Food Chemistry **15** (1984) 93–111

The Formation of Inorganic Sulphur Oxoanion Systems from Sulphur Dioxide in Non-Aqueous Solvents

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(Received: 7 March, 1984)

ABSTRACT

Metal sulphites which are non-ionic in the unsolvated state can be converted by SO_2 *in dimethylsulphoxide (dmso) to ionic metal disulphates, by oxidation with dmso. This conversion of sulphur (IV) to sulphur (VI) is confined to the system dmso–*SO_2*. Other solvent–*SO_2 *systems do not allow this oxidation. Metals can also be converted, some spontaneously, others electrolytically, by dmso–*SO_2 *into disulphates. This reaction involves the sulphoxylate radical ion,* SO_2^-*, and metal ion-pairs,* $M^{x+} \cdots (SO_2^-)_y$*, as intermediates. Other solvent–*SO_2 *systems only allow the formation of dithionites as final products. These oxidations by dmso are considered possible as a result of the presence of S—O—S linkages, which can only arise when the sulphur (IV) group is covalently bound to a metal. Metal oxides are also converted by dmso–*SO_2 *to disulphates. No* SO_2^- *ions arise, and a direct attack of* SO_2 *on the oxide is thought to occur.*

INTRODUCTION

Recent studies (Maylor *et al.*, 1971; Harrison *et al.*, 1983) on the preparation of anhydrous transition metal sulphites have indicated certain features which distinguish them from their hydrated counterparts. The anhydrous sulphites of cobalt, nickel, iron and manganese, for example, are highly insoluble, and probably polymeric. They exhibit a high degree of covalent character, as witnessed by their infra-red spectra

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TABLE 1
Infra-red Bands of Metal Sulphites (cm^{-1})

	ν_1(*sym. str.*)/ν_3(*asym. str.*)		ν_2(*sym. bend*)	ν_4(*asym. bend*)
$CoSO_3$	1 020s	950vs	648s	466w
$NiSO_3$	1 015s	950vs	645s	462w
$FeSO_3$	980sh 900s	942s	620s	470w
$MnSO_3$	1 015m	960s	645s	470w
$MnSO_3.H_2O$	1 040sh 880s	975m	635s	470w
$FeSO_3.3H_2O$	1 020sh 880s	950s	630s	480s
$CaSO_3.0.5H_2O$	975s	950s	668m 650m	520w 485w 455w

vs = very strong; s = strong; m = medium; w = weak; sh = shoulder. All bands are broad.

(see Table 1). It is not clear how, or to what degree, the absence or presence of water of hydration affects the nature of the oxoanion in such compounds, but there is some evidence that the metal ion has a considerable influence on the characteristics of the sulphur oxoanion.

The anhydrous sulphites cannot be made by thermal dehydration of the hydrates, because sulphur dioxide and water are simultaneously expelled. They must be made in non-aqueous media, by means of a metathetical reaction involving metal iodide and tetramethylammonium disulphite, e.g.

$$CoI_2 + (NMe_4)_2S_2O_5 \xrightarrow{\text{acetone}} CoSO_3 + SO_2 + 2NMe_4I$$

The infra-red spectra indicate that the sulphite group co-ordinates to the transition metal by way of oxygen, probably in the form of bridging groups, which is in accord with the general physical characteristics of the compounds, and particularly with a polymeric structure. Comparisons are made with the infra-red spectra of known ionic sulphites (Nakamoto, 1970).

Although there are difficulties in interpreting the spectra as a consequence of the broadness of sulphite bands, there is no doubt that the anhydrous transition metal sulphites contain no free anions. Thermal stability studies (Harrison *et al.*, 1983) also indicate that the behaviour of sulphite anions is dependent on the absence or presence of water in a compound. This may be partly dependent on hydrogen bonding effects between sulphite and water, and the presence of water may also determine

TABLE 2

Infra-red Bands (cm^{-1}) of Metal Disulphates

Co(dmso)$_6$S$_2$O$_7$	*Ni(dmso)$_6$S$_2$O$_7$*	*Fe(dmso)$_6$S$_2$O$_7$*	*Mn(dmso)$_6$S$_2$O$_7$*	*Assignment*
430s	440s			$S_2O_7^{2-}$
			575m	
579s	580s	585m	582m	
595sh	596sh	590m		
680w	680w		670w	dmso
716m	716m			
830s	835s	835s	835s	$S_2O_7^{2-}$
890w	890w			dmso
902w	902w		915s	
945s	942s	945s	948sh	
999s	1 000s	1 000sh	1 002s	
1 056s	1 056s	1 060s	1 060s	$S_2O_7^{2-}$
1 152s	1 152s	1 160s	1 160s	
1 246s	1 246s	1 230s	1 234s	
1 321s	1 320s	1 320w	1 315w	dmso
1 405sh	1 406s			

s = strong; m = medium; w = weak; sh = shoulder. All bands are broad.

whether sulphite is bound through oxygen or sulphur to a metal. Some non-transition metal sulphites are shown to contain sulphite within their hydrates where it is fairly clear that the sulphite is not present as a free anion, as indicated by the infra-red bands (see Table 1). The hemi-hydrate of calcium sulphite, for example, seems to show not only interactions between metal ion and sulphite, but also some hydrogen bonding between sulphite and water. The infra-red spectra of hydrated manganese sulphite and iron(II) sulphite also show they contain sulphite which is, to a large degree, non-ionic. The thermal degradation behaviour reflects these effects, accentuating the distinctions between covalent and ionic sulphite.

It is considered to be precisely a consequence of these covalent characteristics that anhydrous transition metal sulphites are able to react with sulphur dioxide in certain non-aqueous solvents. One binary solvent system of particular interest is dimethylsulphoxide–sulphur dioxide (Maylor *et al.*, 1973). The sulphites are not soluble in sulphur dioxide or dimethylsulphoxide alone, but they do react with the binary system to form metal disulphates, which are obtained as crystalline compounds incorporating several dimethylsulphoxide molecules of crystallisation. In the case of most metals, these are the first preparations of such compounds. They contain the dusulphate group as the free anion. This is indicated by infra-red data shown in Table 2, making comparison with the infrared data for anhydrous potassium and sodium disulphates. It is also indicated by conductivity measurements.

SULPHITE OXIDATION

The mechanism of the formation of these metal disulphates is not very clear. The binary solvent system acts as an oxidising medium, and this is to be contrasted with the water–sulphur dioxide system. The dimethylsulphoxide is considered to be the oxidising agent in view of the fact that dimethyl sulphide is a reaction product. Sulphur dioxide reacts also with anhydrous cobalt sulphate; for example, in dimethylsulphoxide to form cobalt disulphate.

The scheme of reactions for the conversion of cobalt sulphite and cobalt sulphate to disulphite is shown in Fig. 1.

The behaviour of transition metal sulphites and sulphates is to be contrasted with that of the alkali metal analogues; alkali metal sulphites cannot be oxidised by dimethylsulphoxide–sulphur dioxide to disulphate. Conversion only as far as disulphite occurs. This suggests that disulphite may be an intermediate in the conversion of transition metal sulphites to disulphates. The influence of metal is, however, clearly illustrated.

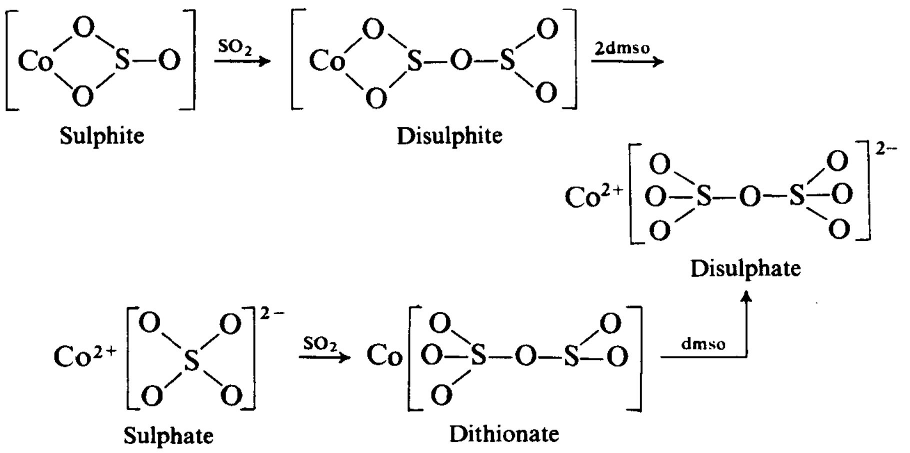


Fig. 1. Conversion of cobalt sulphite and cobalt sulphate to cobalt disulphate.

Disulphite formation is quite likely, since sulphite and sulphur dioxide associate readily.

However, a problem arises in considering the conversion of disulphite to disulphate. The disulphite ion contains an S—S bond, and conversion to disulphate would necessitate a major reorganisation, through bond cleavage. A much more facile conversion can occur if a disulphite containing an S—O—S linkage arises. Although this does not exist for the free ion, free ions are not essential for any considered mechanism. An intermediate disulphite with an S—O—S linkage may arise where a considerable degree of covalent bonding between metal and sulphur oxoanion exists. The facile conversion of cobalt sulphate to disulphate is in accord with this, as is the failure of the alkali metal sulphites to be converted beyond the disulphite stage.

The thermal decomposition of transition metal disulphates shows that sulphate and oxide result by successive loss of sulphur trioxide, according to the scheme:

$$M_x(S_2O_7)_yZ\mathrm{dmso} \rightarrow M_x(S_2O_7)_y \rightarrow M_x(SO_4)_y + ySO_3 \rightarrow M_xO_y + ySO_3$$

The thermal decomposition curves are shown in Fig. 2.

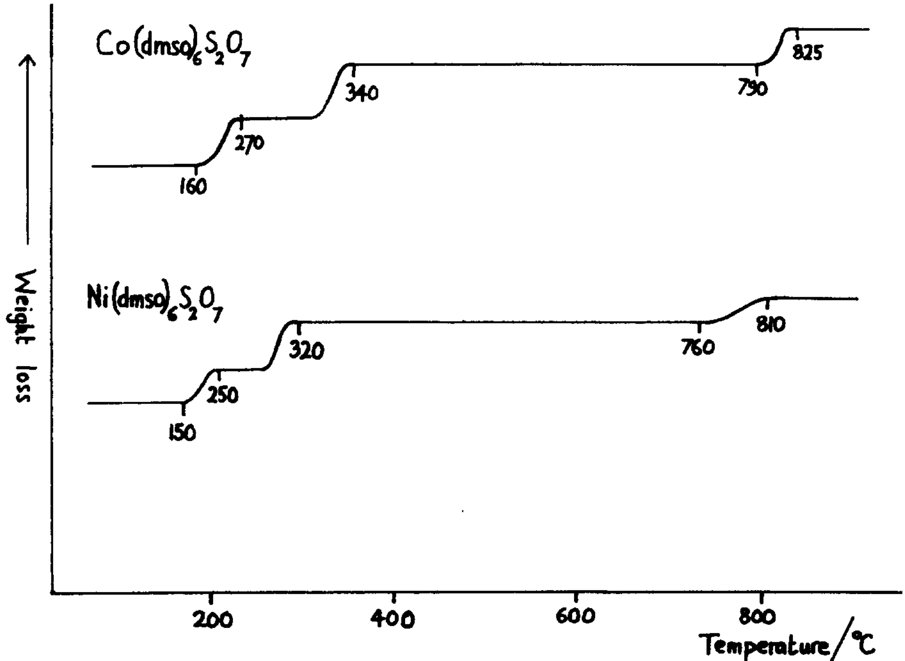


Fig. 2. Thermograms of metal disulphates.

REACTIONS OF METALS

Another method by which sulphur oxoanion compounds arise is by the direct attack of a binary system containing sulphur dioxide on a metal. Several metals behave in this manner (Harrison *et al.*, 1978, 1979). For example, magnesium dissolves quite rapidly in dimethylsulphoxide–sulphur dioxide, giving a highly coloured solution, from which solvated disulphate is formed. In some cases, particularly with zinc, cadmium and tin, dithionite is formed, which is, at a later stage, converted to disulphate. Reaction rates vary considerably. In any group, the lighter metals are more reactive, and the slowest reactions occur where the final oxidation state of the metal is greater than two. Surface effects, such as insoluble coatings of sulphate (in the case of lead, for example) can severely impede reaction. In some cases, pure products cannot be isolated. This is the case with alkali metals and many rare earth metals. In the great majority of cases, however, disulphate is the final product. Some metals within a generally reactive series are completely inert. This is true for chromium, which is the only First Row transition metal to be unattacked by the solvent.

The dimethylsulphoxide–sulphur dioxide system has been the subject

TABLE 3

Absorption Frequencies in the Raman Spectra of dmso, SO_2 and (dmso-SO_2) (cm^{-1})

SO_2	*dmso*	*(dmso-SO_2)*	*Frequency shift in mixed solvent*	*Assignment*
	310	300	−10	C—S—C deformation
	335	335	0	Asymmetric C—S—O deformation
	390	385	−5	Symmetric C—S—O deformation
525		535	+10	ν_2SO_2 bend
	670	670	0	Symmetric C—S stretch
	700	700	0	C—S stretch
	960	950	−10	
	1 050	1 010	−40	S—O stretch
1 145		1 140	−5	ν_1SO_2 stretch
	1 310			C—H deformation
1 335		1 320	−15	ν_3SO_2 asymmetric stretch
	1 420	1 420	0	C—H deformation

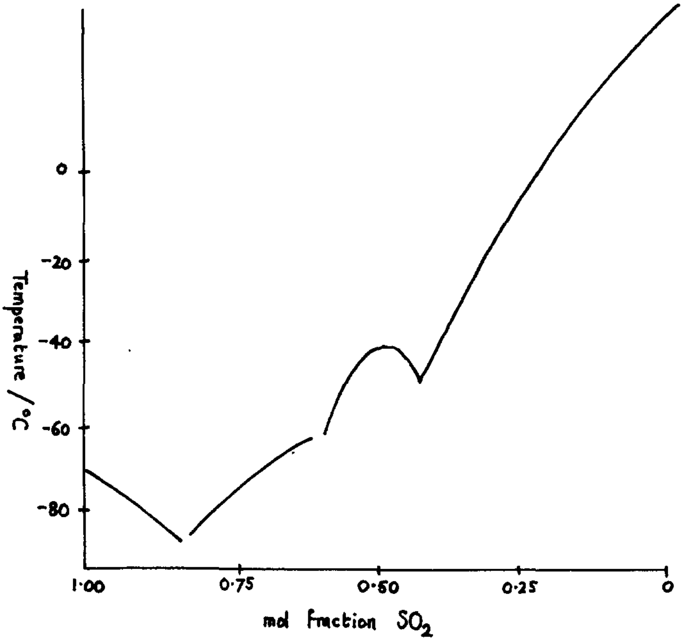
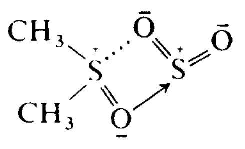


Fig. 3. Phase (melting point-composition) diagram for dmso–SO$_2$.

of considerable study. The mixing of the two components is a very exothermic process. Phase studies clearly show the formation of a 1:1 adduct, as shown in Fig. 3. The Raman bands are shown in Table 3. A shift of 40 cm^{-1} in the S—O stretching frequency of dimethylsulphoxide and a shift of 15 cm^{-1} in the asymmetric stretching frequency (ν_3) of sulphur dioxide are observable on adduct formation. The reduction of the S—O stretching frequency of dimethylsulphoxide in the adduct indicates co-ordination of dimethylsulphoxide to sulphur dioxide through oxygen. The small shift of 40 cm^{-1} suggests that either dimethylsulphoxide is not particularly strongly bound to sulphur dioxide, or that there is perhaps a degree of back co-ordination from the oxygen of sulphur dioxide to the sulphur of dimethylsulphoxide. This is in accord with the structure:



(A)

Such a structure would also be stabilised by the charges carried by the various sulphur and oxygen atoms. A diagnostic pattern (Byler & Shriver,

1976) using $\Delta(\nu_1 - \nu_3)$ from Table 3, for sulphur dioxide in various adducts enables useful support to be given. In the adduct $SbF_5.SO_2$, where sulphur dioxide is known to bond through oxygen, $\Delta = 220\,cm^{-1}$. In the adduct $NMe_2H.SO_2$, where sulphur dioxide bonds through sulphur, $\Delta = 125\,cm^{-1}$, and in adducts of sulphur dioxide with alkali-metal halides, in which sulphur dioxide also bonds through sulphur, $\Delta = 180\,cm^{-1}$. From the Raman spectrum of the dimethylsulphoxide–sulphur dioxide adduct, $\Delta = 180\,cm_{-}^{1}$. This indicates weak bonding through the sulphur of sulphur dioxide, or even bonding through sulphur and oxygen, as seen from the sketch structure (A). In this case, bonding through sulphur and oxygen would almost cancel out their different effects on Δ and give a value close to that observed for pure sulphur dioxide. Other solvent–sulphur dioxide systems also contain adducts, as shown in Table 4.

Although some metal sulphites have been shown to undergo conversion into sulphates and disulphates in dimethylsulphoxide–sulphur dioxide, no evidence exists to indicate that a metal sulphite intermediate is present when metals react directly with the binary solvent system. Metal dithionite has been observed as a transitory product in the case of the more reactive metals such as sodium or tin. This has been considered to happen as a result of the dimerisation of the sulphoxylate (SO_2^-) radical ion, which is formed when the metal reacts with sulphur dioxide, according to the following scheme:

$$M + xSO_2 \rightarrow M^{x+} + x(SO_2^-)$$

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

When metals dissolve in dimethylsulphoxide–sulphur dioxide and in some other binary systems containing sulphur dioxide, two peaks arise in the visible region of the spectrum. One, at 395 nm, corresponds to the brown SO_2^- ion, and the other, which is blue and lies in the region 560–600 nm, and which is dependent on the metal, corresponds, to some

TABLE 4

Solvents which Form Adducts with Sulphur Dioxide

R_3N	C_5H_5N
$OP(NMe_2)_3$	$OP(OMe)_3$
$HCONMe_2$	$HCONH_2$
CH_3CONMe_2	

kind of ion-pair. Both of the absorption peaks are broad, but clearly distinguishable. Both the ion-pairs and the SO_2^- ion are rapidly oxidised in air. The colours of the species can be reversibly discharged at −70 °C to give colourless solutions. In anaerobic conditions at room temperature, the colours are stable for some days, except in the cases of water, methanol and dimethylsulphoxide. The solutions are paramagnetic. The SO_2^- ion arises in concentrated aqueous solutions of sodium dithionite, and has a *g* value of the esr spectrum of 2·007. It is a product of the dissociation of dithionite:

$$S_2O_4^{2-} \rightarrow 2SO_2^-$$

Such solutions are distinctly yellow, giving an absorption at 395 nm. A blue species, absorbing in the region 560–600 nm, is evident in solutions of sodium dithionite in dimethylsulphoxide, and is also formed when sodium amalgam or magnesium is put into dimethylsulphoxide–sulphur dioxide or dimethylformamide–sulphur dioxide. Esr measurements also detect the SO_2^- ion in these solutions.

The blue colour is attributed to some form of metal ion-pair, represented as:

$$[M^{x+} \cdots (SO_2^-)]$$

The exact constitution of this ion-pair is unknown, but solvent molecules would probably occupy other co-ordination sites around the metal. Whether the species is a contact ion-pair or a solvent-separated ion-pair will depend on a number of factors, such as the electropositive character of the metal, the oxidation state of the metal, and the preferred stereochemistry of the complex.

All of such metal ion-pairs detected show a peak in the esr spectrum having $g = 2{\cdot}003$. It appears alongside the peak for the SO_2^- ion, but has a much lower intensity. It is of interest to monitor the visible spectrum of the solution formed when magnesium dissolves in dimethylsulphoxide–sulphur dioxide. Initially, a very deep blue colour is evident. At this stage the visible spectrum detects mostly metal ion-pair, although a small amount of SO_2^- ion is present. Within half-an-hour, the solution changes through brown to yellow, and the spectrum shows mostly SO_2^- ion at this stage.

The SO_2^- ion, which can be generated either by dissociation of dithionite, or by reduction of sulphur dioxide by metal, is observable in several solvents, The blue metal ion-pairs are also observed in several

TABLE 5

Solvent	*Solubility of SO_2 (mol SO_2 per mol of solvent)*	*Dielectric constant*	*Colour change*
Dimethylsulphoxide	1·62	29·8	Blue–brown–yellow (rapid)
Dimethylacetamide	1·58	37·8	Green–brown (moderate)
Dimethylformamide	1·51	36·7	Green–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)
Trimethylphosphate	1·40	20·6	Orange–brown (moderate)
Tris(dimethylamino)phosphine oxide	2·07	30·0	Brown (slow)

Several other solvents investigated permitted no reaction.

solvents, but not all metals give rise to the formation of metal ion-pairs which are stable long enough for a detailed study.

Table 5 illustrates the situation with respect to solvents containing sulphur dioxide which react with magnesium, chosen as one of the most reactive metals.

A number of conclusions can be drawn from the results obtained. Only solvents of high dielectric constant will allow reaction, although some metals fail to react even in cases where a solvent does have a high dielectric constant. A high solubility of sulphur dioxide is not necessary for reaction. The intensity of the coloured species is variable, being greatest in solvents containing the highest concentrations of sulphur dioxide. Rates of reaction vary, being fastest in dimethylsulphoxide, and relatively fast in water, ethanol and formamide. The reactions of a number of metals with solvent–sulphur dioxide systems were studied spectrophotometrically. The results are given in Table 6.

In every case where reaction takes place, the SO_2^- ion arises, and is identified by its absorption peak at 395 nm. The blue metal ion-pairs are not always observable. They are stabilised by the more electropositive metals, especially lithium and sodium, and they do not appear in protic solvents. In all cases, except for iron and magnesium in dimethylsulphoxide–sulphur dioxide, white precipitates of metal dithionite form after a few hours. In dimethylsulphoxide–sulphur dioxide they are subsequently converted to metal disulphate. In the case of the more electropositive metals, the blue metal ion-pairs are predominant. The SO_2^- ion is the dominant species in the case of less electropositive species, There is some dependence on metal ion concentration, also. For example, if magnesium ions are added to a solution of magnesium in dimethylformamide–sulphur dioxide, there is an increase in the concentration of blue metal-ion pairs. The oxidation state of the metal has a very important bearing on the relative amounts of SO_2^- ion and metal ion-pairs which form. If a univalent metal is involved, the following situation is a likely outcome:

$$M + SO_2 \rightarrow M^+ + SO_2^- \rightleftharpoons [M^+ \cdots SO_2^-]$$

The equilibrium position would be dependent on the solvent. For a multivalent metal:

$$M + xSO_2 \rightarrow M^{x+} + xSO_2^- \rightleftharpoons [M^{x+} \cdots SO_2^-] + (x-1)SO_2^-$$

TABLE 6

Visible–uv Spectral Bands (nm) for Solutions of Metals in Solvent–Sulphur Dioxide Systems

Solvent	*Li*	*Na*	*Ca*	*Mg*	*Fe*	*Zn*
Dimethylsulphoxide	395 585	395 590	395 570	395 565	395 550	395
Dimethylacetamide	395 580	395 590	*a*	395 565	*a*	395
Dimethylformamide	395 580	395 585	*a*	395 565	*a*	395
Formamide	*a*	*a*	*a*	395	*a*	*a*
Ethanol	*a*	*a*	*a*	395	390	390
Water	*a*	*a*	*a*	395	390	390
Trimethylphosphate	395 575		*a*	390	*a*	*a*
Tris(dimethylamino)phosphine oxide	395 585		*a*	390 565	395 550	*a*

a = Not clearly distinguishable.

Some order of stability of the ion-pairs is shown as follows:

$$[Li^+ . SO_2^-] \approx [Na^+ . SO_2^-] > [Mg^{2+} . SO_2^-] \geq [Fe^{2+} . SO_2^-] \geq [Zn^{2+} . SO_2^-]$$

The zinc ion-pair must be quite unstable, as its formation could not be detected. The stability is reflected in the absorption maximum, which follows the order:

$[Fe^{2+} . SO_2^-]$	$[Mg^{2+} . SO_2^-]$	$[Li^+ . SO_2^-]$	$[Na^+ . SO_2^-]$
550 nm	565 nm	580–585 nm	585–590 nm

The order of stability of these ion-pairs bears some relation to the degree of solvation of the metal ions in solution. Alkali metal ions are not generally heavily solvated. Thus, the metal ion and SO_2^- ions can come into close proximity and form a stable ion-pair. The ability to form an ion-pair depends very much on the dielectric properties of the solvent. Ion-pair formation is facilitated in solvents with low dielectric constant. In solvents of high dielectric constant, ion-pairs are not observed; only the SO_2^- ion forms.

Another important parameter affecting metal reactivity with sulphur dioxide is the solvent donor number. It appears that a high donor number, as well as a high dielectric constant, is necessary for such reactivity. The dielectric constant does give a rough indication as to whether a reaction will occur. Solvents of high dielectric constant facilitate ionisation of metal and the related reduction of sulphur dioxide to SO_2^- ion. The rate-controlling stage is that of diffusion of metal ions from the metal surface. The development of the coloured species always occurs at the surface of the metal. Solvents with high donor numbers favour the solvation of metal ions and prevent the recombination of metal ion and SO_2^- ion to metal and sulphur dioxide. A study of the behaviour of several solvent–sulphur dioxide systems towards metals has shown how important the parameter's donor number and dielectric constant are. This is shown in Fig. 4. Once a metal has reacted with sulphur dioxide to form a metal ion-pair, the next reaction is the conversion to another metal sulphur oxoanion compound. The second stage in the process is the formation of metal dithionite. This happens in all the binary solvent systems. Dithionite is likely to be formed by dimerisation of the SO_2^- ions present. These may be free SO_2^- ions, or SO_2^- ions produced by dissociation of the metal ion-pairs.

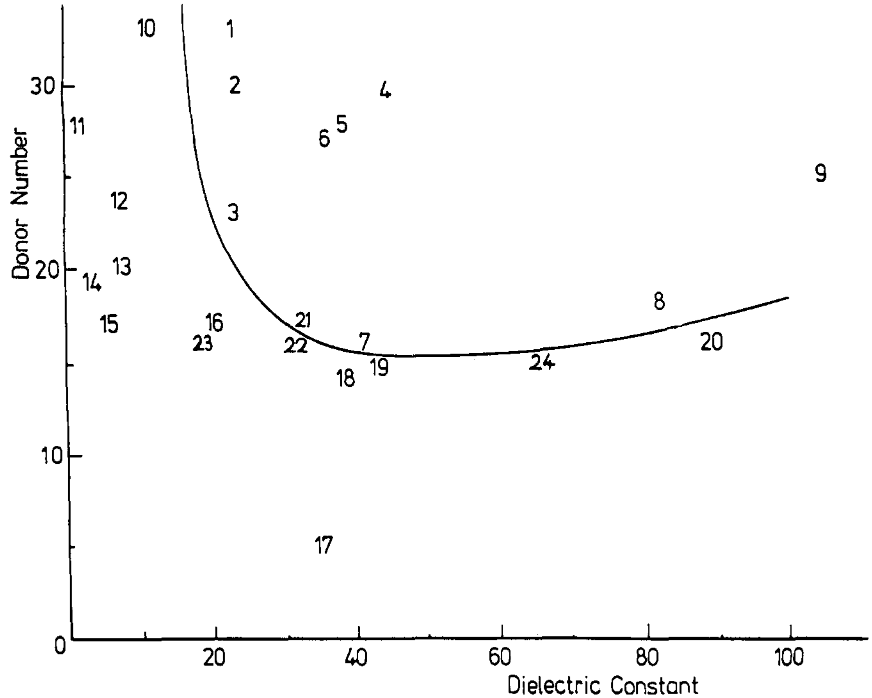
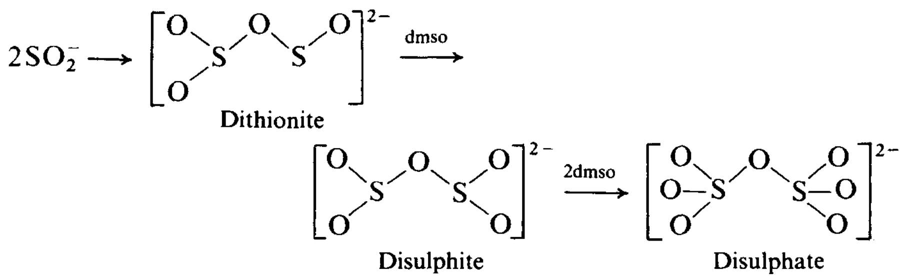


Fig. 4. Dielectric constant versus donor number for (1) methanol, (2) ethanol, (3) trimethylphosphate, (4) dimethylsulphoxide, (5) dimethylacetamide, (6) dimethylformamide, (7) ethylene sulphite, (8) water, (9) formamide, (10) pyridine, (11) dioxan, (12) tributylphosphate, (13) tetrahydrofuran, (14) diethylether, (15) ethylacetate, (16) acetone, (17) nitrobenzene, (18) acetonitrile, (19) sulpholane, (20) ethylene carbonate, (21) phenyl phosphonic dichloride, (22) *n*-propionitrile, (23) *n*-butyronitrile, (24) propylene carbonate.

In dimethylsulphoxide–sulphur dioxide, a further reaction stage occurs. This system is unique in its ability to oxidise sulphur(IV) to sulphur(VI). Although dithionite forms, it is only a transitory stage, being converted through an oxidation process to disulphate, according to the following scheme:



A comparison needs to be made between this process and that of the oxidation of transition metal sulphites to disulphates described earlier. In both situations, it is considered that the most direct and facile oxidation of sulphur(IV) to sulphur(VI) can occur if a disulphite is present which contains an S—O—S linkage. This then presupposes that, in the preceding stage, a dithionate also containing an S—O—S linkage could exist. Such a suggestion is reasonable where the less electropositive metals are being considered, since they are the ones which form highly covalent sulphites where sulphite is very likely to use one or more of its oxygen atoms to bond covalently to the metal. A consequence of this is that an S—O—S linkage is likely at the dithionite stage, simply on consideration of the much reduced negative charge on the sulphur atom in sulphite. Dithionite in the solid state possesses an S—S bond, but this is likely to be much less reactive than dithionite which has an S—O—S linkage. This form would require no rearrangement for the subsequent conversion to disulphate.

ELECTROLYTIC REACTIONS

It is possible, in cases where a metal does not react spontaneously with sulphur dioxide in a binary system, to induce reactivity electrolytically. It has been noted that some metals, notably chromium and the heavier transition metals, did not react even with solvents of high donor number and high dielectric constant. It is possible to electrolyse such metals into solvents which even have low donor numbers and low dielectric constants (such as acetone, nitrobenzene and acetonitrile). The metals are used as sacrificial anodes in an electrolytic cell. Electrolytic dissolution of metal into the binary solvents gives rise to a somewhat complicated mixture, mainly of sulphur oxoanions such as sulphate, dithionite and thiosulphate; in a few cases, sulphide was also detected. In the case of dimethylsulphoxide–sulphur dioxide, the disulphate ion is formed, this being the only binary system able to oxidise sulphur(IV) to sulphur(VI). In this system, the product is mainly or entirely disulphate, and the metal disulphate usually crystallises readily from solution. These were generally similar to the disulphates characterised in earlier work on the spontaneous reactions of metals. The rate of formation of the sulphur oxoanions depends on the current and potential difference maintained in the electrolytic cell. In some cases, the nature of background electrolyte is important. With iron in dimethylsulphoxide–sulphur dioxide, use of tetraethylammonium tetrafluoroborate always led to the formation of a mixture of sulphate and disulphate, whereas use of tetraethylammonium perchlorate always yielded only disulphate. With aluminium, a mixture of sulphate and disulphate resulted, whatever background electrolyte was used. A potential difference of 10 V was used in the cell, giving currents of 40–100 mA. The rate of formation of sulphur oxoanions was also determined by the metal and the state of passivation of the electrodes. Dithionite ions are the source of a high degree of passivation in dimethylsulphoxide–sulphur dioxide, and it is quite possible that the various sulphur oxoanions formed generally in binary solvents containing sulphur dioxide are the cause of considerable passivation. The SO_2^- ion plays an important rôle in the electrolytic conversion of metals to metal sulphur oxoanion compounds in solvent–sulphur dioxide systems. The formation of SO_2^- ion from sulphur dioxide in the presence of a metal probably requires the formation of a reactive adduct involving sulphur dioxide and a solvent, before spontaneous reactivity with metals can occur, and such adducts are known to form, for example, in the case of dimethylsulphoxide. However, such would not be necessary under electrolytic conditions, where electrons are available for the reduction of sulphur dioxide, although the adducts are undoubtedly present. SO_2^- ions have been generated electrolytically from sulphur dioxide in dimethylsulphoxide, dimethylformamide, formamide and dimethylacetamide, using inert electrodes. In cells containing an inert cathode and sacrificial metal anode, SO_2^- ions and metal cations are simultaneously generated during electrolysis. SO_2^- ions and blue metal ion-pairs have both been detected spectroscopically in the vicinity of the cathode surface. The solution is green–yellow.

SO_2^- ions participate in rather complex reactions under electrolytic conditions, producing many sulphur oxoanions. This is to be contrasted with the simple dimerisation of SO_2^- ions to dithionite which takes place when metals dissolve spontaneously in solvent–sulphur dioxide systems. Simple conversion of SO_2^- to disulphite under electrolytic conditions only appears to happen in the case of dimethylsulphoxide–sulphur dioxide. This oxidation of sulphur(IV) to sulphur(VI) as disulphate, which is unique to this system, is the predominant step in the sequence of reactions. In the other binary systems, this oxidation cannot take place, and several interactions of SO_2^- with SO_2, SO_2^- and other sulphur oxoanions are possible, because of the high reactivity of SO_2^- towards sulphur and oxygen.

REACTIONS OF OXIDES

Several metal oxides are now known to react with some solvent–sulphur dioxide systems (Jeffreys *et al.*, 1982). Reaction with dimethylsulphoxide–sulphur dioxide gives rise to the formation of disulphates. As in the case of metals and transition metal sulphites, both components are necessary for reaction. Contrary to the situation with respect to the spontaneous reaction of metals with solvent–sulphur dioxide systems, no evidence exists for the intermediate involvement of SO_2^- ions or metal ion-pairs. The metal ion is already very strongly bound to oxygen in the oxides, and thus probably no competition from SO_2^- would be experienced, indeed, if the latter is formed at all. It seems most likely that the oxide is converted directly, by reaction with sulphur dioxide, into sulphite, which is then solvated by sulphur dioxide to disulphite, which is oxidised by dimethylsulphoxide to disulphate, according to the scheme:

$$MO + SO_2 \longrightarrow MSO_3 \xrightarrow{SO_2} MS_2O_5 \xrightarrow{2dmso} MS_2O_7$$

The mechanism for conversion of sulphate to disulphate was discussed earlier. In view of the nature of bonding in transition metal oxides and sulphites, it is highly likely that a process is occurring which is like that previously outlined.

The factors which are important in determining whether or not an oxide reacts with dimethylsulphoxide–sulphur dioxide are not understood. There appears to be no correlation with metal redox parameters, as witnessed by the high reactivity of the binary system towards cobalt oxide but total lack of reactivity towards nickel oxide. An important factor may be that of lattice defect structure in the oxide.

Other solvent–sulphur dioxide systems, principally dimethylformamide–sulphur dioxide and acetonitrile–sulphur dioxide, react with metal oxides. They are, however, less reactive than dimethylsulphoxide–sulphur dioxide towards oxides, and are, of course, unable to oxidise sulphur(IV) to sulphur(VI). Dithionite and sulphite have been detected amongst the products of reaction of oxides with these other binary systems. Although dimethylsulphoxide–sulphur dioxide is thought of as being an oxidising medium, this appears to be in relation to its behaviour towards sulphur. The oxidation state of a metal seems not to be particularly influenced by the oxidising abilities of the system. The electrolytic dissolution of iron into dimethylsulphoxide–sulphur dioxide gives rise to the formation of iron(III), and although there is a reducing medium in an electrolytic cell, the oxidising power of the solvent appears to be predominant with respect to the metal, as well as sulphur. However, chromium(VI) in chromium(VI) oxide, chromates and dichromates is reduced to chromium(III), vanadium(V) to vanadium(III) and manganese(IV) to manganese(II), and copper(I) is oxidised to copper(II) in dimethylsulphoxide–sulphur dioxide.

Some attempts have been made to discover what the chemical consequences are of adding water to the binary systems dimethylsulphoxide–sulphur dioxide and dimethylformamide–sulphur dioxide. Addition of water introduces the possibility of the formation of bisulphite and sulphite according to:

$$H_2O + SO_2 \rightleftharpoons HSO_3^- + H^+$$
$$HSO_3^- \rightleftharpoons SO_3^{2-} + H^+$$

In considering the reactions of some metal oxides with dimethylsulphoxide–sulphur dioxide systems, for example, it was discovered that addition of up to 20% water merely slowed down the formation of metal disulphate. Addition of more than 20% water brought about the formation of metal sulphite or bisulphite. Clearly, it is to be expected that the point at which the aqueous chemistry is predominant over the non-aqueous chemistry of sulphur dioxide in such situations will be strongly dependent on the organic solvent and perhaps, to a lesser degree, on the metal oxide. In the cases so far investigated, it has not been possible to ascertain what is the extent, if any, of the involvement of SO_2^- ions. That they will be involved is in little doubt, particularly since SO_2^- can exist in equilibrium with dithionite in aqueous solutions, and in cases where metals are reacting, SO_2^- exists both in aqueous and non-aqueous environments.

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