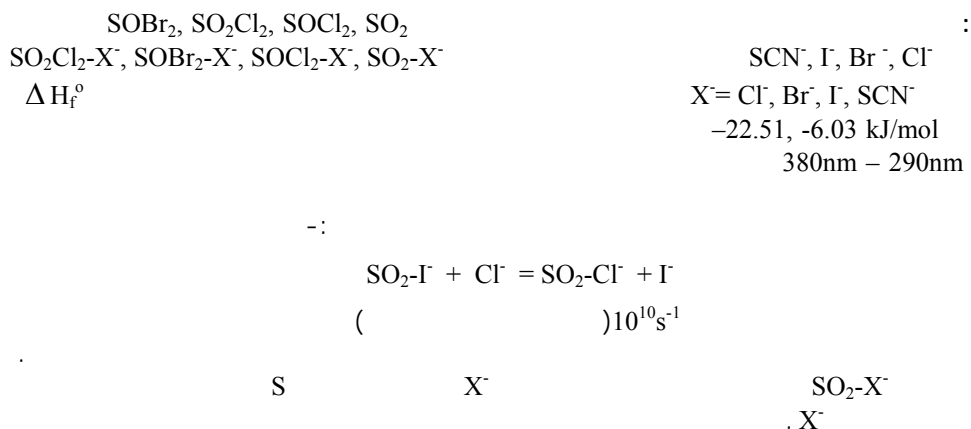


Weak Complexes of Sulfur Compounds with Halide Ligands

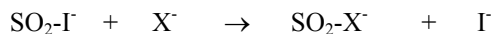
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ABSTRACT: This review summarizes the study of the formation of SO₂-X⁻, SOCl₂-X⁻, SOBr₂-X⁻, SO₂Cl₂-X⁻ complexes (X⁻ = Cl⁻, Br⁻, I⁻, and SCN⁻) in pure and mixed solvents of acetonitrile and dimethylsulfoxide over the past 30 years. Spectrometry (290nm-380nm) was the principal technique used for the investigation, since the enthalpies of formation ΔH_f^o of the above complexes are low (-6.03 — -22.51 kJ/mol). The stability of the complexes depend on the nature of the solvent, acceptor properties of the sulfur compounds, the donor properties of the halide ions and the temperature of the reaction. Also, it was found that the extent of the iodide ion replacement reactions by the other halide depends on the nature of the solvent and the halide ions.



The structures of SO₂-X⁻ compounds are pyramidal, with X⁻ at the top of the pyramid, the S atom at the center, and the angle depends on the nature of the halide ion.

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1. Introduction

Throughout the past 30 years there has been a growing interest in the field of sulfur compounds-halide ligands chemistry. The motivation for this interest has undoubtedly arisen from various sources. Witeckowa and Witok (1955) investigated the reaction between SO_2 and iodine in the gas phase and in solutions by spectrophotometric and kinetic techniques. They suggested that the interaction between HI and SO_2 in aqueous solutions is due to dipole-dipole interaction. Burke and Smith (1959) studied the molecular complexes between HF and SO_2 by infrared spectroscopy. Jander and Tuerk (1962; 1963) studied the adduct of iodine with H_2S in dichloroethane at -95°C . The low enthalpy of formation ($\Delta H_f^\circ = -31.8 \text{ kJ/mol}$) was taken as indication of the charge transfer nature of the adduct formation. Burow (1970) studied

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the solvate formation between SO_2 and Cl^- , Br^- , and I^- ligands in liquid SO_2 . Gutmann (1956) isolated a number of adducts of SOCl_2 and SO_2Cl_2 with halide ligands. Sandhu *et al* (1960; 1962) discussed the tendency of SO_2Cl_2 to form adducts with Lewis acids and Lewis bases. Salama and Wasif *et al* (1971; 1973; 1994) studied the interaction of some organic sulfur compounds and SO_2 , SOCl_2 , SO_2Cl_2 , & SOBr_2 with Cl^- , Br^- , I^- , and SCN^- ligands in acetonitrile (MeCN), dimethylsulfoxide (dmsO) and water (for SO_2 species only).

The collated data are summarized in four parts:

2. Detection, stoichiometry and stability of $\text{SO}_2\text{-X}^-$, $\text{SOCl}_2\text{-X}^-$, and $\text{SO}_2\text{Cl}_2\text{-X}^-$ complex species.
3. Effects of solvents on the stability of complex species.
4. Ligand replacement reactions in complex species and factors which affect them.
5. Structure of $\text{SO}_2\text{-X}^-$ species.

2. Detection, Stoichiometry and Stability of $\text{SO}_2\text{-X}^-$, $\text{SOCl}_2\text{-X}^-$, and $\text{SO}_2\text{Cl}_2\text{-X}^-$ Complex Species

2.1 Detection of Sulfur Complex Species

Figure 1 shows the absorbance peaks of mixtures of SO_2 with (A) tetramethylammonium iodide, (B) tetramethylammonium bromide and (C) tetramethylammonium chloride. Table 1 includes the absorbance peaks of sulfur compounds, SO_2 , SOCl_2 and SO_2Cl_2 with tetramethylammonium halides in which the halide was in abundance of the sulfur compound and in acetonitrile (MeCN) solvent. Similar peaks were obtained in dmsO and water confirming earlier studies (Jander *et al.*, 1937; Seel *et al.*, 1955).

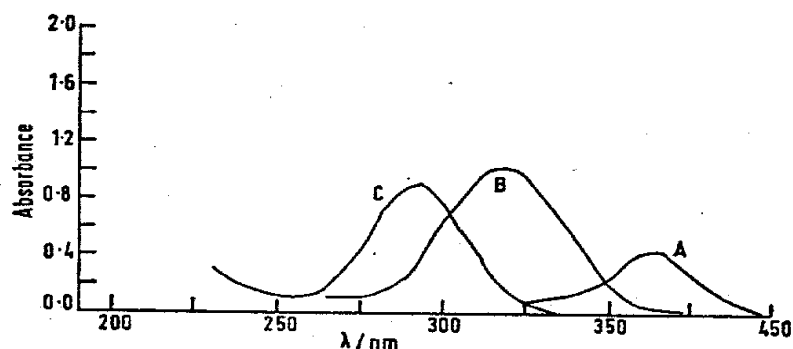


Figure 1. Absorbance peaks of $\text{SO}_2\text{-X}^-$ Species.

Table 1. λ_{max} in MeCN at 298°K

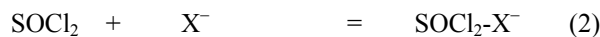
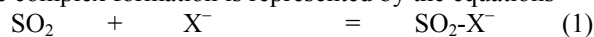
Sulfur compound (S)	S + X ⁻		
	Cl ⁻	Br ⁻	I ⁻
SO_2 (280)nm	292	320	380
SOCl_2 (280)	292	322	382
SO_2Cl_2 (275)	293	322	375

2.2 Stoichiometry and Complex Species

Job's (1928) and Asmus's (1960) methods were used to determine the complex stoichiometry. The former gave the empirical formula while the latter gave its molecular formula. The two methods showed that all complex species were of 1:1 type irrespective of the solvent used (MeCN or dmsO).

2.3 Stability Constants of Complex Species

If the complex formation is represented by the equations



then the equilibrium constants for reactions (1) – (3), which will be defined throughout this article as stability constants, may be represented by the equation

$$K_c = [\text{Complex}]/[\text{S compound}] [\text{X}^-] \quad (4)$$

where the parentheses represent molar concentration of each species and K_c is defined by the units $\text{dm}^3 \text{mol}^{-1}$. The magnitude (or value) of K_c is taken as a measure of the ability of the reacting species to associate in a complex.

Spectrophotometry was the principal technique used to find the concentration of all the terms in equation (4). Two procedures (Salama *et al.*, 1971) were adopted to evaluate K_c : (a) graphical and (b) by calculation from the molar concentrations of reactants and products. Both methods (a & b) depend on the absorbances of individual species before and after they are mixed together. Table 2 (Salama *et al.*, 1971) includes K_c values for $\text{SO}_2\text{-X}^-$, $\text{SOCl}_2\text{-X}^-$ and $\text{SO}_2\text{Cl}_2\text{-X}^-$ in MeCN at 293° or 298°K.

In most cases the difference between K_c values by the graphical and calculation methods does not exceed 5% which may be taken as the limit of the experimental error. The constancy of the K_c data is further evidence to confirm that all the complex species were of a 1:1 type (Salama *et al.*, 1971).

Table 2. Stability Constants of $\text{SO}_2\text{-X}^-$, $\text{SOCl}_2\text{-X}^-$ and $\text{SO}_2\text{Cl}_2\text{-X}^-$ in MeCN at 293° or 298° K

S Compound	SO ₂			SOCl ₂			SO ₂ Cl ₂		
Halide ligand	I ⁻	Br ⁻	Cl ⁻	I ⁻	Br ⁻	Cl ⁻	I ⁻	Br ⁻	Cl ⁻
K _c (Graphical)	37.9	192	348	152	242	367	78	40.6	10.6
K _c (Calculation)	38.5	190	363	150	241	362	77	41	10.2
Temp.°K	298	293	293	298	298	298	298	298	298

2.4 Thermodynamic Constants of $\text{SO}_2\text{-X}^-$, $\text{SOCl}_2\text{-X}^-$ and $\text{SO}_2\text{Cl}_2\text{-X}^-$

Table 3 includes K_c data for $\text{SO}_2\text{-X}^-$, $\text{SOCl}_2\text{-X}^-$ and $\text{SO}_2\text{Cl}_2\text{-X}^-$ over a range of temperatures and their relevant thermodynamic constants. The data in Table 3 point to a weak association between the sulfur compounds (electron acceptors) and the halide ligands (electron donors) of a charge transfer nature (Salama

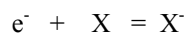
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et al., 1971; Ketelaar *et al.*, 1952; Benesi *et al.*, 1949; Drago, 1959; Rossotti *et al.*, 1969; Andrew *et al.*, 1961). Since the solvents used are polar, they possess varying tendencies to solvate the species in solution (ions, molecules and complex species) and although we are mainly concerned with complex species in acetonitrile, yet a simple interpretation of such enthalpy data will be complicated by solvation and/or dipole interaction. Comparison of the enthalpy data for the different complex species in Table 4 cannot lead to linear correlations.

Table 3. Thermodynamic Constants of $\text{SO}_2\text{-X}^-$, $\text{SOCl}_2\text{-X}^-$ and $\text{SO}_2\text{Cl}_2\text{-X}^-$ in MeCN

Complex Species	$K_c \text{ dm}^3 \text{ mol}^{-1}$	$-\Delta G_f^\circ$ kJ/mol	$-\Delta H_f^\circ$ kJ/mol	$-\Delta S_f^\circ$ J/K/mol
$\text{SO}_2\text{-I}^-$	37.9(298), 34.4(303), 30.8 (308)	8.99	17.5	28.5
$\text{SO}_2\text{-Br}^-$	260(283), 192 (293), 137 (303)	12.7	22.4	32.8
$\text{SO}_2\text{-Cl}^-$	519(284), 400 (293), 348 (303)	14.7	15.1	1.34
$\text{SOCl}_2\text{-I}^-$	190 (288), 150 (298)	12.2	16.9	15.1
$\text{SOCl}_2\text{-Br}^-$	276 (288), 241 (298)	13.6	9.82	-12.6
$\text{SOCl}_2\text{-Cl}^-$	447(288), 362 (298), 264 (308)	14.6	15.4	2.72
$\text{SO}_2\text{Cl}_2\text{-I}^-$	86 (288), 77 (298), 71 (308)	10.8	6.01	-15.9
$\text{SO}_2\text{Cl}_2\text{-Br}^-$	45 (288), 39 (298), 37 (308)	9.20	10.7	4.98
$\text{SO}_2\text{Cl}_2\text{-Cl}^-$	12(288), 10.5 (298), 9.3 (308)	5.76	7.82	6.90

Of the components taking part in the formation of these complexes only the acceptors (sulfur compounds) have UV absorption peaks, SO_2 (280nm), SOCl_2 (280nm) and SO_2Cl_2 (275nm) (Friedman, 1967). The appearance of new peaks due to the formation of the complex species arises from donor-acceptor interactions. These result in spectral shifts for the acceptor which must be a function of the donor character of each halide ligand. An attempt was made to correlate such spectral shifts with the reversible potential for:

Table 4. Stability Constants of $\text{SO}_2\text{-X}^-$, $\text{SOCl}_2\text{-X}^-$, and $\text{SO}_2\text{Cl}_2\text{-X}^-$ in MeCN at 298°K

	Cl^-	Br^-	I^-
$\text{SO}_2\text{-X}^-$	372	160	38
$\text{SOCl}_2\text{-X}^-$	362	241	150
$\text{SO}_2\text{Cl}_2\text{-X}^-$	10.5	41.0	77

The linear plots of Figure 2 supplement this assumption for the different species.

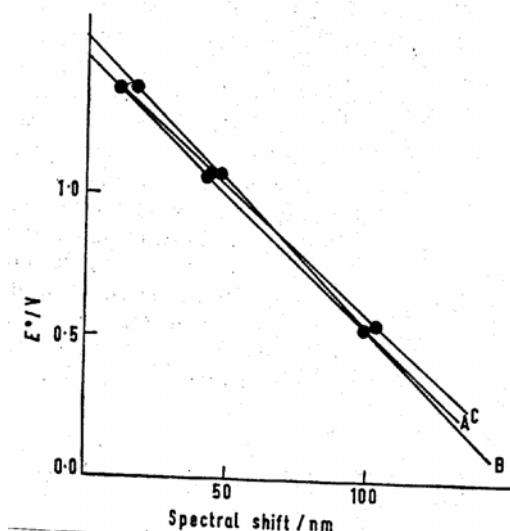


Figure 2. Correlation of E° for the Reaction $e^- + X \rightleftharpoons X^-$ with Acceptor Spectral Shifts: A, $\text{SO}_2\text{-X}^-$; B, $\text{SO}_2\text{Cl}_2\text{-X}^-$; C, $\text{SOCl}_2\text{-X}^-$

2.5 The Donor-Acceptor Nature of the Complex Species

In order to understand the nature of these complexes we shall try to rationalize the stability constants data of Table 4 with the nature of the halide ligands (donors) and the sulfur compounds (acceptors). Table 5 summarizes some important trends (Basolo *et al.*, 1958 ; Gould, 1960).

Table 5. Physical Constants of Halide Ions.

	Cl^-	Br^-	I^-
Ionisation Potential (kJ/mol)	1251	1136	1000
Electron Affinity (kJ/mol)	349	325	295
Hydration Energy of X^- kJ g-ion ⁻¹	356	310	255
Polarisability/Å	2.3	3.3	5.1
Electronegativity	2.83	2.74	2.21

The iodide ion with high polarisability, low electronegativity and easy oxidation is considered to be a soft Lewis base (Pearson, 1963; Day *et al.*, 1969). The chloride ion with low polarisability and high electronegativity is a hard Lewis base. The bromide ion is a borderline Lewis base. The acceptors include SO_2 and SOCl_2 in which the oxidation state of sulfur is four and SO_2Cl_2 in which it is six. SO_2 is a borderline Lewis acid (Pearson, 1963; Day *et al.*, 1969). It acts as a base toward BF_3 to form the adduct $\text{SO}_2\text{-BF}_3$ and as acid towards water. Thionyl chloride SOCl_2 is similar to SO_2 in that it has a lone pair of electrons ($3s^2$) but one of the double bonded oxygen atoms is replaced by two Cl atoms. The S-Cl bond is more polarized than the S-O bond owing to the higher electronegativity of Cl, and would be expected to act as a stronger Lewis acid than SO_2 , or a better acceptor. Sulphonyl chloride SO_2Cl_2 , may be related to SO_3 (known as a hard Lewis acid) (Pearson, 1963; Day *et al.*, 1969) in the same manner as SOCl_2 is related to

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SO₂, and the order of acid strength is SO₂Cl₂ > SOCl₂ > SO₂. The formation of the present complex species is the result of acid-base interactions between the acceptors and the donors and the order of stability given in Table 4 can be discussed on this basis.

2.6 Correlation of the Order of Stability Constants of Different Complexes with Donor-Acceptor Properties

Table 4 shows that the stability of SO₂-X⁻ species falls in the order SO₂-Cl⁻ > SO₂-Br⁻ > SO₂-I⁻. Sulfur (IV) forms coordination compounds owing to the electrophilic and nucleophilic nature of the sulfur atom. The former is due to the availability of the empty 3*d* electron orbitals and the latter to the presence of a lone pair of 3*s*² electrons on the sulfur atom. Thus, in such compounds as SO₂, sulfur acts as a σ-donor only or a Π-acceptor. However, the donor-acceptor properties of the sulfur atom are exhibited almost synonymously. If the donor (or ligand) contains *d*-orbitals of the appropriate symmetry (i.e. not diffuse) back-donation from the sulfur atom to the donor may occur, giving rise to the *d-d* multiple bonding which will strengthen the ligand acceptor bond. The Cl⁻ and Br⁻ ions may accept back-donation but this seems doubtful for the I⁻ ion because the *d*-orbitals become progressively diffuse and less available for back-donation as we go down the halide group. The order of complex stability can be explained on this basis.

This interpretation of the stability constants order is supplemented by the classification of the halide ions as hard (Cl⁻) borderline (Br⁻) and soft (I⁻) bases and of SO₂ as a borderline Lewis acid. The order of stability of the SO₂-X⁻ complex species would follow the strength of the base and SO₂-Cl⁻ species would be the strongest and SO₂-I⁻ the weakest, as actually found. We may now consider the SOCl₂-X⁻ species. Table 6 includes the ratios of stability constants of SO₂-X⁻ and SOCl₂-X⁻ species.

Table 6. Stability Constants Ratios for SO₂-X⁻ and SOCl₂-X⁻ in MeCN

	I ⁻	Br ⁻	Cl ⁻
K _c (SO ₂ -X ⁻)/K _c (SO ₂ -I ⁻)	1.0	4.0	10.0
K _c (SOCl ₂ -X ⁻)/K _c (SOCl ₂ -I ⁻)	1.0	1.6	2.4

Table 4 shows that the order of stability of SOCl₂-X⁻ species is similar to that of SO₂-X⁻ where Cl⁻ > Br⁻ > I⁻. Table 6 shows that the stability constants of SO₂-Cl⁻ and SOCl₂-I⁻ are nearly of the same order of magnitude but K_c(SOCl₂-I⁻) is merely 4 times greater than K_c(SO₂-I⁻) and K_c(SOCl₂-Br⁻) and K_c(SOCl₂-Cl⁻) are only 1.6 and 2.4 times greater than K_c(SOCl₂-I⁻) which calls attention to new factors responsible for the observed change in ratios.

The order of stability constants ratio of SOCl₂-X⁻ species shows that as in the case of SO₂-X⁻ the chloride species is the most stable and the iodide is the least stable. This order suggests that the nature of association between the Cl⁻ and SO₂ is much the same as with SOCl₂. Back-donation may be considered to be the factor contributing to the stability of SOCl₂-X⁻ species. In SOCl₂ the electrophilic nature is enhanced over SO₂ by the replacement of one oxygen atom by two chlorine atoms and the *d*-orbitals of sulfur are more exposed for coordination because the electron cloud is removed by the electronegative chlorine atoms, and this makes SOCl₂ a better Lewis acid than SO₂.

Although the halide ions were classified by Pearson (1963) as Lewis bases of varying strengths and such classification could account for the order of stabilities of SO₂-X⁻ species, the situation may be different with SOCl₂. The increased acceptor character does not appear to have changed or to have affected dramatically the nature of association with the Cl⁻ ligand. For the I⁻ ligand this increased acid character appears to have increased the basicities of the I⁻ and Br⁻ ligands relative to that of the Cl⁻, so SOCl₂ appears to be leveling up the basic character of the I⁻ and Br⁻ ligands towards that of the Cl⁻ ligand. This leveling of relative basicities of the halide ligands appears to be another factor which determines the ratios of Table 6.

A third factor relevant to Table 6 is the increased ionic radii and polarisabilities of the donors. Table 5 shows that the Γ ligand is the most polarisable of the halide ions. Other factors remaining equal, an increase in the polarisability of the donor would make the donor-acceptor interaction stronger. The dipole moments of SO_2 and SOCl_2 are 1.61 and 1.60D respectively. If polarisability was the only factor one would expect the iodide complex to be the most stable. This was not so, indicating that back-donation is a still more important factor in deciding the nature of association of the halide ligands with SOCl_2 . Sulphonyl chloride, SO_2Cl_2 , is the strongest acceptor of this group of sulfur compounds; it has the highest dipole moment (1.86 D). The d -orbitals of sulfur here are the most exposed for coordination than in the other acceptors. The order of stability of its halide ligand complexes is: $\text{SO}_2\text{Cl}_2\text{-I}^- > \text{SO}_2\text{Cl}_2\text{-Br}^- > \text{SO}_2\text{Cl}_2\text{-Cl}^-$ which is the reverse of $\text{SO}_2\text{-X}^-$ and $\text{SOCl}_2\text{-X}^-$ species (Table 4) suggesting that back-donation cannot be strong in the formation of $\text{SO}_2\text{Cl}_2\text{-X}^-$ complexes.

The increased acidity of SO_2Cl_2 seems now to be very important. In the presence of such a relatively strong Lewis acid the three Lewis bases appear to lose their identity and are of merely equal strength. Thus the leveling effect observed for SOCl_2 is probably more strongly displayed. In protonic systems this leveling explains why benzoic acid and sulfuric acid are equally strong in liquid ammonia while water, alcohol, ketones... etc are equally strong bases in pure sulfuric acid (Bell, 1965; Waddington, 1965).

It appears that increased polarisability towards Γ^- , the increased polarity towards SO_2Cl_2 and the increased leveling effect can account for the order of stability constants observed for $\text{SOCl}_2\text{-X}^-$ complex species. The effect of polarisability of the halide ligands on the order of stability of some metal complexes has been reported (Gould, 1960).

We may conclude that as the acceptor is changed from SO_2 to SO_2Cl_2 the nature of association also changes. With SO_2 $d_{II}\text{-}d_{II}$ multiple bonding from back-donation makes its association with halide ligands quite strong but with SO_2Cl_2 the dipole-dipole interaction seems to be a weaker force of association, as shown from ΔH_f° values in Table 3 and the K_c values of Table 4.

3. Solvent Effects on Stability of $\text{SO}_2\text{-X}^-$, $\text{SOCl}_2\text{-X}^-$ and $\text{SO}_2\text{Cl}_2\text{-X}^-$

3.1 Pure Solvents

Solvent molecules are not impartial in chemical processes and the extent to which they participate sometimes overshadows that of the other species in the reaction media. This is because the solvent represents the environment in which a chemical reaction takes place and in most cases plays the role of a donor or acceptor. The role of environment and solvent effects on chemical reactions has been discussed by a number of workers (Bell, 1965; Waddington, 1965; Frost *et al.*, 1961; Benson, 1960; Amis, 1965; Gutmann, 1967, 1971; Grunwald, 1949). The K_c values for $\text{SO}_2\text{-X}^-$, $\text{SOCl}_2\text{-X}^-$ and $\text{SO}_2\text{Cl}_2\text{-X}^-$ in MeCN, dmsO and water recorded in Table 7 illustrate the solvent effects.

Table 7. Stability Constants for $\text{SO}_2\text{-X}^-$, $\text{SOCl}_2\text{-X}^-$ and $\text{SO}_2\text{Cl}_2\text{-X}^-$ in MeCN, dmsO and water at 298° K. (a = MeCN, b = dmsO, and c = water)

X^-	Cl^-		Br^-			Γ^-		
	a	b	a	b	c	a	b	c
$\text{SO}_2\text{-X}^-$	372	26	160	21	0.22	38	12	0.36
$\text{SOCl}_2\text{-X}^-$	362	18	241	21		150	35	
$\text{SO}_2\text{Cl}_2\text{-X}^-$	10	36	41	14		71	6	

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Comparison of K_c data is limited to the values in MeCN and dmsO. With the exception of $\text{SO}_2\text{Cl}_2\text{-X}^-$ species, the stability constants of different complexes decreased by a factor of nearly 20 in dmsO as compared to MeCN which is shown from the data in Table 8.

Table 8. Comparison of Stability Constants in MeCN and dmsO $K_c(\text{MeCN})/K_c(\text{dmsO})$ at 298°K.

X^-	Cl^-	Br^-	I^-
$\text{SO}_2\text{-X}^-$	15	8	3
$\text{SOCl}_2\text{-X}^-$	20	11	4
$\text{SO}_2\text{Cl}_2\text{-X}^-$	0.3	3	13

The data in Tables 7 and 8 express significant changes in complex stabilities between MeCN and dmsO, as the K_c values are lower in dmsO than in MeCN. There are at least two possible roles that can be played by dmsO (or water) in affecting the stabilities of the complex species. It may solvate the halide ligands, which prevents them from interacting with the acceptors, i.e. sulfur compounds, or it may act as a competing acceptor, i.e. competes against SO_2 , SOCl_2 , and SO_2Cl_2 and thus makes a complex species with the ligands and perhaps it may play the two roles depending on the environmental conditions. Table 8 shows some horizontal and vertical trends.

The data in column (1) show maximum decrease in K_c for $\text{SO}_2\text{-Cl}^-$ and also for $\text{SOCl}_2\text{-Cl}^-$ in dmsO. This can be attributed to solvation of the Cl^- ligand and possibly ion-dipole interaction in view of the high dipole moment of dmsO (4.3D). In these species, stabilization results from back-donation (Mines *et al.*, 1972; Chadwick, 1973) from sulfur 3d-orbitals to the donor ligand. Minimum effect is shown for $\text{SO}_2\text{Cl}_2\text{-Cl}^-$ where $K_c(\text{MeCN})/K_c(\text{dmsO})$ equals 0.3, which shows the importance of polarization and not back-donation in stabilizing $\text{SO}_2\text{Cl}_2\text{-Cl}^-$ species.

In column (2) ratios for $\text{SO}_2\text{-Br}^-$ and $\text{SOCl}_2\text{-Br}^-$ are nearly half those reported for the Cl^- species, which is regarded as reflecting the lower tendency to solvation of the Br^- ligand as compared to Cl^- by dmsO. In column (3) the ratios of $\text{SO}_2\text{-I}^-$ and $\text{SOCl}_2\text{-I}^-$ are nearly $\frac{1}{4}$ of the values for the Cl^- species. This shows the lower tendency of I^- ligands to solvate and this is not unexpected due to the larger ionic size of I^- .

The horizontal trends in $\text{SO}_2\text{-X}^-$ and $\text{SOCl}_2\text{-X}^-$ appear to agree with the conclusion that solvation of the donor ligands by dmsO is important in decreasing the stability constants compared with those in MeCN and that this lowering is maximal with Cl^- ligands and minimal with I^- ligands. The K_c values in water appear to support this view.

For $\text{SO}_2\text{Cl}_2\text{-X}^-$ the horizontal trend is reversed compared to that shown by $\text{SO}_2\text{-X}^-$ and $\text{SOCl}_2\text{-X}^-$. This supports the view that the nature of association in $\text{SO}_2\text{Cl}_2\text{-X}^-$ is different from that in $\text{SO}_2\text{-X}^-$ and $\text{SOCl}_2\text{-X}^-$ (Salama *et al.*, 1971), the former being mainly ion-dipole interaction and the latter back-donation as mentioned earlier. The lowering in stability constants of $\text{SO}_2\text{Cl}_2\text{-I}^-$ and $\text{SO}_2\text{Cl}_2\text{-Br}^-$ is evidence that ion-dipole interaction is particularly strong between dmsO and iodide ion (Salama *et al.*, 1991), which is understandable in view of the higher dipole moment of dmsO compared with SO_2Cl_2 . The data in Table 8, column (3) for the iodide species show that ion-dipole interaction outweighs solvation, while those in column (1) show that solvation has the greater effect.

3.2 Mixed Solvents: (MeCN-dmsO)

Few workers have reported on chemical processes in mixed solvents and also specified the role of solvent. The work to be outlined reports on the stability of $\text{SO}_2\text{-X}^-$, $\text{SOCl}_2\text{-X}^-$ and $\text{SO}_2\text{Cl}_2\text{-X}^-$ in MeCN-dmsO mixed solvent, and Table 9 (Salama *et al.*, 1978) includes the K_c data of these complex species in MeCN, dmsO and mixtures of the two solvents at 298°K.

The data in columns 2 and 6 were quoted from Table 2. One feature appears throughout Table 9. The stability constants of all complex species, at 298°K, vary with solvent composition. In order to rationalize

the K_c values we shall discuss the horizontal and vertical trends in Table 9.

Table 9. Stability Constants for $\text{SO}_2\text{-X}^-$, $\text{SOCl}_2\text{-X}^-$, and $\text{SO}_2\text{Cl}_2\text{-X}^-$ in MeCN, dmsO, and their mixtures at 298°K

Complex	dmsO	MeCN+dmsO			MeCN
		1:3	1:1	3:1	
$\text{SO}_2\text{-I}^-$	12.1	14.1	24.7	36.7	37.9
$\text{SO}_2\text{-Br}^-$	21.0	14.5	24.1	40.1	40.1
$\text{SO}_2\text{-Cl}^-$	26.0	35.5	50.0	52.4	372.0
$\text{SOCl}_2\text{-I}^-$	35.0	40.2	58.9	223.5	150.0
$\text{SOCl}_2\text{-Br}^-$	21.0	22.9	34.2	71.7	241.0
$\text{SOCl}_2\text{-Cl}^-$	18.0	66.7	73.8	113.0	362.0
$\text{SO}_2\text{Cl}_2\text{-I}^-$	6.0	30.1	50.1	142.2	76.0
$\text{SO}_2\text{Cl}_2\text{-Br}^-$	14.0	15.5	24.6	36.2	41.0

3.3 The $\text{SO}_2\text{-X}^-$ Species

The K_c values of $\text{SO}_2\text{-I}^-$ change gradually between the limits set for MeCN and dmsO as the solvent composition changes. In MeCN-dmsO solvent (3:1) the K_c value is reduced by 2.7% compared with that in 25% dmsO solvent. For $\text{SO}_2\text{-Br}^-$ and $\text{SO}_2\text{-Cl}^-$ the K_c values are reduced in the same solvent by 75% and 85% respectively. (The K_c value in MeCN is taken as a reference in each case). Solvation of Br^- and Cl^- ligands by dmsO is clearly greater than that for the I^- ligand. A similar conclusion was reached when K_c for the same species were determined in MeCN and dmsO (Salama *et al.*, 1975). To correlate the variations in K_c values with solvent composition it should be remembered that the molecules of different solvents can act as donors and/or acceptors. Even if both solvent molecules have donor or acceptor character a slight difference in the donor or acceptor properties between different solvent molecules will invite donor-acceptor interaction between them. The nature of such interactions in non-protic solvent mixtures such as MeCN-dmsO has not been studied before (Waddington, 1965).

Over a wide range of molecular ratios of MeCN and dmsO one expects such interactions to exhibit different patterns which depend on the structural and geometrical characters of the molecules. We shall call this solvent-solvent interaction and may define it in terms of donor-acceptor interaction or perhaps association which vary with solvent composition.

Such solvent-solvent interactions may occur at the expense of other interactions in solution. For example in MeCN-dmsO containing SO_2 molecules and Cl^- ligands and $\text{SO}_2\text{-Cl}^-$ complex species the following interactions are likely to occur (a) Cl^- -dmsO, (b) Cl^- -MeCN, (c) SO_2 -dmsO, (d) SO_2 -MeCN and (e) MeCN-dmsO. The stability constant of the $\text{SO}_2\text{-Cl}^-$ species is determined by the relative magnitudes of such interactions, a strong Cl^- -solvent interaction (solvation) would reduce the stability of $\text{SO}_2\text{-Cl}^-$ species, since this steric factor may prevent, to some extent, SO_2 and Cl^- from approaching each other for coordination. On the other hand a strong MeCN-dmsO interaction would allow more SO_2 to coordinate with Cl^- ligands and K_c values become greater than the limits set for each solvent.

The data for $\text{SO}_2\text{-X}^-$ show that MeCN-dmsO interaction accounts partly for the change in K_c with solvent changes. Ligand solvation is also important in determining K_c values. The K_c data show that while the I^- -solvent interaction is relatively weak and reduces K_c by 2.7% (in 25% dmsO relative to its value in MeCN) those of Cl^- -solvent interactions and Br^- -solvent interactions are much stronger and reduce K_c by 85% and 75% for $\text{SO}_2\text{-Cl}^-$ and $\text{SO}_2\text{-Br}^-$ respectively.

3.4 The $\text{SOCl}_2\text{-X}^-$ and $\text{SO}_2\text{Cl}_2\text{-X}^-$ Series

The K_c values for $\text{SOCl}_2\text{-Cl}^-$ and $\text{SOCl}_2\text{-Br}^-$ fall between the limits set for MeCN and dmsO but that for $\text{SOCl}_2\text{-I}^-$ species exceeds the upper limit in MeCN by 30% (in 25% dmsO solvent). A change in solvent

composition from 50 to 25% dmsO is coupled with a sudden change in K_c for $\text{SOCl}_2\text{-I}^-$. It appears that over this critical range of solvent composition the solvent-solvent interaction reaches its maximum. The nature of this interaction is not yet clear but is detectable from vapor pressure measurements (Salama *et al.*, 1985). Such interactions have freed sufficient I^- ligands and SOCl_2 molecules for coordination which makes K_c 30% greater than the value in MeCN. With $\text{SOCl}_2\text{-Cl}^-$ and SOCl_2Br^- (in 25% dmsO solvent) the K_c values are reduced by 69% and 71% from the value in MeCN. Thus, despite strong solvent-solvent interaction the Br^- -solvent and Cl^- -solvent interactions have outweighed solvent-solvent interactions. A similar argument applies to $\text{SO}_2\text{Cl}_2\text{-I}^-$ and $\text{SO}_2\text{Cl}_2\text{-Br}^-$ where K_c increases by 61% for the iodide species and decreases by 15% for the bromide species.

3.5 Vertical Correlations in Table 9

3.5.1 The Iodide Complex Series

Although K_c values for $\text{SOCl}_2\text{-I}^-$ and for $\text{SO}_2\text{Cl}_2\text{-I}^-$ in 25% dmsO are 30% and 64% greater than the value in MeCN we find that K_c for $\text{SO}_2\text{-I}^-$ is 2.7% less than its value in MeCN. Such differences in behavior are probably due to differences in the manner in which the I^- ligand is coordinated to the three acceptors. The I^- ligand is polarisable with diffuse *d*-orbitals suitable for ion-dipole interaction. The dipole moment of the three acceptors are in the order SO_2 (1.61D) SOCl_2 (1.60D) and SO_2Cl_2 (1.86D). In 25% dmsO solvent strong solvent-solvent interaction favors $\text{SO}_2\text{Cl}_2\text{-I}^-$ coordination so that the K_c value exceeds that in MeCN by 64%. The acceptor character of SOCl_2 is enhanced by the replacement of one O atom in SO_2 by 2 Cl atoms and coordination by ion-dipole interaction is relatively stronger with I^- than with SO_2 . Solvent-solvent interaction helps coordination of SOCl_2 to I^- and results in a K_c value which exceeds that in MeCN by 30%. For $\text{SO}_2\text{-I}^-$ the ion-dipole interaction is probably so weak that is nearly balanced by solvent-solvent interaction and K_c is slightly reduced by 2.7%.

3.5.2 The Bromide and Chloride Complex Series

The decrease in the K_c values for $\text{SO}_2\text{-Br}^-$, $\text{SOCl}_2\text{-Br}^-$ and $\text{SO}_2\text{Cl}_2\text{-Br}^-$ (in 25% dmsO solvent) by 76, 71 and 15% respectively resulted from Br^- -solvent interaction. The difference arises from differences in the modes of coordination of the three acceptors. For SO_2 and SOCl_2 back-donation is the principal mechanism by which coordination takes place to S(IV). For $\text{SO}_2\text{-Br}^-$ and $\text{SOCl}_2\text{-Br}^-$ solvent-solvent interaction is outweighed by Br^- -solvent interaction and K_c is reduced accordingly. For $\text{SO}_2\text{Cl}_2\text{-Br}^-$ coordination occurs by an ion-dipole mechanism involving S(VI). The Br^- ligand, being a borderline Lewis base, responds favorably to this mechanism and by its solvation by dmsO slightly outweighs solvent-solvent interaction and K_c is reduced to a smaller extent than in the other bromides.

For $\text{SO}_2\text{-Cl}^-$ and $\text{SOCl}_2\text{-Cl}^-$ back-donation is the principal mechanism for coordination. In both species the Cl^- -solvent interaction outweighs solvent-solvent interaction and K_c values are reduced by 85 and 69% respectively. This differing effect on K_c might be due to selective solvation in the presence of different acceptors which we may describe as chemical environmental factors.

3.6 Evidence for Solvent-Solvent Interactions

3.6.1 Spectroscopic

Using the IR (infra red) techniques, it is found that the S=O vibration band of dmsO appears at 1080cm^{-1} and on addition of MeCN the band is shifted to 1070cm^{-1} . The $\text{C}\equiv\text{N}$ vibration band of MeCN appears at 2250cm^{-1} and adding dmsO at $x_1 = 0.5$ ($x_1 = \text{mol fraction}$) the band is shifted to 2240cm^{-1} (Salama *et al.*, 1985).

Using Raman spectra it is found that the S = O vibration band appears at 1044cm^{-1} and on adding MeCN a peak appears at 1062cm^{-1} while that at 1044cm^{-1} disappears. For MeCN the $\text{C}\equiv\text{N}$ vibration band appears at 2255cm^{-1} and on addition of dmsO the band disappears gradually. The observed vibrational shifts

may be taken as evidence for solvent-solvent interaction through adduct formation of the type represented by Figure 3.

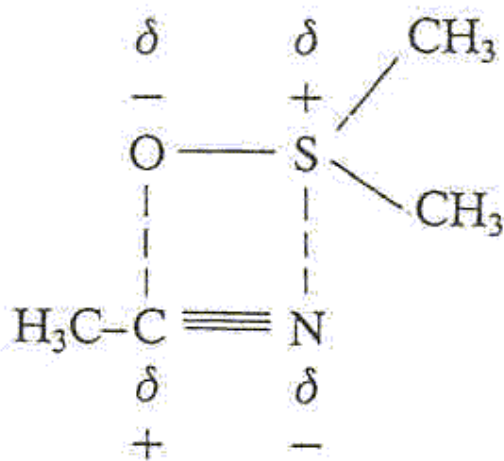


Figure 3. MeCN-dmsO Adduct

3.6.2 Vapor-Pressure, Viscosity, and Excess Functions from Refractive Index, Dielectric Constant and Volume

Further confirmation for solvent-solvent interaction was obtained from measurements of vapor pressure and viscosity of MeCN-dmsO mixtures. Table 10 includes vapor pressure, viscosity, ΔH_{vap} , ΔS_{vap} , and ΔH_{vis} of the mixtures over the whole composition range.

Table 10. Vapour pressures and viscosities of MeCN-dmsO mixtures

10(a). Vapour Pressure Data

25% MeCN	$t/^{\circ}\text{C}$	61.6	69.0	75.6	80.7	85.7	
	p/mmHg	58.0	72.0	84.0	99.0	115.5	
50% MeCN	$t/^{\circ}\text{C}$	29.0	34.5	39.9	45.0	49.0	54.0
	p/mmHg	69.7	76.1	95.6	115.6	136.3	163.6
75% MeCN	$t/^{\circ}\text{C}$	28.4	33.1	38.5	43.7	49.4	
	p/mmHg	78.9	95.4	119.4	147.9	186.9	
80% MeCN	$t/^{\circ}\text{C}$	28.4	33.4	38.9	45.1	51.6	
	p/mmHg	84.7	106.5	134.0	160.0	213.0	

10(b). Viscosity Data

$t/^{\circ}\text{C}$	25.0	30.0	35.0
MeCN	3.55	3.38	3.30×10^{-4} Pas
75%MeCN	5.17	4.89	4.73
50%MeCN	7.44	7.04	6.68
25%MeCN	11.71	10.85	10.16
dmsO	19.57	17.88	16.40

WEAK COMPLEXES OF SULFUR COMPOUNDS

10(c). Thermodynamic Data for Vaporization and Viscosity

Solvent	MeCN	80% MeCN	75% MeCN	50% MeCN	25% MeCN	dmsO
ΔH_{vap} kJ/mol	33.2	31.8	33.3	29.1	28.2	52.9
ΔS_{vap} J/K/mol	96.0	87.1	91.4	72.9	62.7	95.8
ΔH_{vis} kJ/mol	5.48	6.57	7.74	8.24	10.6	13.3

Figure 4 shows a plot of ΔH_{vap} and ΔH_{vis} against solvent composition. The plots are not linear and deviate over the composition range 50–70% (maximum deviation which may be taken to indicate solvent-solvent interaction). The ΔS_{vap} data show a minimum value at 75% dmsO suggesting maximum order for the system at this composition with probable formation of MeCN-dmsO adduct.

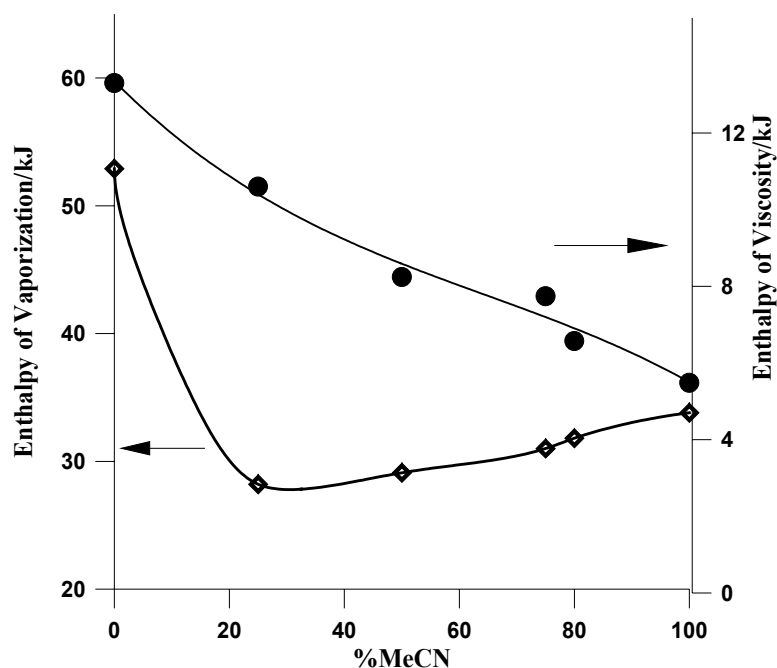


Figure 4. Plot of Enthalpy of Vaporization/kJ (●) and Enthalpy of Viscosity /kJ (◆) against %MeCN

The excess functions from refractive index n^E , dielectric constant ϵ^E and densities V^E of MeCN-dmsO mixtures are given in Table 11 (Salama *et al.*, 1985). The data in Table 11 show that the magnitude of any excess function reaches a maximum at approximately 1:1 composition. This is again taken to indicate solvent-solvent interaction.

Table 11. Excess Functions of MeCN-dmsO mixtures at 298°K
11(a). Refractive Index (n^E)

x_1	0.1319	0.2676	0.4258	0.6899	0.7836	0.8697
n^E	0.0030	0.0076	0.0087	0.0102	0.0065	0.0039

11(b). Dielectric Constant (ϵ^E)

x_1	0.1319	0.2676	0.4258	0.6009	0.6899	0.7836	0.8697
ϵ^E	0.5710	0.9540	1.3180	1.4910	1.3680	1.1960	0.8630

11(c). Volume (V^E). (x_1 = mole fraction of dmsO)

x_1	0.1006	0.3066	0.6037	0.7061	0.8083	0.8999	0.9455
V^E	-0.1300	-0.2523	-0.2519	-0.1773	-0.1275	-0.0876	-0.0486

3.7 A Thermodynamic View of Solvent Effects on The Stability of $\text{SO}_2\text{-X}^-$, $\text{SOCl}_2\text{-X}^-$ and $\text{SO}_2\text{Cl}_2\text{-X}^-$

3.7.1 The Significance of ΔG_f° of Complexes in Relation to Solute-Solvent Interactions:

Table 12 includes the standard free energies of formation ΔG_f° of $\text{SO}_2\text{-X}^-$ and $\text{SOCl}_2\text{-X}^-$ in MeCN, dmsO, and their mixtures.

Table 12. $-\Delta G_f^\circ$ (kJ/mol) of complex species in different solvents at 298°K

	dmsO	dmsO: MeCN			MeCN
		3:1	1:1	1:3	
$\text{SO}_2\text{-I}^-$	6.19	6.57	8.03	9.00	9.08
$\text{SO}_2\text{-Br}^-$	7.61	6.74	7.91	9.20	8.49
$\text{SO}_2\text{-Cl}^-$	8.12	8.95	9.75	10.9	10.6
$\text{SOCl}_2\text{-I}^-$	8.87	9.20	10.2	13.5	12.5
$\text{SOCl}_2\text{-Br}^-$	7.61	7.82	8.79	10.7	13.7
$\text{SOCl}_2\text{-Cl}^-$	7.20	10.5	10.7	11.8	14.6

The data in Table 12 show that for every complex species there are several free energy minima, each corresponding to a different solvent composition. This situation is only possible if a change in the solvent composition affects continuously the coordinating ability of the halide ligand (X^-) with the sulfur acceptor (SO_2 or SOCl_2) and partially hinders them from complex formation and which was described as solvation. Preliminary studies (Wasif, unpublished work) show that halide ion solvation in MeCN and dmsO falls in the order $\text{Cl}^- > \text{Br}^- > \text{I}^-$, which agrees with their ionic radii and charge densities.

Solvation of the sulfur acceptors was studied in the present work by UV spectroscopy. Figure 5 shows the absorbance of SOBr_2 in (a) MeCN, (b) dmsO and (c) 1:1 mixed solvent of MeCN-dmsO. It shows three distinct species which obey Beer's law. The intermediate absorbance of the 1:1 mixed solvent shows that SOBr_2 forms an absorbing species of intermediate character between the species in dmsO and MeCN. There are two possibilities in which this could happen: (1) The formation of a constant ratio of the adduct species $\text{SOBr}_2\text{-MeCN}$ and $\text{SOBr}_2\text{-dmsO}$, (2) that SOBr_2 makes a species with a mixed solvent adduct e.g. ($\text{SOBr}_2\text{-MeCN:dmsO}$). Using CCl_4 as solvent the species $\text{SOBr}_2\text{-MeCN}$ and $\text{SOBr}_2\text{-dmsO}$ were detectable and their stability constants are given in Table 13.

The data in Table 13 show that solvents MeCN and dmsO play a competing role against halide ligands in their coordination with the sulfur acceptors. The data also show dmsO to have a greater destabilizing role

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Table 13. Stability Constants of Adducts of MeCN and dmsO with Sulfur Compounds at 298°K.

A	SO ₂	SOCl ₂	SOBr ₂	SO ₂ Cl ₂
dmsO-A	2.82	6.86	3.73	17.79
MeCN-A	0.34	0.07	0.11	0.68

for the complex species than does MeCN, by its strong ability to solvate the halide ligands and the sulfur compounds.

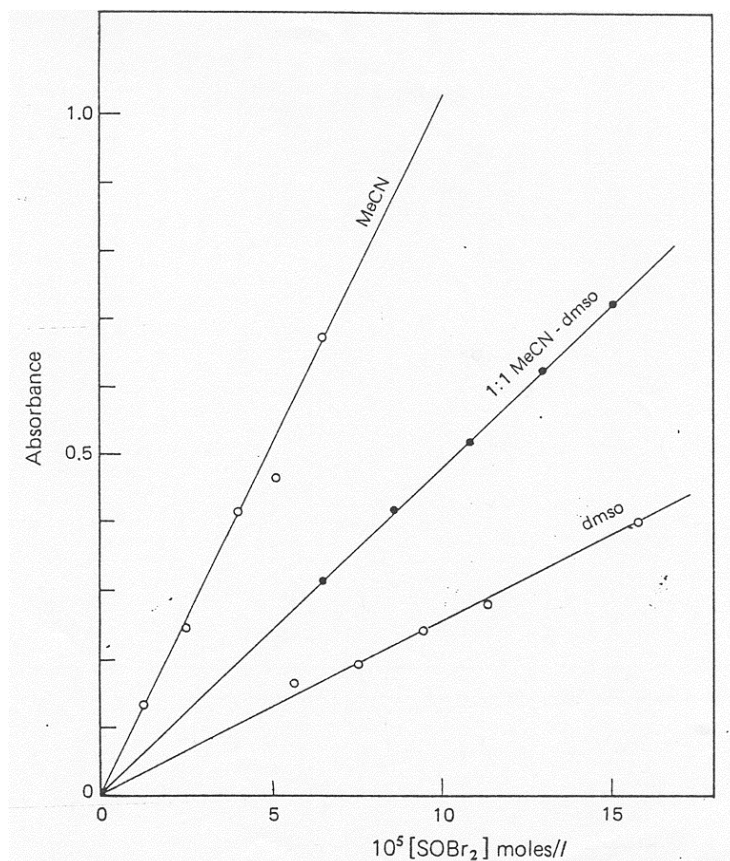


Figure 5. Dependence of Absorbance of SOBr₂ On Solvent Mole Fraction

3.7.2 The Dependence of ΔH_f° and ΔS_f° of Complex Species on Solvent Composition:

A second thermodynamic aspect would be to consider the significance of ΔH_f° and ΔS_f° for complex species in mixed solvents. Table 14 includes the standard thermodynamic constants for the formation of the complex species SOBr₂-Cl⁻ and SOBr₂-Br⁻.

Table 14 shows that the standard enthalpy of formation varies as the solvent composition changes from MeCN to dmsO. For SOBr₂-Br⁻ ΔH_f° is nearly 10 times greater in MeCN than in dmsO but for SOBr₂-Cl⁻ it is nearly 5 times greater than the value in dmsO. Such differences in ΔH_f° values suggest that the

measured enthalpy of formation is a rather complex function. It does not probably represent the heat of formation of the complex species but other heat terms are possibly embodied in this term such as heats of solvation of the halide ligands and sulfur compounds in MeCN and dmsO. If ΔH_f° be taken as a rough measure for the complex stability, then data in Table 14 would show that the complex species $\text{SOBr}_2\text{-X}^-$ ($\text{X}^- = \text{Cl}, \text{Br}$) are more stable in MeCN than they are in dmsO. A thorough discussion of the significance of ΔH_f° data requires a knowledge of the heats of solvation of the different species in both solvents which are not at present available. This situation permits a qualitative discussion of ΔH_f° data. Since solute-solvent interactions are a dynamically changing process we may expect the magnitude of $\Delta H_{\text{solvation}}$ values to change over the solvent concentration range, which is confirmed directly from Table 14. With this situation in mixed polar solvents a discussion of ΔS_f° values would be difficult to interpret.

Table 14. Thermodynamic constants of $\text{SOBr}_2\text{-Cl}^-$ and $\text{SOBr}_2\text{-Br}^-$ in MeCN, dmsO and their Mixtures at 298°K.

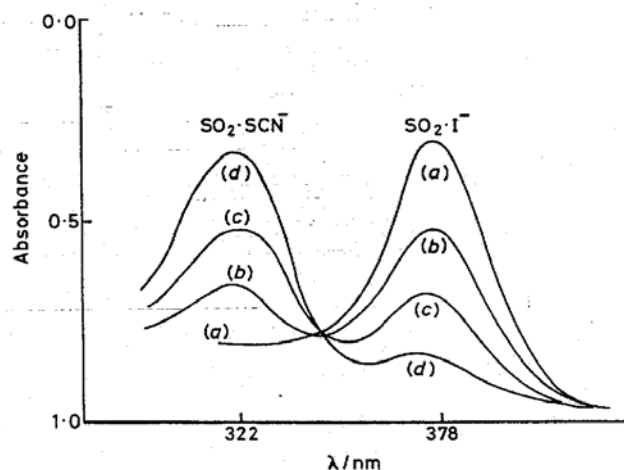
	dmsO	dmsO: MeCN			MeCN
		3:1	1:1	1:3	
$\text{SOBr}_2\text{-Br}^-$					
$K_c \text{ dm}^3 / \text{mol}$	12	19	25	32	203
$-\Delta G_f^\circ \text{ kJ/mol}$	5.86	7.36	8.03	8.66	13.3
$-\Delta H_f^\circ \text{ kJ/mol}$	1.88	4.60	4.60	20.1	19.2
$\Delta S_f^\circ \text{ J/K/mol}$	13.4	9.20	11.3	-38.5	-20.1
$\text{SOBr}_2\text{-Cl}^-$					
$K_c \text{ dm}^3 . \text{mol}^{-1}$	19	36	40	79	100
$-\Delta G_f^\circ \text{ kJ/mol}$	7.36	8.95	9.20	10.9	11.5
$-\Delta H_f^\circ \text{ kJ/mol}$	1.88	10.0	9.62	16.3	10.0
$\Delta S_f^\circ \text{ J/K/mol}$	18.4	-2.93	-1.26	-18.0	5.02

4. Ligand Replacement Reactions

The coordination of different ligands (Cl^- , Br^- , I^- or SCN^-) with the same sulfur acceptors giving varying stability constants suggested that they are differently coordinated and could accordingly be able to replace each other with the same acceptor. Equation (5) shows a general replacement reaction between $\text{SO}_2\text{-I}^-$ and X^- ($\text{X}^- = \text{Cl}, \text{Br}, \text{SCN}$) and Figure 6 illustrates a spectrophotometric scan when SCN^- is added to $\text{SO}_2\text{-I}^-$ in MeCN (Salama *et al.*, 1978).



WEAK COMPLEXES OF SULFUR COMPOUNDS

Figure 6. Replacement of I^- by SCN^- in MeCNa) No SCN^- , b) $[\text{SCN}^-] / [\text{I}^-] = 0.4$, c) $[\text{SCN}^-] / [\text{I}^-] = 1$, d) $[\text{SCN}^-] / [\text{I}^-] = 2$

In Figure 6 the gradual addition of SCN^- solution causes a gradual disappearance of the $\text{SO}_2\text{-I}^-$ peak at 378 nm and appearance of a new peak at 322 nm for the $\text{SO}_2\text{-SCN}^-$ species. Table 15 includes the results of the above replacement reactions.

Table 15. Replacement Reactions in MeCN, dmsO and Water at 298° K*

(a) In MeCN	Reaction	$[\text{Cl}^-] : [\text{I}^-]$
	1) $\text{Cl}^- + \text{SO}_2\text{-I}^-$	0.05(5), 0.10(8), 0.15(12), 0.20(15), 0.30(19), 0.40(23)
	2) $\text{Cl}^- + \text{SOCl}_2\text{-I}^-$	0.05(4), 0.10(7), 0.15(11), 0.20(15), 0.30(18), 0.40(22)
	3) $\text{Cl}^- + \text{SO}_2\text{Cl}_2\text{-I}^-$	0.05(2), 0.10(3.5), 0.15(5.5), 0.20(8), 0.30(10), 0.40(12.5)
		$[\text{Br}^-] : [\text{I}^-]$
	4) $\text{Br}^- + \text{SO}_2\text{-I}^-$	0.05(1.5), 0.10(3), 0.20(5), 0.30(8), 0.40(10)
	5) $\text{Br}^- + \text{SOCl}_2\text{-I}^-$	0.05(2), 0.10(3.6), 0.20(5.8), 0.30(7.7), 0.40(9.3)
	6) $\text{Br}^- + \text{SO}_2\text{Cl}_2\text{-I}^-$	0.05(2.5), 0.10(4), 2.20(6), 0.30(8), 0.40(9.4)
		$[\text{SCN}^-] : [\text{I}^-]$
	7) $[\text{SCN}^-] + \text{SO}_2\text{-I}^-$	0.20(-), 0.50(2), 1.0(3), 2.5(4), 4.0(6)
	8) $[\text{SCN}^-] + \text{SO}_2\text{Cl}_2\text{-I}^-$	0.20(-), 0.50(1.8), 1.0(2.9), 2.5(4), 4.0(5.9)
(b) In dmsO	Reaction	$[\text{Cl}^-] : [\text{I}^-]$
	9) $\text{Cl}^- + \text{SO}_2\text{-I}^-$	0.05(3), 1.0(5), 1.5(7), 2.0(10), 3.0(13), 4.0(17)
	10) $\text{Cl}^- + \text{SOCl}_2\text{-I}^-$	0.50(3), 1.0(4), 1.5(6), 2.0(9), 3.0(12), 4.0(15)
	11) $\text{Cl}^- + \text{SO}_2\text{Cl}_2\text{-I}^-$	2.0(8), 4.0(16)
		$[\text{Br}^-] : [\text{I}^-]$
	12) $\text{Br}^- + \text{SO}_2\text{-I}^-$	0.50(4), 1.0(6), 2.0(11), 4.0(13)
	13) $\text{Br}^- + \text{SOCl}_2\text{-I}^-$	0.50(4), 1.0(5), 1.5(7), 2.0(10)
(c) In water	14) $\text{Cl}^- + \text{SO}_2\text{-I}^-$	4.0(3), 8.0(5), 12.0(7)

*No replacement was observed by $[\text{SCN}^-]$ in dmsO. Percentage replacements of the iodide species are given in parentheses.

In all the above reactions the extent (or magnitude) of replacement depends on the stability constant for the reactant and product complex species. Table 16 includes the K_c data for reactants and products in the

replacement reactions. Another factor which determines the magnitude of the replacement is the Lewis basic character of the ligands and a third factor appears to be related to the donor and acceptor number of the solvent used (Salama *et al.*, 1971; Pearson, 1963; Day *et al.*, 1969).

Table 16. Stability Constants for Reactants and Products in Replacement Reactions at 298°K

X ⁻	Cl ⁻	Br ⁻	I ⁻	SCN ⁻
SO ₂ -X ⁻	372	160	38	65
SOCl ₂ -X ⁻	362	240	150	77
SO ₂ Cl ₂ -X ⁻	10	41	77	298

4.1 Correlation of Stability Constants with Ligand Replacement

4.1.1 The Cl⁻-I⁻ Reaction

The data in Table 15 show that in the presence of two halide ligands, Cl⁻ and I⁻ and acceptors such as SO₂, SOCl₂ and SO₂Cl₂ in MeCN solvent the thermodynamics would be more favorable for SO₂-Cl⁻ and SOCl₂-Cl⁻ than for SO₂-I⁻ and SOCl₂-I⁻. We may add that K_c(SO₂-Cl⁻) is nearly equal to K_c(SOCl₂-Cl⁻) and both are much higher than K_c(SO₂Cl₂-Cl⁻) in the ratio 37: 36: 1. Such a large difference in stability constants makes replacement of I⁻ by Cl⁻ much easier for SO₂-I⁻ and SOCl₂-I⁻ than it is for SO₂Cl₂-I⁻. The data in Table 15 and the plot of Figure 7 illustrate this observation and we note that the percentage replacement in SO₂-I⁻ and SOCl₂-I⁻ fall at a low [Cl⁻]/[I⁻] on the same line and are much higher for SO₂Cl₂-I⁻. The replacement reaction, equation (6), seems anomalous in view of the K_c(SO₂Cl₂-I⁻) / K_c(SO₂Cl₂-Cl⁻) ratio = 8. That this reaction, equation (6), can take place despite the reversed order of stability constants for reactant and product can only be due to the relative abundance of the Cl⁻ ligand which seems to outweigh the difference in stability constants. Table 15 shows that a 20% disappearance of SO₂-I⁻ requires a ligand ratio of 0.35:1 while in the case of SO₂Cl₂-I⁻ ligand ratio [Cl⁻] / [I⁻] = 1 : 1 was necessary for the same percentage replacement. By changing the ligand ratio we are merely increasing the chances of effective collisions leading to a replacement by the more abundant ligand.

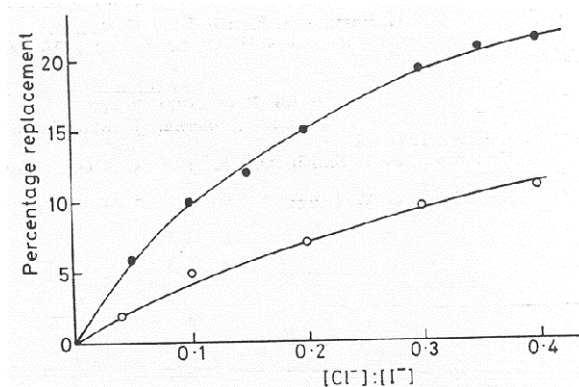


Figure 7. Comparison of Replacement Reactions by added Cl⁻ in MeCN at 298°K (●) SO₂-I⁻ and SOCl₂-I⁻ ; (○) SO₂Cl₂-I⁻

4.1.2 The Br^- - I^- and SCN^- - I^- Reactions

The magnitudes of replacement for the ligands Br^- and SCN^- are not widely different (Table 15). This is not unexpected since the stability constants for $\text{SO}_2\text{-Br}^-$, $\text{SOCl}_2\text{-Br}^-$ and $\text{SO}_2\text{Cl}_2\text{-Br}^-$ are in the ratio 4:6:1 and for $\text{SO}_2\text{-SCN}^-$ and $\text{SOCl}_2\text{-SCN}^-$ and $\text{SO}_2\text{Cl}_2\text{-SCN}^-$ are in the ratio 1: 1.2 : 2.4. Figure 8 shows a comparison of the replacing ability of the SCN^- ligand with that of Cl^- and Br^- ligands. The replacing ability of ligands fall in order $\text{Cl}^- > \text{Br}^- > \text{SCN}^-$, which parallels their Lewis base character as hard, borderline and soft respectively (Pearson, 1963; Day *et al.*, 1969).

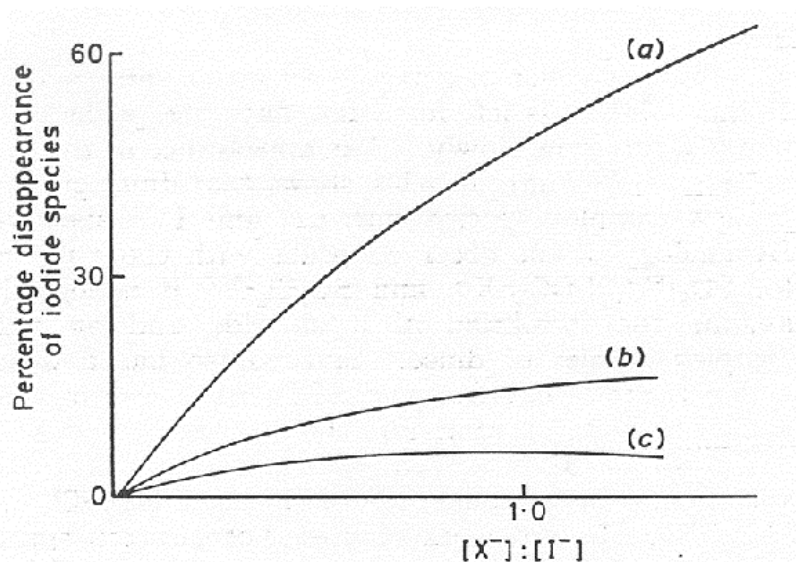


Figure 8. Comparison of Amounts of Replacements of I^- in $\text{SOCl}_2\text{-I}^-$

4.2 The Role of Solvents in Replacement Reactions

Table 15 and Figure 9 show the effect of solvents on the reaction $\text{SO}_2\text{-I}^- + \text{X}^-$ where $\text{X}^- = \text{Cl}^-$. For a ligand ratio $[\text{Cl}^-]/[\text{I}^-] = 4$ the extent of replacement is 70% in MeCN but only 16% in dmsO and less than 2% in water. Clearly a change of solvent greatly affects the degree of replacement.

In dmsO two factors are operative: a) dmsO may solvate the Cl^- ligand and b) dmsO may act as a potential acceptor at its S atom and compete with SO_2 in solution. The conclusion that dmsO acts as a potential acceptor was reached using the observation of the spectrum of a solution containing Cl^- and I^- ligands. This solution shows slow growth of two peaks at 292 nm and 365 nm and the rate of peaks growth depends on the ligand concentration and a rate constant was found to be $2 \times 10^{-2} \text{ min}^{-1}$ at 298°K.

The replacement reaction $\text{SO}_2\text{-I}^- + \text{Cl}^- = \text{SO}_2\text{-Cl}^- + \text{I}^-$ in dmsO is ionic with a rate constant of 10^{10} sec^{-1} and therefore the addition of Cl^- to $\text{SO}_2\text{-I}^-$ in dmsO is accompanied by the disappearance of the peak at 378nm ($\text{SO}_2\text{-I}^-$) and the emergence of the new peak at 292 nm ($\text{SO}_2\text{-Cl}^-$). If this solution is left for some time the peaks at 292nm and 365nm will slowly appear for the complex species of dmsO with Cl^- and I^- ligands respectively. The sulfur atom in dmsO will be the acceptor center with the following structures: $\text{OMe}_2\text{S-Cl}^-$ and $\text{OMe}_2\text{S-I}^-$ respectively.

Recent work on photoelectron spectroscopy of sulfur compounds favors this view (Guest *et al.*, 1972; Buncel *et al.*, 1975). Water appears to be a more drastic solvating agent towards the Cl^- ligand which results in a low degree of replacement with high ligand ratio of $[\text{Cl}^-]/[\text{I}^-] = 12$.

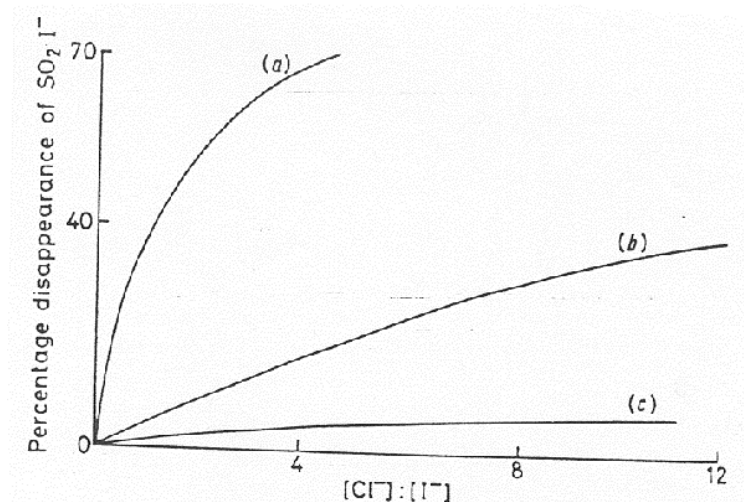


Figure 9. Effect of Solvents on the Reaction $\text{SO}_2\text{-I}^- + \text{Cl}^- \rightarrow \text{SO}_2\text{-Cl}^- + \text{I}^-$ in a) MeCN, b) dmsO and c) water at 298°K.

4.3 Replacement Reactions in Mixed Solvents

Table 17 includes the replacement reaction data for the $\text{SO}_2\text{-I}^- + \text{Cl}^-$ reaction in MeCN-dmsO mixed solvent. For all runs the ligand ratio was $[\text{Cl}^-]/[\text{I}^-] = 4$. The replacement percentage of iodide is given in parentheses. As the percentage of dmsO in the solvent increases the ability of Cl^- to replace I^- diminishes. Here it is possible that the solvating power of dmsO towards Cl^- makes it sterically difficult to replace the I^- in $\text{SO}_2\text{-I}^-$.

Table 17. Replacement Reaction of $\text{SO}_2\text{-I}^- + \text{Cl}^-$ in MeCN-dmsO Mixture at 298°K

dmsO%	0.00(70%)	25(53%)	50(32%)	75(20%)	100(17%)
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5. Structure of $\text{SO}_2\text{-X}^-$

The structures of $\text{SO}_2\text{-X}^-$ ($\text{X}^- = \text{F}, \text{Cl}, \text{Br} \text{ \& } \text{I}$) (Latajka *et al.*, 1995) were investigated using ab initio method at the electron correlation level with effective core potential double zeta valence basis set with polarization functions. It has been found that the minimum on the potential energy surface corresponds to the C_s structure of the complexes whereas the planar C_{2v} structure is the transition state for the inversion process. The stability of $\text{SO}_2\text{-X}^-$ complexes fall in the order $\text{SO}_2\text{-F}^- > \text{SO}_2\text{-Cl}^- > \text{SO}_2\text{-Br}^- > \text{SO}_2\text{-I}^-$.

Careful studies of the potential energy surfaces of the complexes clearly indicates that only one structure corresponds to the minimum. The X^- is in close contact with the S atom having a positive total charge. The intermolecular distance $R(\text{S} \cdots \text{X})$ increases in this series with the increase of the atomic number of X^- . The shortest intermolecular distance is noted for $\text{SO}_2\text{-F}^-$ complex. Replacement of F^- by Cl^- increases the distance by 2.61Å and successive replacements by Br^- and I^- ligands cause an increase in $R(\text{S} \cdots \text{O})$ value by about 0.3Å.

The complex formation slightly distorts the SO_2 subunit. The SO bond is stretched while the OSO bond angle slightly decreases in comparison with the values for the isolated SO_2 subunit. Perturbation of the geometrical structure of the SO_2 subunit is essentially pronounced with the F^- ligands.

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SO₂-X⁻ complexes are not planar and have C_s symmetry. The nonplanarity of the complex is denoted by α which measures the angle between the C₂ axis of the SO₂ subunit and the S...X axis. In the series of SO₂-X⁻ complexes the angle decreases from 71° for the SO₂-F⁻ complex to 61° for the SO₂-I⁻ complex which makes this complex less pyramidal.

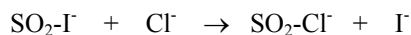
Since in this series the intermolecular distance has increased from 1.93 Å for the SO₂-F⁻ complex to 3.25 Å for the SO₂-I⁻ complex, the dipole-charge interaction becomes most important and in consequence the SO₂-I⁻ is less pyramidal.

In conclusion we may report that SO₂-F⁻ has a rigid pyramidal structure while SO₂-I⁻ is the least pyramidal in the above series of SO₂-X⁻ complex species.

6. Conclusion

The formation of the complex species SO₂-X⁻, SOCl₂-X⁻, SO₂Cl₂-X⁻ and SOBr₂-X⁻ where (X⁻ = Cl⁻, Br⁻, I⁻ and SCN⁻) was reported during the last thirty years.

The above complexes are weak of charge transfer nature and can not be isolated from solution but can be detected by spectrophotometry. Their enthalpies of formation ΔH_f^o vary between -22.5 and -6.0 kJ/mol. The stabilities of the above complexes depend on the solvent used, the acceptor properties of the S_{compound}, the basic nature of the halide ligands and the temperature of the system. Ligand replacements of the following type:



showed that the reaction is quite fast 10¹⁰ s⁻¹ (detectable by Laser Technique) and is universal throughout all the complex species studied.

The geometry of SO₂-X⁻ species suggest a pyramidal type with acute angle for X⁻ = Cl⁻ and less for X⁻ = I⁻.

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