, and/or the identity of the cations present the radical anion in solution can appear in a variety of forms: $[SO_2]^{\cdot -}\text{-}SO_2$;[15] $[SO_2]^{\cdot -}\text{-}xSO_2$ (blue species);[14] $([SO_2]^{\cdot -})_2$, (or $[S_2O_4]^{2-}$, dithionite);[14] $SO_2\cdot[S_2O_4]^{2-}$ (red species).[14] The absorption maximum of the blue species varies between 550 and 590 nm depending on the cation present. The cation dependency of the absorption frequency indicates that either contact or solvent-separated ion pairing occurs between the metal cation and the $[SO_2]^{\cdot -}$ radical anion.[5,9] The affinity of many dipolar aprotic solvents for sulphur dioxide means that, in solution, the $[SO_2]^{\cdot -}$ anions are probably heavily solvated by further SO_2–solvent interactions.

From the phase studies[11] on SO_2–dmso mixtures we have shown that adducts with the compositions $2SO_2\cdot$dmso and $SO_2\cdot$dmso exist. Raman spectroscopic studies[10] confirmed these species as well as providing the evidence for a third adduct of stoicheiometry $SO_2\cdot$2dmso. Although the structural details of these adducts are, as yet, unavailable it can be reasonably assumed that association occurs through either 'end-on' [(**I**)], or 'sideways-on' [(**II**)] addition. These structures are similar to


(**I**)


(**II**)


(**III**)

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† Part 8 is ref. 11.

those of the addition product known to occur between N_2O_4 and dmso,[16] and for which isotopic exchange experiments have confirmed oxygen exchange between optically active sulphoxide and N_2O_4.[17,18]

In the light of a few further simple experiments, and a recent improvement in the understanding of the compositions of these binary solvent mixtures, this new appraisal of the mechanistic pathway of the dissolution processes is presented.

Discussion

(*a*) *Dissolution of Metals into* dmso–SO_2 *Media.*—The $2SO_2{\cdot}$dmso species is important because its existence affords a simple explanation of the route to the disulphate anion, $[S_2O_7]^{2-}$, which contains the S–O–S linkage as its nucleus. With species (**III**) as an initial reactant in the process there is no need to postulate either direct formation of the unknown S–O–S linkage in an anion with stoicheiometry $[S_2O_5]^{2-}$, with S in the S^{IV} formal oxidation state, or its indirect formation by an intramolecular rearrangement of the well known S–S bonded disulphite, $[S_2O_5]^{2-}$. The second case constitutes the weak link of our previous proposal[4] for the mechanism; there is no evidence that the S–S linkage of $[S_2O_5]^{2-}$ can break and reassemble in an isomeric form containing the S–O–S group of atoms.

Adduct (**III**) provides a starting point for the formation of a radical ion containing the S–O–S group, $[\text{dmso}{\cdot}OS{\cdot}O{\cdot}SO_2]^{\bullet -}$. Two possible routes to its formation may be written: either equation (1) followed by equation (2), or by equation (3) (Scheme). We favour the successive steps through equations (1) and (2) because there is sound experimental evidence that both the spontaneous and the electrolytic dissolution of metals involves solvated $[SO_2]^{\bullet -}$ irrespective of the cosolvent. Following the formation of this radical, stepwise additions of dmso [as indicated by equations (4), (5), and (6)], through a series of successive radical anions, leads to $[S_2O_7]^{\bullet -}$. At any one of these steps the sulphoxide bond of an associated dmso molecule may break to leave its O atom on the radical with the release of dms. Finally, electron exchange from another radical anion to $[S_2O_7]^{\bullet -}$ can produce the disulphate anion, as in equation (7).

$$M + SO_2 \longrightarrow [SO_2]^{\bullet -}_{(\text{solv.})} + M^+ \qquad (1)$$

$$[SO_2]^{\bullet -}_{(\text{solv.})} + [\text{dmso}{\cdot}SO{\cdot}O{\cdot}SO_2] \longrightarrow [\text{dmso}{\cdot}SO{\cdot}O{\cdot}SO_2]^{\bullet -} + SO_2 \qquad (2)$$

$$M + [\text{dmso}{\cdot}SO{\cdot}O{\cdot}SO_2] \longrightarrow M^+ + [\text{dmso}{\cdot}SO{\cdot}O{\cdot}SO_2]^{\bullet -} \qquad (3)$$

$$[\text{dmso}{\cdot}SO{\cdot}O{\cdot}SO_2]^{\bullet -} + \text{dmso} \longrightarrow [O_2S{\cdot}O{\cdot}SO_2]^{\bullet -} + 2\text{dms} \qquad (4)$$

$$[O_2S{\cdot}O{\cdot}SO_2]^{\bullet -} + \text{dmso} \longrightarrow [O_2S{\cdot}O{\cdot}SO_3]^{\bullet -} + \text{dms} \qquad (5)$$

$$[O_2S{\cdot}O{\cdot}SO_3]^{\bullet -} + \text{dmso} \longrightarrow [O_3S{\cdot}O{\cdot}SO_3]^{\bullet -} + \text{dms} \qquad (6)$$

$$[S_2O_7]^{\bullet -} + [SO_2]^{\bullet -}_{(\text{solv.})} \longrightarrow [S_2O_7]^{2-} + SO_{2(\text{solv.})} \qquad (7)$$

Scheme.

(*b*) *Dissolution of Metals into other* SO_2*–Cosolvent Systems.*—If the cosolvent with SO_2 is not dmso, but a solvent with high donicity and high dielectric constant such as dmf, dma, hmpa, *etc.*, the product is the metal dithionite. This is also the end product of the sacrificial anodic dissolution process of metals into those mixtures in which the cosolvent has low or moderate donicity and/or low or moderate dielectric constant. For these cases the situation is obvious. Oxidation of the metal to the metal cation produces solvated $[SO_2]^{\bullet -}$ [process (1) of the Scheme] and the consequent dimerisation of this gives $[S_2O_4]^{2-}$ from which the metal dithionite results; $2[SO_2]^{\bullet -} = [S_2O_4]^{2-}$.

(*c*) *The Dissolution of Metal Sulphites.*—In the case of the oxidation of transition-metal sulphites to disulphates, observed in dmso–SO_2 but not in dmso alone, the first stage is the simple addition of SO_2 to the $SO_3{}^{2-}$ anion to give the soluble S–S bonded disulphite; equation (8). The next step is not the

$$SO_2 + M(SO_3) \longrightarrow M^{2+} + [O_2S{\cdot}SO_3]^{2-} \qquad (8)$$

oxidation of S–S bonded $[S_2O_5]^{2-}$ originally proposed,[4] but appears to be the production of solvated $[SO_2]^{\bullet -}$ by an electron transfer between the transition metal cation with the solvent; equation (9).

$$M^{x+} + SO_2 \longrightarrow M^{(x+1)+} + [SO_2]^{\bullet -}_{(\text{solv.})} \qquad (9)$$

The process outlined in (*a*) above then occurs because dmso not only oxidises the S^{IV} of the S–O–S linkage to S^{VI}, as in equations (1)—(6) of the Scheme, but also transfers O atoms to the intermediate S–O–S bridged anions with release of dms. Evidence that this mechanism must proceed through a series of S–O–S bridged species is as follows: (*i*) deep coloured solutions are observed[19,20] when iron(II), cobalt(II), and copper(I) sulphites dissolve in dmso–SO_2 (the generation of $[SO_2]^{\bullet -}$ was not appreciated at the time of the initial observations); (*ii*) non-transition metal sulphites (Na_2SO_3, $MgSO_3$, *etc.*) remain unoxidised by dmso–SO_2; and (*iii*) S–S bonded disulphites, and dithionites, cannot be oxidised by dmso alone. The argument is also supported by experiments which have shown how the addition of transition-metal salts, such as $MnCl_2$ and $CoCl_2$, to solutions of SO_2 in dmf produces $[SO_2]^{\bullet -}$. Dimethylformamide was chosen as the solvent for this experiment because $[SO_2]^{\bullet -}$ exists in dmso mixtures at low concentration only due to the oxidising power of this solvent.

(*d*) *Dissolution of Metal Oxides.*—In the dissolution of transition metal oxides a step prior to those outlined above must be included, namely the generation of sulphite, $[SO_3]^{2-}$, from SO_2 and oxide ion. Further addition of SO_2 to $[SO_3]^{2-}$ produces the soluble disulphite. The process can then proceed through generation of the solvated $[SO_2]^{\bullet -}$ radical anion as in (*a*) and (*c*) above.

In the special case of the reaction of Cu^I and Cu^{II} oxides with dmf–SO_2 mixtures Cu metal is precipitated.[21] First, addition of SO_2 to the oxide anion occurs with the formation of $[SO_3]^{2-}$, and some reduction in the case of Cu^{II} oxide; equations (10)—(12). The Cu_2SO_3 formed (probably in solution as disulphite), undergoes a disproportionation involving the reduction of $[S_2O_5]^{2-}$ to $[S_2O_4]^{2-}$ and oxidation of Cu^I to Cu^{II}; equation (13). The copper dithionite then undergoes further disproportionation to produce Cu metal with regeneration of SO_2; equation (14).

$$Cu_2O + SO_2 \longrightarrow Cu_2SO_3 \qquad (10)$$

$$CuO + SO_2 \longrightarrow CuSO_3 \qquad (11)$$

$$2CuSO_3 + CuO \longrightarrow CuSO_4 + Cu_2SO_3 \qquad (12)$$

$$Cu_2(S_2O_5) + 2SO_2 \longrightarrow Cu(S_2O_5) + Cu(S_2O_4) \qquad (13)$$

$$Cu(S_2O_4) \longrightarrow Cu + 2SO_2 \qquad (14)$$

Two items of experimental evidence support this. First, both Cu^I and Cu^{II} and SO_2 coexist in the solution, and the presence of $[SO_2]^{\bullet-}$ radical anions is confirmed spectroscopically from the intense sharp absorption band observed at 395 nm. Secondly, Cu metal, in a solution of dmf–SO_2, partially dissolves and soon comes to equilibrium with copper ions and $[SO_2]^{\bullet-}$ radical anions. So this is another example, such as those outlined in section (*c*), of the reduction of SO_2 to $[SO_2]^{\bullet-}$ by a transition-metal ion in solution. The reactions can be summarised as in equations (15) and (16).

$$Cu_2O + SO_2 \longrightarrow Cu(SO_3) + Cu \quad (15)$$

$$3CuO + 2SO_2 \longrightarrow Cu(SO_4) + Cu(SO_3) + Cu \quad (16)$$

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