Reactions in Mixed Non-aqueous Systems containing Sulphur Dioxide. Part 1. The Dissolution of Main-group Metals in the Binary Mixture Dimethyl Sulphoxide–Sulphur Dioxide

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The metals M = Mg, Al, In, or Sn react with the mixed non-aqueous solvent dimethyl sulphoxide (dmso)–sulphur dioxide to form the metal disulphates, and Sr, Ba, or Pb react with the same system to form the metal sulphates. Other metals (Li, Na, Be, Ca, Ga, Tl, Sb, or Bi) dissolve in the mixed solvent, but so far it has not been possible to characterise the products. Phase studies and a Raman spectroscopic investigation indicate 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.

A RECENT communication[1] reported the reaction of metals with the mixed non-aqueous system dimethyl sulphoxide–sulphur dioxide. The metals M = Mg, Al, In, or Sn dissolve in the mixed solvent to form crystalline metal disulphates $M_x(S_2O_7)_y{\cdot}z$dmso, but Sr, Ba, or Pb dissolve to form only the metal sulphates. The metals Li, Na, Be, Ca, Ga, Tl, Sb, or Bi dissolve in the mixed solvent, but no pure products have yet been isolated. The metals dissolve neither in dmso nor in SO_2 separately, and the mixed solvent is required for dissolution of metal to occur and for the oxidation of S^{IV} to S^{VI}.

TABLE 1

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

$Mg(dmso)_6(S_2O_7)$	$Al_2(dmso)_{12}(S_2O_7)_3$	$In_2(dmso)_{12}(S_2O_7)_3$	$Sn(dmso)_6(S_2O_7)_2$	Assignment
430s	415s	432 (sh)		$[S_2O_7]^{2-}$
	445s	457s	488m	
		462 (sh)	495s	
575s		576s	580w	$[S_2O_7]^{2-}$
582s	580s	585s	592w	
695s		644s	655w	dmso
835s	835s	840s	835m	$[S_2O_7]^{2-}$
907m		912s	900s	dmso
945s	955s	950s	942 (sh)	
960s			950s	
970 (sh)		984s	985m	
1 005s		1 010s	1 010s	$[S_2O_7]^{2-}$
1 015s		1 026s	1 030s	
1 057s	1 050s	1 056s	1 056s	
		1 125s	1 130 (sh)	
			1 140s	
1 160s		1 163s	1 155s	
		1 226s		dmso
1 240s			1 235s	
1 315m	1 320m	1 320m	1 325m	

The products were characterised by elemental analysis for metal, sulphur, carbon, and hydrogen, thermogravimetric analysis, and i.r. spectroscopy. Some metals react completely with the mixed solvent within a few hours, others react more slowly. The state of division of the metal has a marked effect on the rate of reaction, and some metals, particularly Sr, Ba, and Pb, become passive with a coating of insoluble sulphate. The solvated disulphates are hygroscopic solids. They dissolve readily in water, but, as in the case of the alkali-metal disulphates, the disulphate ion is probably hydrolysed to the $[HSO_4]^-$ ion. They are quite soluble in dmso. The i.r. bands of the solvated disulphates are shown in Table 1. The S–O stretching frequency of dmso is at 1 053 cm^{-1}. In the complexes, if the bands at 1 000—900 cm^{-1} are assigned to the S–O stretching frequencies, there is a shift of 50—150 cm^{-1} when dmso 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 the spectrum of anhydrous potassium disulphate and the reported spectrum of sodium disulphate[2] clearly indicate the presence of the disulphate ion. The thermal decomposition of the solvated metal disulphates has been studied up to 1 000 °C. The compound $Mg(dmso)_6(S_2O_7)$ begins to lose dimethyl sulphoxide at 120 °C and formation of an intermediate solvate, $Mg(S_2O_7){\cdot}$dmso, was observed at 260—350 °C. Further heating results in the loss of sulphur trioxide and dmso, and $Mg[SO_4]$ exists from 430 °C. The compound $Al_2(dmso)_{12}(S_2O_7)_3$ begins to lose dmso at 100 °C, and at 440 °C $Al_2(SO_4)_3$ is obtained. No evidence was obtained for any intermediate dimethyl sulphoxide complexes. Further heating results in the loss of SO_3, and Al_2O_3 exists from 600 °C. The compound $Sn(dmso)_6(S_2O_7)_2$ begins to lose dmso at

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[1] W. D. Harrison, J. B. Gill, and D. C. Goodall, *J.C.S. Chem. Comm.*, 1976, 540.

[2] A. Simon and H. Wagner, *Z. anorg. Chem.*, 1961, **311**, 102.

180 °C, and at 470 °C $Sn(SO_4)_2$ is obtained. No evidence was obtained for any intermediate dimethyl sulphoxide complexes. Further heating results in the loss of SO_3, and SnO_2 exists from 950 °C.

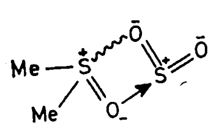
It is important to consider the steps involved in the oxidation of metal to metal disulphate. Dimethyl sulphide forms during the reaction and was collected (b.p. 37 °C). It is clear that dimethyl sulphoxide is acting as an oxidising species. It is not clear at this stage whether all the oxygen for the oxidation arises from dmso. Phase studies indicate the existence of a discrete 1 : 1 adduct (m.p. −38 °C) of dmso and SO_2. The adduct cannot be prepared from SMe_2 and SO_3. Raman spectroscopic studies support the formation of such an adduct. The bands are shown in Table 2.

TABLE 2

Bands (cm^{-1}) in the Raman spectra of dmso, SO_2, and dmso–SO_2

SO_2	dmso	dmso–SO_2	Band shift (cm^{-1}) in mixed solvent	Assignment
	310	300	−10	C–S–C deform.
	335	335	0	asym. C–S–O deform.
	390	385	−5	sym. C–S–O deform.
525		535	+10	$\nu_2(SO_2)$ bend
	670	670	0	sym. C–S str.
	700	700	0	C–S str.
	960	950	−10	
	1 050	1 010	−40	S–O str.
1 145		1 140	−5	$\nu_1(SO_2)$ str.
	1 310	1 320		C–H deform.
1 335			−15	$\nu_3(SO_2)$ asym. str.
	1 420	1 420	0	C–H deform.

There is a shift of 40 cm^{-1} in the S–O stretching frequency of dmso and a shift of 15 cm^{-1} in the asymmetric stretching frequency (ν_3) of SO_2 when adduct formation occurs. The lowering of the S–O stretching frequency of dmso in the adduct indicates co-ordination of dimethyl sulphoxide to SO_2 through oxygen. However, the small shift of 40 cm^{-1} suggests that either dmso is not very strongly bound to SO_2 or there is possibly some back-co-ordination from the oxygen of sulphur dioxide to the sulphur of dimethyl sulphoxide. This tends to favour the adduct, as does the situation with respect to the charges carried by the various oxygen and sulphur atoms. A diagnostic pattern can be established, using $\Delta(\nu_1 - \nu_3)^3$, from Table 2, for sulphur dioxide in various adducts. For example, in the adduct $SbF_5 \cdot SO_2$, where sulphur dioxide bonds through oxygen, $\Delta = 220$ cm^{-1}. In the adduct $NMe_2H \cdot SO_2$, where sulphur dioxide bonds through sulphur, $\Delta = 125$ cm^{-1}, and in the adducts of sulphur dioxide with alkali-metal halides, where SO_2 also bonds through sulphur, $\Delta = 180$ cm^{-1}.



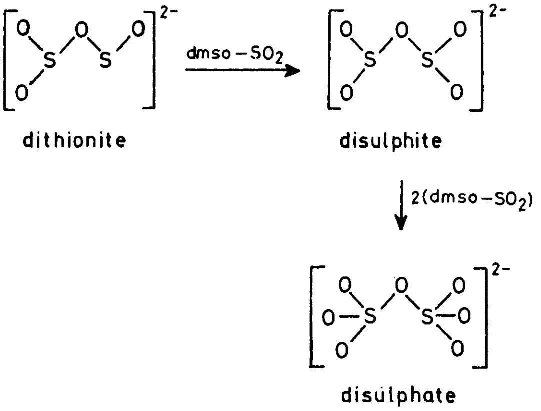
From the Raman spectrum of the dimethyl sulphoxide–sulphur dioxide adduct, $\Delta = 180$ cm^{-1}, indicating weak bonding through the sulphur of SO_2, or perhaps bonding through sulphur and oxygen, as shown earlier. In the latter case, bonding through oxygen and sulphur will tend to cancel out their different effects on Δ and give a value close to that for pure SO_2 (190 cm^{-1}).

A possible mechanism for the oxidation, involving the formation of metal sulphite as one of the intermediates, has already been outlined.[1] However, although some metal sulphites [4] undergo conversion into sulphates and disulphates in the presence of dmso and SO_2, there is no evidence to show that, when metals react directly with dmso–SO_2 to form metal disulphates, a metal sulphite intermediate is involved. In the case of the more reactive metals (M = Li, Na, or Sn) formation of metal dithionite has been observed. This is considered to occur as a result of dimerisation of the $[SO_2]^-$ radical ion, formed when the metal reacts with sulphur dioxide [equations (1) and (2)]. Formation of the $[SO_2]^-$ ion

$$M + xSO_2 \longrightarrow M^{x+} + x[SO_2]^- \quad (1)$$

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

had been observed when sodium dissolves in a mixture of dmso and SO_2.[3]



The metal dithionites are oxidised to metal disulphates by the mixed solvent dmso–SO_2. It appears that neither single component of the mixed solvent will bring about the oxidation. It is not yet clear exactly how the dmso–SO_2 adduct releases its oxygen in the oxidative process. Rinker and Lynn [5] had observed the formation of a very reactive form of dithionite, which they considered to be the form containing an S–O–S link, $[SO_2 \cdot SO_2]^{2-}$. Although in the solid state dithionites have the S–S link, $[O_2S \cdot SO_2]^{2-}$, the form with the S–O–S link may well be the reactive intermediate in the oxidative process. This intermediate is particularly attractive, in that it can be oxidised by dmso–SO_2 to disulphate without any rearrangement, and a transi-

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[3] M. C. R. Symons and R. Atkins, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967, p. 146.

[4] R. Maylor, J. B. Gill, and D. C. Goodall, *J.C.S. Dalton*, 1973, 534.

[5] R. G. Rinker and S. Lynn, *Ind. and Eng. Chem.* (*Product Res. and Development*), 1969, **8**, 338.

tionary disulphite having an S–O–S link may form, as is considered to be the case when transition-metal sulphites are converted into disulphates:[3]

EXPERIMENTAL

All the operations were carried out in a closed system under dry nitrogen. Nitrogen and sulphur dioxide were dried by passing the gases separately through concentrated sulphuric acid and phosphorus(V) oxide. Filtrations were carried out under a nitrogen stream, using a sinter tube. Diethyl ether was distilled and dried with sodium.

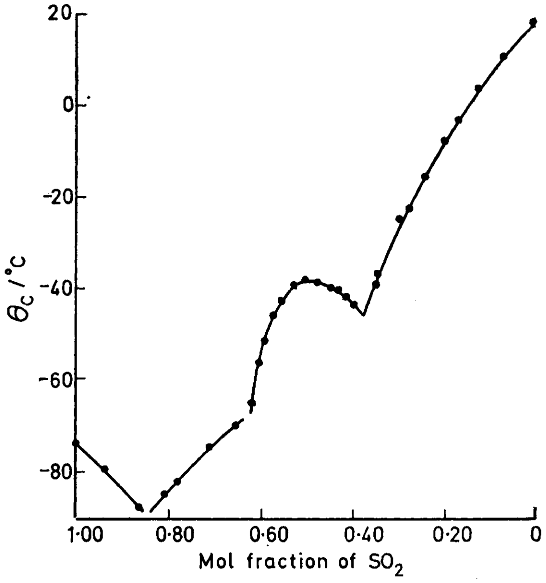
Preparations.—$Mg(dmso)_6(S_2O_7)$. Finely divided magnesium was added to freshly distilled dimethyl sulphoxide (10 cm^3) and the mixture was saturated with sulphur dioxide. The mixture was retained in a closed container and left until no more metal dissolved. The solution was filtered, and diethyl ether added to the filtrate. A colourless crystalline solid precipitated, was filtered off, washed with diethyl ether, and pumped for 12 h (Found: C, 21.8; H, 5.55; S, 38.45. Calc. for $C_{12}H_{36}MgO_{13}S_8$: C, 21.55; H, 5.40; S, 38.35%).

$Al_2(dmso)_{12}(S_2O_7)_3$ (Found: C, 19.1; H, 4.85; Al, 3.55. Calc. for $C_{24}H_{72}Al_2O_{33}S_{18}$: C, 18.95; H, 4.80; Al, 3.55%) and $In_2(dmso)_{12}(S_2O_7)_3$ (Found: C, 16.9; H, 4.20; S, 34.15. Calc. for $C_{24}H_{72}In_2O_{33}S_{18}$: C, 17.0; H, 4.25; S, 34.0%) were prepared similarly as colourless crystalline solids.

$Sn(dmso)_6(S_2O_7)_2$. The method described above for the magnesium complex was followed, with slight modification. After the initial fairly rapid reaction a white solid formed, which was allowed to stand for 1 week until most of it 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, 14.8; H, 3.60; S, 33.75. Calc. for $C_{12}H_{36}O_{20}S_{10}Sn$: C, 15.3; H, 3.85; S, 34.1%).

Physical Measurements.—The melting point of the dimethyl sulphoxide–sulphur dioxide adduct was determined from the phase diagram, obtained by plotting melting point against mol fraction of SO_2 in dmso. Temperatures were measured to ±1.0 °C by an accurate alcohol thermometer, immersed in the samples contained in a refrigerated bath of silicone fluid. The phase diagram is shown in the Figure.

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. Scattered radiation was analysed by a double-grating Coderg (model type PHO) spectrometer.



Phase diagram of melting point against composition for dmso–SO_2

Thermogravimetric curves were obtained using a Stanton thermobalance. Aluminium was determined gravimetrically as aluminium oxide. C, H, and S were determined by Mr. A. Hedley of this department.

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