

Spectroscopic Studies of Charge Transfer Complexes

VIII. Sulphoxides and Iodine Cyanide

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The complexes between five sulphoxides and iodine cyanide have been studied by spectroscopic methods. Charge transfer absorption bands have been observed in the ultraviolet region with maxima at 220–240 m μ . Considerable changes occurred in the infrared spectra of the sulphoxides when iodine cyanide was added. Formation constants (K_c) for the 1:1 complexes in carbon disulphide were obtained from intensity changes of the S–O stretching bands. The basicities of the sulphoxides were mostly influenced by inductive effects. Iodine and iodine monochloride were found to perturb the infrared sulphoxide bands even more than iodine cyanide. For dimethyl sulphoxide these spectral changes were closely related to those observed on complex formation to metal halides, on hydrogen bonding and on sulphoxide self association.

During the recent years, several investigators have studied the ligand properties of the sulphoxides to metal halides^{1–3} and boron halides^{4,5} by spectroscopic methods. These studies revealed that the sulphoxides generally coordinate through the oxygen atom, but coordination through sulphur has been reported^{1,4} for some platinum and palladium complexes. Moreover, the sulphoxides have been found to form strong hydrogen bonds^{6,7} with alcohols and phenols and to associate with many solvents.^{8–10} The simplest sulphoxide, dimethyl sulphoxide, is highly associated in the liquid state¹¹ as well as in mixtures¹² with benzene and carbon tetrachloride.

The interesting coordinating properties of the sulphoxides and the use of dimethyl sulphoxide as a non-aqueous solvent have initiated a study of the donor properties of the sulphoxides towards halogens in this laboratory. In the present paper the complex formation in solution between 5 different sulphoxides and iodine cyanide is reported. Furthermore, infrared spectral data for the sulphoxide-iodine and sulphoxide-iodine monochloride systems have been included in the present study for comparison. In forthcoming papers the sulphoxide-iodine complexes will be reported as obtained from visible and ultraviolet data.

EXPERIMENTAL

Chemicals. Dimethyl sulphoxide from Fluka AG was dried with barium oxide, distilled *in vacuo* and purified by fractional crystallization. Diethyl sulphoxide and methyl phenyl sulphoxide were prepared by oxidizing^{13,14} the corresponding sulphides with dinitrogen tetroxide at -70°C . They were purified by distillation *in vacuo* and repeated fractional crystallization. Diphenyl sulphoxide was prepared by oxidizing¹⁵ the sulphide with hydrogen peroxide in acetic acid and was purified by fractional crystallization from ligroine. Dibenzyl sulphoxide from Fluka was treated with active carbon and purified by fractional crystallization from benzene. The melting points and the infrared spectra agreed with the data given in the literature. Because of the strong hygroscopic properties of the sulphoxides, precautions were taken not to expose the samples to the atmospheric humidity. Iodine cyanide was prepared according to Bak and Hillebert¹⁶ and purified by recrystallization from chloroform. Iodine and iodine monochloride were purified as described earlier,¹⁷ while carbon disulphide and heptane, *Uvasole* from Merck, were used as solvents without further purification.

The spectra were recorded immediately after the solutions were prepared. In addition, the spectra were re-run after 1 h and 24 h. It was found that negligible changes in the sulphoxide-iodine cyanide systems occurred with time. However, in the sulphoxide-iodine solutions marked time dependent changes were observed for higher iodine concentrations. With iodine monochloride these changes were much faster and they occurred so rapidly with iodine monobromide that the complex formation could not be studied.

Instrumental. The infrared spectra were recorded with a Perkin-Elmer model 21 spectrophotometer equipped with sodium chloride optics. The sealed cell had a thickness of 0.053 cm, the temperature was measured to $27 \pm 1^{\circ}\text{C}$, and a variable thickness cell was used for solvent compensation. A Beckman DK-1 recording spectrophotometer was used in the ultraviolet region. Quartz cells of thickness 1.00 cm were used and the temperature kept at $20 \pm 0.2^{\circ}\text{C}$.

RESULTS

Infrared spectra. When iodine cyanide, iodine or iodine monochloride was added to a solution of a sulphoxide in carbon tetrachloride or carbon disulphide, some distinct spectral changes occurred. These changes included band displacements as well as marked intensity variations. Moreover, for each of the sulphoxides studied, the most important spectral changes occurred around 1050 cm^{-1} . While complete vibrational assignments have been reported only for dimethyl sulphoxide,^{18,19} it is well known that the strong sulphoxide bands in this region, are mainly connected with the S—O stretching mode.²⁰ When iodine cyanide, iodine or iodine monochloride was added, the free S—O stretching

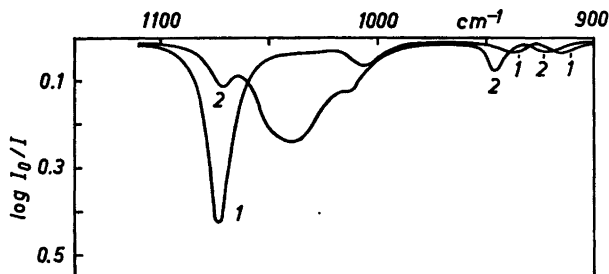


Fig. 1. Infrared spectrum of dimethyl sulphoxide-iodine cyanide in carbon disulphide at a cell thickness of 0.053 cm. (1) Sulphoxide $1.954 \times 10^{-3}\text{ M}$. (2) Sulphoxide $1.954 \times 10^{-3}\text{ M}$ and ICN $5.264 \times 10^{-2}\text{ M}$.

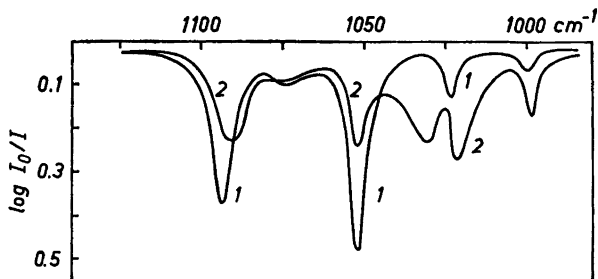


Fig. 2. Infrared spectrum of diphenyl sulphoxide-iodine cyanide in carbon disulphide at a cell thickness of 0.053 cm. (1) Sulphoxide 2.008×10^{-2} M. (2) Sulphoxide 2.008×10^{-3} M and ICN 5.211×10^{-2} M.

band was reduced in intensity and a new band appeared, displaced towards lower frequencies. It is assigned as the S—O stretching band of the complex. The infrared spectra of dimethyl sulphoxide and diphenyl sulphoxide and the mixed sulphoxide-iodine cyanide solutions are given in Figs. 1 and 2, respectively. Furthermore, the infrared bands perturbed on complex formation are listed in Table 1 for dimethyl sulphoxide and diethyl sulphoxide and in Table 2 for dibenzyl sulphoxide, methyl phenyl sulphoxide and diphenyl sulphoxide. Only the spectral data observed between 1400 and 650 cm^{-1} in carbon disul-

Table 1. Infrared bands ^{a,b} of dimethyl sulphoxide and diethyl sulphoxide perturbed on complex formation.

Donor	Free donor	Acceptor			Species	Approximate mode	
		ICN	I ₂	ICl			
Dimethyl ^c sulphoxide	1318 w ^d	1318 vvw	1318 m	1318 m	A''	sym C—H def	
	1300 s	1300 s	1300 vvw	1300 vvw	A'		sym C—H def
	1072 vs	1036 vs	1021 vs	1011 vs	A'		S—O stretch
	1051 vw	1051 w		1051 w			
	1035 vw		1032 m	1032 m	A''	methyl rock	
	1007 s	1014 s	1013 s	1013 s	A'	methyl rock	
	943 m	948 s	952 s	953 s	A''	methyl rock	
	918 s	925 s	930 m	939 m	A'	methyl rock	
	683 s	694 m	699 m	700 m	A''	antis. C—S stretch	
Diethyl sulphoxide	1069 vs	1018 vs	1004 vs	995 vs		S—O stretch	
	1061 w	1054 s	1058 w	1058 w			
	1045 w	1045 vw	1045 vw	1045 vw			
	1038 vw	1038 s	1035 vw	1035 vw			
	1024 m	1024 m	1024 vw	1024 vw			
	972 w	969 s	968 m	959 s			

^a Only the region 1400—650 cm^{-1} included.

^b Solvent: carbon disulphide.

^c Assignments for dimethyl sulphoxide from Ref.¹⁹

^d The intensities are abbreviated as follows: s = strong, m = medium, w = weak, v = very.

Table 2. Infrared bands ^{a,b} of dibenzyl sulphoxide, methyl phenyl sulphoxide and diphenyl sulphoxide perturbed on complex formation.

Donor	Free donor	Acceptor		
		ICN	I ₂	ICl
Dibenzyl sulphoxide	1074 vs ^c	1074 s	1074 w	1074 w
	1057 vs	1023 vs	1010 vs	981 vs
	1032 m	1032 s	1030 w	1030 w
	1004 w	1004 m	1003 s	1003 s
Methyl phenyl sulphoxide	1093 vs	1092 vs	1092 s	1091 s
	1074 m	1072 m	1072 w	1073 vw
	1058 vs	1033 vs	1019 vs	992 vs
	1025 s	1024 vs	1028 s	1026 vw
	1000 m	999 m	999 s	1003 s
	950 s	953 s	954 vs	957 vs
	929 m	932 m	933 m	936 m
Diphenyl sulphoxide	1094 vs	1092 s	1089 s	1087 s
	1075 w	1076 w	1076 vw	1077 vw
	1053 vs	1030 vs	1016 vs	984 vs
	1023 s	1021 vs	1027 s	1028 m
	999 m	996 s	996 vs	1003 s
	673 m	672 m	670 m	664 m

^a Only the region 1400–650 cm⁻¹ included.

^b Solvent: carbon disulphide.

^c For abbreviations see Table 1.

phide are included in these tables. However, no distinct spectral changes were observed in the region 4000–1600 cm⁻¹. Because of the substitution reactions taking place in the iodine monochloride and to a lesser extent in the iodine solutions, these data are somewhat less reliable than those obtained for the iodine cyanide systems.

The variations in intensities of the free sulphoxide S—O stretching bands were employed to determine the formation constants of the molecular complexes. Actual measurements of the integrated areas of the free sulphoxide peaks were carried out at different iodine cyanide concentrations. The formation constants were calculated according to the method described earlier,²¹ assuming 1:1 complexes. It is a prerequisite that the areas of the free S—O stretching bands are proportional to the free sulphoxide concentrations. This was independently found to be the case for sulphoxide concentrations smaller than approximately 0.1 M. For higher dimethyl sulphoxide concentrations, however, significant deviations occurred, probably caused by association. This is to be discussed in some detail for dimethyl sulphoxide in the following paper.²² In the present measurements the concentrations were kept around 0.04 M for diethyl sulphoxide and around 0.02 M for the other sulphoxides. For each sulphoxide the spectra were recorded at five iodine cyanide concentrations varying from 0.01 to 0.08 M and good agreement was found between the calculated formation constants. The assumption of 1:1 stoichiometry is

Table 3. Formation constants and spectral data for the S—O stretching bands in the free sulphoxides and in the complexes with iodine cyanide.^a

Donor sulphoxide	Free donor			Complexes			$\Delta\nu$ cm ⁻¹	K_f^b lM ⁻¹	B_c/B_s^c
	ν cm ⁻¹	$B_s \times 10^{-4}$ lM ⁻¹ cm ⁻²	$\nu_{1/2}$ cm ⁻¹	ν cm ⁻¹	$B_c \times 10^{-4}$ lM ⁻¹ cm ⁻²	$\nu_{1/2}$ cm ⁻¹			
Dimethyl	1072	1.6	13	1036	2.1	30	36	86	1.3
Diethyl	1069	1.0	18	1018	1.4	20	51	157	1.4
Dibenzyl	1057	1.0	12	1023	1.8	21	34	61	1.8
Methyl phenyl	1058	0.7	7	1033	1.7	17	25	35	2.4
Diphenyl	1053	0.8	6	1030	1.4	15	23	32	1.8

^a Solvent: carbon disulphide.

^b Temperature $27 \pm 1^\circ\text{C}$.

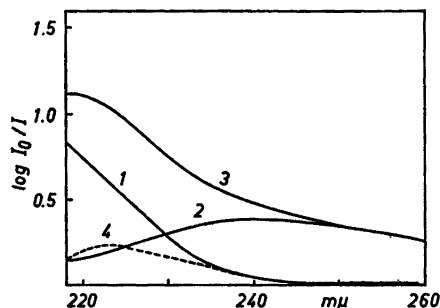
^c B_s and B_c denote the apparent molar integrated absorption intensities of the free sulphoxide and the complex, respectively.

therefore supported for these complexes, at least for donor and acceptor concentrations of the same order of magnitude.

The average formation constants calculated for the iodine cyanide complexes are listed in Table 3. The experimental uncertainties were somewhat larger for the aromatic compounds because of the difficult wing corrections of the free S—O band made necessary by the overlapping neighbouring aromatic bands. When similar calculations were made for the iodine complexes obtained under the same conditions, formation constants equal to 11.2, 8.0, and 3.2 l/mole were found for dimethyl sulphoxide, dibenzyl sulphoxide and diphenyl sulphoxide, respectively. Furthermore, semiquantitative results for the iodine monochloride complexes indicated formation constants of the order of magnitude 200 and 60 l/mole for dimethyl sulphoxide and diphenyl sulphoxide, respectively. However, the iodine and iodine monochloride complexes could not be accurately determined from the infrared data because of substitution reactions. For measurements in the visible and ultraviolet regions very small halogen concentrations were employed and under these conditions accurate formation constants can be determined.²²

Ultraviolet spectra. Because the sulphoxide-iodine cyanide complexes are supposedly of the charge transfer type, they are expected to have absorption bands in the ultraviolet region. Haszeldine²³ has reported ultraviolet absorption bands below $240 \text{ m}\mu$ for iodine cyanide complexes with various n and π donors. In the present study a solution of iodine cyanide in heptane was found to have a low intensity band with maximum at $241 \text{ m}\mu$. Furthermore, the aliphatic sulphoxides have very intense absorption near $210 \text{ m}\mu$ while the aromatic compounds also absorb strongly at longer wave lengths. Fig. 3 shows the absorption curves for the dimethyl sulphoxide-iodine cyanide system. In the region around $250 \text{ m}\mu$ the mixed solution absorbed less than the superposition of the component absorption. At lower wave lengths, however, the absorption exceeded that of the components, the difference $E = E(\text{DMSO} + \text{ICN}) - E(\text{DMSO}) - E(\text{ICN})$ where E denotes the absorbance, reached a maximum around $223 \text{ m}\mu$. The absorption maxima obtained for

Fig. 3. Ultraviolet absorption spectrum of dimethyl sulphoxide-iodine cyanide in heptane at 20°C and a cell thickness 1 cm. (1) Sulphoxide 3×10^{-4} M. (2) ICN 2.36×10^{-3} M. (3) Sulphoxide 3×10^{-4} M and ICN 2.36×10^{-3} M. (4) Constructed charge transfer band.



the sulphoxide-iodine cyanide complexes are listed in Table 4. Because of the low solubilities and the high absorptions of the components in this region, considerable difficulties were encountered when observing the charge transfer maxima. Therefore, no determination of the molecular formation constants could be obtained from these data, neither could the molecular extinction coefficients ϵ be determined.

DISCUSSION

The ultraviolet spectroscopic data revealed that the sulphoxide-iodine cyanide complexes are of the charge transfer type. Moreover, the ultraviolet absorption bands are situated below 240 $m\mu$ as expected.²³ It appears from Table 4 that there is a monotonic relationship between the wave lengths of the charge transfer maxima of the sulphoxide-iodine cyanide and the sulphoxide-iodine systems. This order is probably the one of decreasing ionization potentials of the donors, but no ionization potentials have been reported for these compounds.

The data listed in Tables 1 and 2 show that generally the same spectral changes took place when iodine cyanide, iodine or iodine monochloride was added to a sulphoxide. In most cases, the same infrared bands were perturbed when the sulphoxide formed complexes with any of the three acceptors. Moreover, when the five different sulphoxides were complexed to iodine cyanide,

Table 4. Ultraviolet absorption band of the sulphoxide-iodine cyanide complexes.^a

Donor	Conc. Donor M	Conc. ICN M	ν_{\max} ICN $m\mu$	$\nu_{\max}^{b,c}$ I_2 $m\mu$
Dimethyl sulphoxide	3×10^{-4}	2.4×10^{-3}	223	272
Diethyl sulphoxide	3	2.4	225	283
Dibenzyl sulphoxide	2	2.3	229	285
Methyl phenyl sulphoxide	1.5	2.4	234	285
Diphenyl sulphoxide	0.8	2.1	235	290

^a Solvent: heptane.

^b The sulphoxide-iodine complexes were dissolved in carbon tetrachloride.

^c Data to be published shortly.

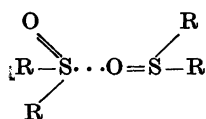
iodine and iodine monochloride, corresponding infrared bands were perturbed. The variations in the S—O stretching frequencies as listed in Table 3 are particularly striking. A lowering of the A=B double bond stretching frequency when B donates a lone pair electron to a halogen X—X₁ has been observed in halogen complexes to C=O groups^{21,24,26} and P=O groups.²⁷⁻²⁹ In the nitriles, however, a raise in the C≡N stretching frequency was observed³⁰ on complex formation to iodine monochloride. When two oscillators A=B and X—X are coupled, the A=B stretching frequency should be raised. A lowering must therefore be interpreted as a decrease in the A=B bond order that more than outweighs the kinematic effect.

While some controversy³¹ has existed as to the nature of the S—O bond in sulphoxides and sulphones, theoretical work,³² dipole moments,³³ vibrational spectra¹⁹ and electron diffraction data³⁴ strongly suggest that the sulphur oxygen bond is a double link with some coordinate bond character. The S—O bond probably results from $p\pi \rightarrow d\pi$ bonding from O to S superposed on the S—O σ -bond. Donation of a lone pair electron from the oxygen to the iodine should decrease the $p\pi \rightarrow d\pi$ bonding and lower the S—O bond order, resulting in a decreased S—O stretching frequency. On the other hand, donation of a lone pair electron from sulphur to iodine should increase the $p\pi \rightarrow d\pi$ bonding and the S—O stretching frequency should be raised. Recent structure determinations, using X-ray crystallographic methods by Eriks and by Hansson and co-workers have verified the earlier spectroscopic results¹⁻⁵ that the sulphoxides form complexes with some metal halides or boron halides over the oxygen atom. Thus, in $\text{BF}_3(\text{CH}_3)_2\text{SO}$, $\text{SbCl}_5(\text{C}_6\text{H}_5)_2\text{SO}$ and $\text{SnCl}_4 \cdot 2(\text{CH}_3)_2\text{SO}$ the S—O distances are slightly longer than in the pure sulphoxides.³⁵ The present data, therefore, leave no doubt that the five sulphoxides studied form complexes in solution with iodine cyanide, iodine and iodine monochloride over the oxygen atom. Furthermore, the amount of X-ray crystallographic work on (n,σ) complexes by Hassel and co-workers³⁶ strongly suggests that in iodine cyanide as well as in iodine monochloride, the iodine atom is linked to the donor.

While the enthalpy changes connected with the complex formation to iodine cyanide have not been measured, the formation constants listed in Table 3 probably express the relative basicities of the sulphoxides. It seems as if the inductive effects are largely responsible for the donor properties. Thus, the aromatic sulphoxides are the weaker donors because the electronegative phenyl groups make the lone pair electrons at the oxygen less available for donation. As expected, diethyl sulphoxide is a stronger donor than dimethyl sulphoxide. The data support the conclusions drawn by different investigators that there is very little conjugation in the aromatic sulphoxides.^{33,37,38} Conjugation would have increased the donor strength of the aromatic sulphoxides relative to the aliphatic ones as observed *e.g.* in the aldehydes.²¹

The data in Tables 1 and 2 disclose that the shifts and intensity changes increase in the order $\text{ICN} < \text{I}_2 < \text{ICl}$, indicating enhanced donor-acceptor interaction in this order. Measurements might thus reveal that the change in enthalpy ($-\Delta H$) is smaller for the iodine cyanide than the iodine complexes in spite of the higher value for K_c and $-\Delta G$ in the former, thus pointing to a very different entropy term in the two complexes.

It seems significant that the spectral differences between dimethyl sulphoxide when dissolved in chloroform⁶ and carbon tetrachloride closely parallel those listed in Table 1 regarding shifts and intensity changes. The same changes are reported in the 1050 cm^{-1} region when phenol is added to dimethyl sulphoxide dissolved in carbon disulphide.⁹ Finally, when the concentration of dimethyl sulphoxide in carbon disulphide is increased to the pure liquid, a number of frequency shifts and intensity variations occur in the 1200–650 cm^{-1} region closely related to those reported in Table 1. Thus, complex formation to the halogens, iodine cyanide, several metal halides, hydrogen bonding to chloroform and phenol, or self association, which according to Lindberg¹² involves



intermolecular bonds, result in very similar perturbations in the infrared spectrum of dimethyl sulphoxide. The related spectral perturbations suggest a similarity between all these complexes brought about by the oxygen donating a lone pair electron to the acceptor.

The normal coordinate work by Horrocks and Cotton¹⁹ shows that there is a considerable mixing of the symmetry coordinates of the same species in dimethyl sulphoxide. A considerable part of the potential energy of the ν_7 (the S—O stretch) is derived from the rocking motions of species A' . On the other hand the rocking modes (ν_8 and ν_9) have a considerable contribution from the S—O stretching. It is therefore not surprising that the 1007 and 918 cm^{-1} rocking bands are perturbed on complex formation. In spite of the coupling of these modes the 1072 cm^{-1} band in dimethyl sulphoxide as well as the corresponding S—O stretching bands in the other sulphoxides vanish when all the donor molecules are complexed in the presence of a very high acceptor concentration. Moreover, the formation constants calculated for the iodine complexes agree satisfactorily with those obtained from the visible and ultraviolet data.

The strong band at the high frequency side of the S—O stretching band situated at 1074, 1093, and 1094 cm^{-1} for dibenzyl, methyl phenyl and diphenyl sulphoxide, respectively, are also reduced in intensity on complex formation. These bands are probably mainly connected with aromatic skeleton vibrations,⁸ borrowing intensity from the S—O stretching. As the latter is displaced on complex formation, the former should decrease in intensity with a slight frequency shift as observed (Table 2).

It seems as if many of the enhancements and shifts of the sulphoxide bands in the region 1050–950 cm^{-1} can be explained in terms of changes in the Fermi resonance from the S—O stretching band when the latter is displaced on complex formation. The 1023 and the 999 cm^{-1} bands of diphenyl sulphoxide, tentatively assigned⁵ as C—H deformation and ring deformation modes can be used as examples. In the iodine cyanide complex the S—O stretching peak is situated at 1030 cm^{-1} and both the 1023 and 999 cm^{-1} are displaced slightly towards longer wave lengths, the high frequency band being more enhanced

than the other. The S—O stretching frequency is situated at 1016 cm^{-1} in the iodine complex. Thus, the 1023 cm^{-1} band is shifted to shorter, the 999 cm^{-1} band to longer wave length, both being enhanced. Finally, in the iodine monochloride complex with the S—O stretching band situated at 984 cm^{-1} both the 1023 and the 999 cm^{-1} bands are shifted to shorter wave lengths, the neighbouring 999 cm^{-1} band being strongly enhanced.

This research has been supported by *Norges Almenvitenskapelige Forskningsråd*.

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Received September 30, 1963.

Acta Chem. Scand. **18** (1964) No. 1