Reactions in Mixed Non-aqueous Systems containing Sulphur Dioxide. Part 2.† The Dissolution of Transition Metals in the Binary Mixture Dimethyl Sulphoxide–Sulphur Dioxide, and Ion-pair Formation involving the Sulphoxylate Radical Ion in Mixed Solvents containing Sulphur Dioxide

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The metals (Ti, V, Mn, Fe, Co, Ni, Cu, Zn, and Cd) react with the mixed non-aqueous solvent dimethyl sulphoxide–sulphur dioxide to form the metal disulphates. Other metals (M = Ce, Pr, Eu, Dy, or U) dissolve in the mixed solvent, but it has not been possible to characterize the products. 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 non-aqueous solvents containing sulphur dioxide. A correlation has been established between dielectric constant, donor number, and the reactivity of metals in solvents containing sulphur dioxide.

A RECENT communication[1] reported the reaction of metals with the mixed non-aqueous system dimethyl sulphoxide–sulphur dioxide. The metals dissolve neither in dimethyl sulphoxide (dmso) nor in sulphur dioxide separately, the mixed solvent being required for dissolution of metal and for oxidation of sulphur(IV) to sulphur(VI). The metals Ti, V, Mn, Fe, Co, Ni, Cu, Zn, and Cd dissolve in the mixed solvent to form crystalline metal disulphates $M_x(S_2O_7)_y \cdot z(\text{dmso})$, characterized by elemental analysis, thermogravimetric analysis, and i.r. spectroscopy while Ce, Pr, Eu, Dy, and U dissolve in the mixed solvent but no pure products have yet been isolated. 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 reaction rate. The mixed solvent appeared completely inert towards chromium.

TABLE 1

Infrared bands (cm^{-1}) of metal disulphates

$[Mn(dmso)_6][S_2O_7]$	$[Fe(dmso)_6][S_2O_7]$	$[Cu(dmso)_6][S_2O_7]$	$[Zn(dmso)_6][S_2O_7]$	$[Cd(dmso)_6][S_2O_7]$	Assignment
			420s	420s	$[S_2O_7]^{2-}$
			440s		
575m		575m	577s	578s	$[S_2O_7]^{2-}$
582m	585m				
	590m	590m	595s	598s	
670w		670w	680w	675w	dmso
835s	835s	835s	835s	835s	$[S_2O_7]^{2-}$
915s		900 (sh)	902w		dmso
948 (sh)	945s	940s	950s	950s	
956s	955 (sh)				
970m					
1 002s	1 000 (sh)	1 000s	1 000s	990s	$[S_2O_7]^{2-}$
1 012s	1 008s			1 012s	
1 060s	1 060s	1 050s	1 052s	1 058s	
	1 120w	1 110s			
1 160s	1 160s	1 150s	1 155s	1 160s	
1 234s	1 230s	1 240s	1 240s	1 240s	dmso
1 315w	1 320w	1 320w	1 320m	1 320m	

The solvated disulphates are hygroscopic solids which dissolve readily in water, and are quite soluble in dmso. The i.r. bands of solvated disulphates are shown in Table 1. Those of the solvated disulphates of cobalt(II) and nickel(II) are recorded elsewhere.[2] The S–O stretching frequency of dmso occurs at 1 053 cm^{-1}. Thus, if the bands at 900—1 000 cm^{-1} of the complexes are also assigned to the S–O stretching frequencies, there is a shift of 50—150 cm^{-1} when dimethyl sulphoxide co-ordinates to the metals. The shift in each case is to a lower frequency compared to the free solvent, and indicates co-ordination to the metal through oxygen. Comparisons of the spectra of the disulphates with that of anhydrous potassium disulphate and the reported spectrum of sodium disulphate[3] clearly indicate the presence of the disulphate ion.

The thermal decomposition of solvated metal disulphates has been studied up to 1 000 °C. Data for the solvated disulphates of Co^{II} and Ni^{II} have been reported elsewhere.[2] The compound $[Mn(dmso)_6][S_2O_7]$ begins to lose dimethyl sulphoxide and sulphur trioxide at 120 °C, and at 400 °C $Mn[SO_4]$ is obtained; $[Fe(dmso)_6][S_2O_7]$ loses dmso and SO_3 at 110 °C, and at 740 °C Fe_2O_3 is obtained. The compound $[Cu(dmso)_6][S_2O_7]$ loses dmso at 105 °C and formation of $Cu[S_2O_7]$ was observed at 240—280 °C. Further heating results first in the loss of SO_3 to give $Cu[SO_4]$ from 320—340 °C, and then in the loss of more SO_3 to give CuO which exists from 780 °C. The compound $[Zn(dmso)_6][S_2O_7]$ loses dmso and SO_3 at 100 °C and $Zn[SO_4]$ exists from 420 to 440 °C. Further heating results in the loss of more SO_3 to give ZnO from 900 °C. The compound $[Cd(dmso)_6][S_2O_7]$ loses dmso and SO_3 at 120 °C and at 330 °C, $Cd[SO_4]$ is obtained. No evidence was obtained

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† Part 1 is ref. 4.

for any intermediate dimethyl sulphoxide complexes.

The steps involved in the oxidation of metal to metal disulphate have already been reviewed in some detail.[4] Metals are generally converted by dimethyl sulphoxide–sulphur dioxide into metal disulphate, but in the case of the more reactive metals (Li, Na, Sn, Zn, or Cd) formation of metal dithionite was observed. Rinker[5] has shown that an aqueous solution of sodium dithionite contains a paramagnetic species, $[SO_2]^-$, in low concentrations (*ca.* 10^{-6} mol dm^{-3}), formed by dissociation of the dithionite ion [equation (1)]. A concentrated aqueous

$$[S_2O_4]^{2-} \rightleftharpoons 2[SO_2]^- \qquad (1)$$

solution of sodium dithionite is perceptibly yellow, and shows in the u.v. spectrum the presence of a species absorbing at 395 nm.

We have shown that when magnesium dissolves in dimethyl sulphoxide–sulphur dioxide a remarkable series of colour changes occurs. As the metal dissolves a deep blue colour of high intensity develops, which becomes black, then changes through brown to yellow. Spectrophotometric investigation shows that two absorbing species are formed, one at *ca.* 395 nm (the low-energy end of the band trails into the visible region) and which is responsible for the brown colour, and a second which has a broad absorption with a maximum in the 560—590 nm region and which is responsible for the blue colour. Magnesium dissolves in the mixed solvent dimethyl sulphoxide–sulphur trioxide to form magnesium disulphate, but no colours are observed. Therefore it appears that SO_2 is a likely precursor of both coloured species.

The brown species is probably formed as in (2), and

$$Mg + 2SO_2 \longrightarrow Mg^{2+} + 2[SO_2]^- \qquad (2)$$

is the same as the species observed in aqueous sodium dithionite solution. A *g* value of 2.007 was obtained from e.s.r. measurements, and this accords with the presence of $[SO_2]^-$ ions.[6] When sodium dithionite is placed in dimethyl sulphoxide a blue colour is observed. Rinker and Lynn[7] had already noticed a blue colour when sodium amalgam reacts with the mixed solvent dimethylformamide–sulphur dioxide, and a paramagnetic species similar to that observed in aqueous solutions was detected.

We have confirmed that the species responsible for the blue colour observed by Rinker and Lynn is identical with that which can be produced when sodium amalgam reacts with dimethyl sulphoxide–sulphur dioxide. Both species absorb at 585 nm. The blue species we had observed when magnesium reacts with dimethyl sulphoxide–sulphur dioxide is also produced when magnesium dissolves in dimethylformamide–sulphur dioxide, and gives rise to an absorption at 565 nm. Therefore it appears that more than one blue species exists, depending on the nature of the metal.

TABLE 2

Reaction of magnesium in solvents containing sulphur dioxide

Solvent	Solubility of SO_2 (mol SO_2 per mol of solvent)	Dielectric constant	Reaction of solution with Mg	Colour change
Dimethyl sulphoxide	1.62	29.8	positive	blue → black → brown (rapid)
Dimethylacetamide	1.58	37.8	+	brown (moderate)
Dimethylformamide	1.51	36.7	+	brown (moderate)
Formamide	0.38	109.5	+	orange-brown (very rapid)
Ethanol	0.29	25.0	+	orange (very rapid)
Water	0.02	78.3	+	orange (very rapid)
Trimethyl phosphate	1.40	20.6	+	orange-brown (moderate)
Tris(dimethylamino)phosphine oxide	2.07	30.0	+	brown (slow)
Tetrahydrothiophen 1,1-dioxide	1.09	42.0	—	
Nitrobenzene	0.34	34.8	—	
Nitromethane		35.9	—	
Ethyl acetate	0.85	6.02	—	
Acetonitrile	0.65	36.2	—	
Diethyl ether	0.22	4.3	—	
Dioxan	1.32	3.1	—	
Tetrahydrofuran	1.00	7.6	—	
Pyridine	1.45	12.3	—	
Acetone	0.61	20.7	—	

The $[SO_2]^-$ radical ion 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. It can be observed in many solvents and absorbs at *ca.* 395 nm, irrespective of the solvent and metal ions present.

Rinker and his co-workers[5,8] had observed both blue and brown species whilst investigating methods for the preparation of sodium dithionite from sodium and SO_2 in several non-aqueous solvents. However, the explanations for the existence of the coloured species appear inconsistent and inadequate. In order to gain some insight into the processes involved when a metal dissolves in a solvent containing SO_2, we investigated the reaction of magnesium with sulphur dioxide in a wide range of solvents. The results are recorded in Table 2.

The following conclusions can be drawn from the results: (*i*) only a solvent of high dielectric constant ($\varepsilon > 20$) will permit reaction, although in some cases reaction does not occur even if the solvent has a high dielectric constant; (*ii*) high solubility of SO_2 is not a requirement for reaction; (*iii*) the intensity of the coloured species varies considerably, and is highest in solvents containing the greatest amounts of dissolved SO_2; (*iv*) the rates of reaction vary considerably, being greatest in dimethyl sulphoxide, and quite rapid in formamide, water, and ethanol.

A series of experiments was carried out in which the reactions of a variety of metals with dilute solutions of SO_2 in the reactive solvents were investigated spectrophotometrically. The results are shown in Table 3. The following observations can be made. (*i*) In all cases where reaction occurs, $[SO_2]^-$ forms and is observed at *ca.* 395 nm. (*ii*) The blue species is not always observed, and is apparently stabilized by the more electropositive metals (Li or Na); it does not appear in protic solvents. (*iii*) The maximum intensity of the blue species varies from 560 to 590 nm, and depends on the metal ion present. (*iv*) The colours, once formed, are stable for many days, except in the cases of water and ethanol where they disappear rapidly and in dimethyl sulphoxide where they disappear after 1 d. (*v*) Except in the cases of magnesium and iron in dimethyl sulphoxide, white precipitates of metal dithionite form after a few hours. (*vi*) Both blue and brown species can be reversibly discharged at −70 °C to give colourless solutions. (*vii*) Both blue and brown species are rapidly discharged in air. (*viii*) For the more electropositive metals the blue species is dominant, while with less electropositive metals the brown species ($[SO_2]^-$) is dominant; with zinc no blue species is seen.

TABLE 3

Spectral bands (nm) in the visible and u.v. region of solutions of metals in solvents containing sulphur dioxide

Solvent	Li		Na		Ca		Mg		Fe		Zn	
Dimethyl sulphoxide	395	585	395	585	395	570	395	565	395	(550)	400	n.o.
Dimethylacetamide	395	580	395	585	*a*		395→565		*a*		400	n.o.
Dimethylformamide	395	580	395	580	*a*		395→565		*a*		400	n.o.
Formamide	*b*		*b*		*b*		395	n.o.	*c*	n.o.	*c*	n.o.
Ethanol	*b*		*b*		*b*		395 [d]	n.o.	390 [d]	n.o.	385 [d]	n.o.
Water	*c*		*b*		*b*		395 [d]	n.o.	390 [d]	n.o.	380 [d]	n.o.
Trimethyl phosphate	395	575	395	585	*a*		390	n.o.	*a*		*c*	
Tris(dimethylamino)phosphine oxide	395	585	395	585	*a*		395	565	395	(550)	*c*	

n.o. = Species not observed.

[a] Reaction too slow to be seen. [b] Side reactions occur. [c] Reaction not investigated. [d] Colour transient.

When increasing amounts of anhydrous lithium chloride were added to brown solutions of magnesium in dimethyl formamide–sulphur dioxide the change in colour of the solution and the spectra indicated that the relative proportion of the blue and brown species changed in favour of the blue species at the expense of the brown species. Conversely, when anhydrous magnesium nitrate was added to a blue solution of lithium in dimethyl formamide–sulphur dioxide the spectrum did not change. The absorption maximum of the blue species remained almost constant, but broadened to 560—585 nm, and the intensity of the brown species decreased slightly. Clearly, it is not just specific ions which stabilize the blue and brown species. The solution of magnesium in dimethyl formamide–sulphur dioxide gives rise predominantly to the formation of the brown species, yet when magnesium ions are added to a solution of lithium in dimethyl formamide–sulphur dioxide there is no increase in the proportion of the brown species, which one would expect if the presence of magnesium ions favoured the formation of this species. When magnesium ions are added to the brown solution of magnesium in dimethyl formamide–sulphur dioxide the proportion of the blue species actually increases. Thus, it appears that the formation of the blue species depends not so much on the type of ion present as on the amount of ions present. When a metal dissolves in a solution of SO_2 in a solvent different amounts of $[SO_2]^-$ radical ions form, according to the valence of the metal; if the brown species is free $[SO_2]^-$ and the blue species is an ion pair, then all the experimental observations made by

$$\mathrm{M} + x\mathrm{SO_2} \longrightarrow \mathrm{M}^{x+} + \underset{\text{(brown)}}{x[\mathrm{SO_2}]^-} \rightleftharpoons \underset{\text{(blue)}}{[\mathrm{M}^{x+}\cdot\mathrm{SO_2}^-]} + (x-1)[\mathrm{SO_2}]^- \qquad (3)$$

us and in earlier work can be explained [equation (3)]. 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; in the case of zinc the ion pair appears to be relatively unstable, since we did not observe its formation. The order of stability observed is as follows:

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

The ion pairs absorb at different wavelengths, as deduced from the observed variation in position of the absorption maximum of the blue species, which follows the order:

$$\begin{array}{cccc} [\mathrm{Fe^{2+}\cdot SO_2^-}] & [\mathrm{Mg^{2+}\cdot SO_2^-}] & [\mathrm{Li^+\cdot SO_2^-}] & [\mathrm{Na^+\cdot SO_2^-}] \\ 550\text{ nm} & 560\text{—}565\text{ nm} & 585\text{ nm} & 585\text{—}590\text{ nm} \end{array}$$

The order of stability of the ion pairs is a reflection of the state of solvation of the metal ions in solution. In the cases of lithium and sodium ions, which are not heavily solvated, the metal ion and $[SO_2]^-$ can make a close contact and form a stable ion pair. The ability to form an ion pair also depends considerably on the dielectric properties of the solvent. Solvents of low dielectric constant favour ion-pair formation, but if the solvent has a dielectric constant greater than 50, no ion pairs form and only the brown $[SO_2]^-$ is observed.

An explanation can now be given for the rapid sequence through which the coloured species can be observed when magnesium dissolves in dimethyl sulphoxide–sulphur dioxide. The reaction is rapid, and the blue species is soon observed, but as the reaction progresses large amounts of blue and brown species build up. Eventually, complete absorption from 350 to 650 nm (almost all the visible region) occurs, and the solution is black. When all the magnesium has dissolved, $[SO_2]^-$ and the ion pair $[Mg^{2+}\cdot SO_2^-]$ are gradually oxidized and the colour of the solution fades to the yellow of the dimethyl sulphide–sulphur dioxide adduct. If the above theory is correct, then if $[SO_2]^-$ can be generated in solution in the absence of metal ions only a brown solution should arise. In order to test this hypothesis solutions of SO_2 in dimethylformamide, dimethyl sulphoxide, dimethylacetamide, and formamide were electrolyzed, using carbon electrodes. The solutions in each case became brown, and the absorption spectra confirmed the presence of $[SO_2]^-$. No blue species were detected.

It remains to be explained why metals react with sulphur dioxide in some solvents but not in others. Although the solvent must have a high dielectric constant for reaction to occur, many solvents of high dielectric constant do not permit reaction between metal and SO_2. We have observed a relation between donor number, as defined by Gutmann,[9] and whether a reaction will occur: if the donor number is >20 the reaction is likely to occur. If we consider both donor number and dielectric constant together, we find that in order for a reaction between a metal and SO_2 to occur the solvent must have both a high donor number and a high dielectric constant.

The dielectric constant gives an approximate guide as to whether a reaction will occur. Thus a solvent of high dielectric constant will favour ionization of the metal and formation of $[SO_2]^-$. 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 recombination of a metal ion and $[SO_2]^-$ to give metal and SO_2.

EXPERIMENTAL

All operations were carried out as in Part 1.[4] Solutions for spectroscopic investigations were obtained by placing a small amount of a metal into a sample of a stock solution of sulphur dioxide in the required solvent (*ca.* 10^{-1} mol dm^{-3}). The colours were allowed to develop, 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 SP 8000 spectrophotometer.

In the following cases, the method described for the corresponding magnesium compound[4] was followed: $[Ti(dmso)_6][S_2O_7]_2$, colourless crystalline solid (Found: C, 17.2; H, 4.05; S, 34.3. Calc. for $C_{12}H_{36}O_{20}S_{10}Ti$: C, 16.5; H, 4.20; S, 36.9%); $[V_2(dmso)_{12}][S_2O_7]_3$, green crystalline solid (Found: C, 18.65; H, 4.70; S, 37.1. Calc. for $C_{24}H_{72}O_{33}S_{18}V_2$: C, 18.4; H, 4.65; S, 36.8%); $[Mn(dmso)_6][S_2O_7]$, yellow crystalline solid (Found: C, 20.05; H, 5.35; Mn, 7.75. Calc. for $C_{12}H_{36}MnO_{13}S_8$: C, 20.6; H, 5.20; Mn, 7.85%); $[Fe(dmso)_6][S_2O_7]$, pale green crystalline solid (Found: C, 20.4; H, 5.45; Fe, 7.75. Calc. for $C_{12}H_{36}FeO_{13}S_8$: C, 20.55; H, 5.20; Fe, 7.95%); $[Co(dmso)_6][S_2O_7]$, pale pink crystalline solid (Found: C, 20.45; H, 5.30; Co, 8.30. Calc. for $C_{12}H_{36}CoO_{13}S_8$: C, 20.5; H, 5.15; Co, 8.35%); $[Ni(dmso)_6][S_2O_7]$, green crystalline solid (Found: C, 20.3; H, 5.30; Ni, 8.30. Calc. for $C_{12}H_{36}NiO_{13}S_8$: C, 20.5; H, 5.15; Ni, 8.35%); and $[Cu(dmso)_6][S_2O_7]$, pale blue crystalline solid (Found: C, 20.4; H, 5.30; Cu, 8.80. Calc. for $C_{12}H_{36}CuO_{13}S_8$: C, 20.35; H, 5.10; Cu, 9.00%).

Hexakis(dimethyl sulphoxide)zinc(II) *Disulphate*.—The method described for the corresponding magnesium compound was followed, but with slight modification. After the initial fairly rapid reaction, a white solid formed, which was allowed to stand for 1 week until most of the solid had dissolved to form a colourless solution. The solution was filtered and diethyl ether added to the filtrate. A colourless crystalline solid precipitated, was filtered off, washed with diethyl ether, and pumped for 12 h (Found: C, 20.35; H, 5.30; Zn, 9.35. Calc. for $C_{12}H_{36}O_{13}S_8Zn$: C, 20.3; H, 5.10; Zn, 9.20%).

The compound $[Cd(dmso)_6][S_2O_7]$ was prepared similarly as a colourless crystalline solid (Found: C, 18.95; H, 5.05; S, 33.8. Calc. for $C_{12}H_{36}CdO_{13}S_8$: C, 19.05; H, 4.80; S, 33.85%).

Physical Measurements.—Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer as Nujol mulls. Thermogravimetric curves were obtained using a Stanton thermobalance. Metals were determined gravimetrically: manganese as ammonium manganese(II) phosphate monohydrate, iron as iron(III) oxide, cobalt as cobalt(II) tetrathiocyanatomercurate(II), nickel as dimethylglyoximatonickel(II), copper as dipyridinedithiocyanatocopper(II), and zinc as ammonium zinc phosphate. Carbon, H, and S were determined by Mr. A. Hedley of this department.

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