

Spectroscopic Studies of Charge Transfer Complexes

X. Methyl Phenyl Sulphoxide and Diphenyl Sulphoxide with Iodine

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The charge transfer complexes of methyl phenyl sulphoxide and diphenyl sulphoxide with iodine have been studied in the visible and ultraviolet regions. In dilute carbon tetrachloride solutions these complexes are of the 1:1 type. The thermodynamic functions have been determined from the absorption data in the visible region. The sulphoxide-iodine charge transfer bands were superposed on the strong sulphoxide bands.

Compared with dimethyl sulphoxide the present sulphoxides were weaker donors as inferred from the functions ΔG or ΔH . This was expected from the very low conjugation between the S=O bond and the phenyl rings.

The complex between dimethyl sulphoxide (DMSO) and iodine has been studied by spectroscopic methods¹ in the visible and ultraviolet regions. These data revealed that the complex was of the charge transfer type with a strong ultraviolet absorption band at 272 m μ and a blue shifted visible iodine band at 446 m μ when dissolved in carbon tetrachloride. Moreover, from investigations by infrared spectroscopic technique² it was concluded that a number of sulphoxides formed complexes to iodine as well as to iodine cyanide and iodine monochloride over the oxygen atom. Recently Drago *et al.*³ have studied the dimethyl sulphoxide and tetramethylene sulphoxide complexes with iodine in the visible region and reported the thermodynamic functions. In order to obtain more information about these complexes, methyl phenyl sulphoxide (MPSO) and diphenyl sulphoxide (DPSO) have been investigated with iodine in the present study. The corresponding data for diethyl sulphoxide and some cyclic sulphoxides will be reported shortly.⁴

EXPERIMENTAL

The samples of MPSO and DPSO were the same as those used in the earlier study.² Because of the hygroscopic properties of the sulphoxides, great precautions were taken to exclude water vapour during the handling and storage of these samples. Reagent grade iodine from Merck was used. It was found that carbon tetrachloride, Merck, *Uvasole* for ultraviolet spectroscopy, could be used as a solvent without further purifications. Stock

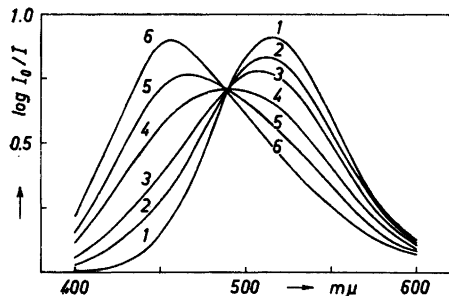


Fig. 1. Visible absorption spectra of MPSO and iodine (9.423×10^{-4} M) in carbon tetrachloride at 20°C for 1 cm cell. The concentrations (M) of MPSO are: (1) zero; (2) 0.01725; (3) 0.03457; (4) 0.08451; (5) 0.1409, and (6) 0.2535.

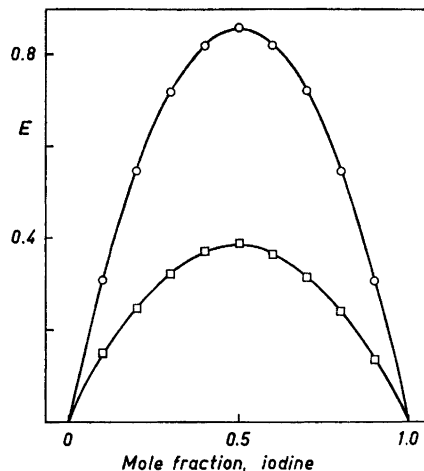


Fig. 2. Method of continuous variation of the MPSO-iodine (O 285 mμ) and the DPSO-iodine (□ 300 mμ) system in carbon tetrachloride at 20°C. The absorbance of the solution minus the calculated component absorbance was plotted versus the mole fraction of iodine. The total concentration of sulphoxide plus iodine was 0.00812 M.

solutions of iodine and the sulphoxides were prepared by weighing into 100 ml volumetric flasks. The mixed solutions were prepared by pipetting into 25 ml volumetric flasks.

The ultraviolet and visible spectra were recorded with a Beckman DK-1 recording spectrophotometer equipped with a thermostated cell holder. The data at 20°C were also obtained independently on a Zeiss P.M.Q. II spectrophotometer. Matched pairs of ground glass stoppered silica cells of path length 1.000 cm were used. The mixed solutions were recorded immediately and negligible spectral changes occurred after 20 minutes and after 24 h. As reported previously² the sulphoxides react irreversibly with iodine at high halogen concentrations, however, MPSO and DPSO were less reactive than DMSO.

RESULTS

Methyl phenyl sulphoxide. When MPSO was added to a solution of iodine in carbon tetrachloride the visible absorption band at 517 mμ was displaced to 454 mμ. As shown in Fig. 1 the blue shifted peak overlapped partly the free iodine band and an isosbestic point was observed at 489 mμ. For MPSO concentrations exceeding approximately 0.2 M the absorption curves passed under the isosbestic point as observed for DMSO.¹ The method of continuous variation⁵ was applied to this system. The components absorption was subtracted from the total absorption in the ultraviolet region and plotted against the mole fraction of iodine. It appears from Fig. 2 that a distinct maximum was obtained for $[\text{MPSO}] = [\text{I}_2]$, characteristic of a 1:1 complex.

Different series of MPSO-iodine solutions with the iodine concentrations kept constant and the MPSO concentration varying, were recorded in the visible region at various temperatures. The formation constants and the extinc-

Table 1. Formation constants, extinction coefficients and thermodynamic functions for the MPSO— I_2 complex in CCl_4 , obtained from the blue shifted iodine band.^a

Temp. °C	430 m μ		440 m μ		450 m μ		460 m μ	
	K_c M ⁻¹	ϵ M ⁻¹ cm ⁻¹	K_c M ⁻¹	ϵ M ⁻¹ cm ⁻¹	K_c M ⁻¹	ϵ M ⁻¹ cm ⁻¹	K_c M ⁻¹	ϵ M ⁻¹ cm ⁻¹
13.5	7.1	1120	7.0	1290	7.1	1400	7.2	1360
20	6.4	1100	6.4	1270	6.4	1380	6.8	1350
30	5.3	1060	5.3	1240	5.4	1370	5.4	1350
— ΔH^b	3.27		3.10		3.17		3.17	
— ΔG_{25}^c	1.03		1.02		1.04		1.05	
— ΔS^d	7.5		7.0		7.1		7.1	

Mean values — $\Delta H^b = 3.2 \pm 0.4$; — $\Delta G_{25}^c = 1.03 \pm 0.05$; — $\Delta S^d = 7.2 \pm 0.5$.

^a The values were calculated from absorption data of 11 different MPSO— I_2 solutions. $I_2 = 1.123 \times 10^{-3}$ M, MPSO varied from 0.018116 M to 0.1998 M using 1 cm cells.

^b ΔH in units of kcal/mole.

^c ΔG_{25} is in units of kcal/mole

^d ΔS is in units of e.u.

tion coefficients of the molecular complexes were calculated independently from the Scott⁶ and the Nash⁷ representations at various wave lengths. The experimental points were fitted with straight lines using the least squares method. The average values calculated from two independent sets of curves are listed in Table 1, the values at 430 and 440 m μ obtained by the Scott and those at 450 and 460 m μ obtained by the Nash representations. From these data the thermodynamic functions ΔH , ΔG_{25} and ΔS were calculated by standard procedures.

In the ultraviolet region MPSO shows a single strong absorption band at 253 m μ when dissolved in cyclohexane,⁸ while in ethanol two bands appear,⁹ one essentially unchanged, the other situated at 238 m μ . It has therefore been concluded¹⁰ that the band in cyclohexane is a superposition of the $n \rightarrow \pi$ band and the 1L_b band of benzene. The mixed solutions of MPSO and iodine in carbon tetrachloride show a strong ultraviolet absorption band superposed on the MPSO band and the low intensity iodine absorption¹¹ at 280 m μ . With an equal concentration of MPSO and iodine in the reference beam the strong sulphoxide and the iodine absorptions were subtracted and the complex charge transfer band appeared with a peak at 285 m μ . The low wave length side of this band could not be observed because of the very strong sulphoxide absorption. However, the empirical relationship by Briegleb¹² may be valid: $\Delta\bar{\nu}_{\frac{1}{2}}/2(\bar{\nu}_{\max} - \bar{\nu}_L) = 1.2$, $\Delta\bar{\nu}_{\frac{1}{2}}$ is the half intensity width, $\bar{\nu}_{\max}$ is the peak frequency and $\bar{\nu}_L$ the long wave length frequency for which $\epsilon = \frac{1}{2} \epsilon_{\max}$, $\bar{\nu}_{\max} - \bar{\nu}_L$ is approximately 2.5×10^3 cm⁻¹ giving 6.0×10^3 cm⁻¹ for the half intensity width $\Delta\bar{\nu}_{\frac{1}{2}}$.

A series of MPSO-iodine solutions was recorded at 20°C in the ultraviolet region, the iodine concentration kept at 3.769×10^{-4} M and the MPSO concentration varying from 0.008643 M to 0.1459 M. Only the long wave length tail below 305 m μ could be used in the quantitative calculations because of the strong MPSO absorption at the CT-maximum (ϵ_{MPSO} (285 m μ) =

150 M⁻¹ cm⁻¹). The formation constants obtained at 20°C by the Scott representation gave the following values: 6.0, 5.7, 5.4, and 5.1 M⁻¹ obtained at 305, 310, 315, and 320 mμ, respectively. These formation constants are all lower than those listed in Table 1.

The molecular extinction coefficient of the *CT*-peak at 285 mμ was estimated at 20°C, assuming $K_c = 6.8 \text{ M}^{-1}$ and it was found $\epsilon_{CT} (285 \text{ m}\mu) \approx 8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$.

Diphenyl sulphoxide. The mixed solutions of iodine and DPSO had a visible absorption band at 459 mμ overlapping the free iodine band. Sets of curves, having the same iodine concentrations had an isobestic point at 493 mμ for DPSO concentrations not exceeding 0.2 M. Again, as shown in Fig. 2, the method of continuous variation gave curves revealing a 1:1 complex.

Series of DPSO-iodine solutions were recorded in the visible region at four different temperatures. The formation constants, molecular extinction coefficients and thermodynamic functions for the DPSO-iodine complex are listed in Table 2.

DPSO has a strong ultraviolet absorption band at 267 mμ when dissolved in cyclohexane.⁹ The mixed solutions of DPSO and iodine in carbon tetrachloride showed a charge transfer absorption band around 290 mμ superposed on the DPSO absorption as shown in Fig. 3. The distance $\bar{\nu}_{\text{max}} - \bar{\nu}_L$ was approximately $2.3 \times 10^3 \text{ cm}^{-1}$, suggesting a value $\Delta\bar{\nu}_{\frac{1}{2}} = 5.5 \times 10^3 \text{ cm}^{-1}$. Attempts were made to determine the formation constant at 20°C from the *CT* band. A series of mixed solutions was recorded, the iodine concentrations being $4.257 \times 10^{-4} \text{ M}$ and the DPSO concentration varying from 0.01228 M to 0.1842 M. The following formation constants (K_c) were obtained: 2.9, 2.7, 2.5, and 2.4 M⁻¹ obtained at 320, 325, 330, and 335 mμ, respectively, by the Scott representation. These values are much lower than those obtained from the

Table 2. Formation constants, extinction coefficients and thermodynamic functions for the DPSO-I₂ complex in CCl₄, obtained from the blue shifted iodine band.^a

Temp °C	430 mμ		440 mμ		450 mμ		460 mμ	
	K_c M ⁻¹	ϵ M ⁻¹ cm ⁻¹	K_c M ⁻¹	ϵ M ⁻¹ cm ⁻¹	K_c M ⁻¹	ϵ M ⁻¹ cm ⁻¹	K_c M ⁻¹	ϵ M ⁻¹ cm ⁻¹
10	4.70	990	4.82	1100	4.88	1180	4.86	1220
20	3.92	990	4.03	1090	4.09	1180	4.15	1190
25	3.63	980	3.78	1070	3.76	1150	3.70	1190
40	2.91	950	2.98	1060	2.99	1140	2.97	1190
$-\Delta H^b$	2.80		2.76		2.87		2.92	
$-\Delta G_{25}^c$	0.76		0.78		0.78		0.79	
$-\Delta S^d$	6.8		6.6		7.0		7.1	

Mean values $-\Delta H^b = 2.8 \pm 0.3$; $-\Delta G_{25}^c = 0.78 \pm 0.03$; $-\Delta S^d = 6.9 \pm 0.5$.

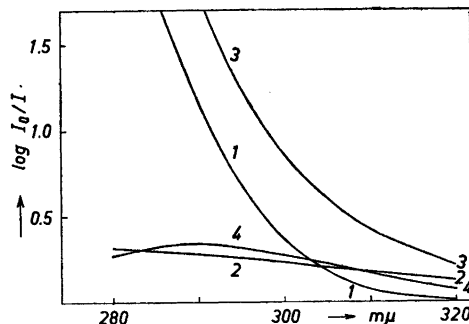
^a The values were calculated from absorption data of 10 different DPSO-I₂ solutions. I₂ = $1.349 \times 10^{-3} \text{ M}$, DPSO varied from 0.01921 M to 0.2882 M using 1 cm cells.

^b ΔH in units of kcal/mole.

^c ΔG_{25} in units of kcal/mole.

^d ΔS in units of e.u.

Fig. 3. The ultraviolet absorption spectra of DPSO at 20°C in carbon tetrachloride: Curves (1) 0.00255 M DPSO; (2) 0.00466 M iodine, and (3) 0.00255 M DPSO + 0.00466 M iodine. Curve (4) is the complex absorption obtained by placing the solutions (1) and (2) in the reference beam.



blue shifted iodine band in Table 2. However, they have been obtained from absorption data at the long wave length wing more than 30 $m\mu$ from the *CT* peak. By assuming $K_c = 4.0 \text{ M}^{-1}$ at 20°C, the molecular extinction coefficient at the *CT* peak was estimated to $\epsilon_{CT} (290 \text{ m}\mu) \approx 7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$.

DISCUSSION

The observations made in the ultraviolet, visible and infrared² regions support the conclusion that the sulphoxides form (n, σ) charge transfer complexes with iodine. Moreover, the infrared data demonstrate that the sulphoxides are bonded to iodine from the oxygen.^{2,3} Evidently, the oxygen lone pair electrons are more readily available for donation than those on the sulphur. For MPSO, DPSO, as well as DMSO the continuous variation plots indicated no tendency to form any higher complexes. Thus, the electron density on the sulphur has been drastically reduced in the sulphoxides compared to the sulphides. Secondly, the donation of an electron pair from the oxygen probably reduces the electron density on the sulphur further, making them unavailable for donation. This is in agreement with the considerable bulk of information in the literature showing that donors with two or more donor sites generally form 1:1 complexes with iodine.¹³⁻¹⁵

In the DMSO-iodine system,¹ it was found that the charge transfer absorption peak underwent a bathochromic shift with higher donor concentrations. Moreover, the formation constants (K_c) calculated from absorption data at the long wave length side of the *CT*-peak gave too low values for high DMSO concentrations. For the present systems, however, donor concentrations higher than 0.1 M were necessary in order to engage 30–40 % of the iodine into complex formation. Furthermore, the long wave length wing quite far from the *CT* band maxima was the only region available for quantitative calculations. The formation constants (K_c) calculated from this absorption region demonstrate the following features: (1) They are lower than the values obtained in the visible region. (2) They increase towards the *CT* maximum. These findings can both be explained as a bathochromic shift of the *CT* band with higher MPSO or DPSO concentrations. The same conclusions can be drawn from an absorption matrix scheme according to Liptay.¹⁶ Thus, from the same set of absorption curves recorded in the ultraviolet region of the DPSO-iodine system, an absorption matrix was formed. The absorption values at 320,

325, 330, 335, 340, 345, and 350 $m\mu$ were employed and the matrix normalized at 320 $m\mu$. The rows in the (ζ_{ik}) matrix¹⁶ were not equal as expected for a 1:1 complex, but the elements ζ_{ik} increased towards higher DPSO concentrations. This indicates the existence of more than one complex,¹⁶ but may in the present case be interpreted in terms of a bathochromic shift of the *CT* band with higher DPSO concentration. Similar observations were made for the MPSO-iodine absorption matrix. It seems reasonable that for MPSO and DPSO as well as for DMSO¹ this shift is caused by a dielectric effect and presumably also an association effect. High dipole moments¹⁷ and dielectric constants have been observed for the sulphoxides. At higher sulphoxide concentrations the energy of the excited dative state should be reduced,¹⁸ followed by a lower energy transition $h\nu_{CT}$. Moreover, dipole-dipole interactions and a possible "cage"-effect of free sulphoxide molecules surrounding a complex molecule may lead to the same effect. Finally, an association of sulphoxides has been observed for DMSO¹⁹ and would be expected also for MPSO and DPSO, resulting in a perturbation of the electronic transition energy.

It appears from Tables 1 and 2 that the formation constants (K_c) calculated from the blue shifted iodine band do not vary significantly in the observed region. Moreover, corresponding measurements performed at 20°C with a 5 cm absorption cell and five times lower iodine concentrations gave the same formation constants. If the data in Tables 1 and 2 are compared with those obtained for DMSO^{1,3} it appears that the latter is the stronger donor towards iodine. The formation constants as well as the enthalpies of formation increase in the order DPSO, MPSO, and DMSO. Furthermore, the blue shifts of the visible iodine band increased in the same order (58, 63, and 71 $m\mu$, respectively). Finally, the infrared shifts assigned to the S=O stretching frequency on complex formation to iodine were 37, 39, and 51 cm^{-1} , respectively,² indicating increasing interaction in this order. Thus the thermodynamic functions as well as the spectroscopic data in the visible and infrared regions demonstrate the order of basicity towards iodine.

It has been concluded that very little conjugation exists in the aromatic sulphoxides²⁰ because if the sulphur *d* orbital is overlapping the oxygen *p* orbital with maximum efficiency, it cannot do so with the *p* orbital on the α -carbon-atom. This assumption has been verified by thermochemical work²¹ assigning the same bond energy to the S=O bond irrespective of the substituents R_1 and R_2 in $R_1R_2S=O$.

The order of increasing basicity towards iodine is also in agreement with the assumption of very small conjugation in MPSO and DPSO. Thus, the inductive effect of the electronegative phenyl groups reduces the electron density on the oxygen in MPSO and DPSO compared to DMSO. If the S=O bond had been strongly conjugated with the phenyl groups in MPSO and DPSO the π -electron density on the oxygen would increase, counteracting the negative inductive effect. It was found,²² *e.g.*, that benzaldehyde was a stronger donor to iodine than acetaldehyde. The lower basicity of MPSO and DPSO compared with DMSO therefore support the conclusion of low conjugation in the sulphoxides.

The donor properties of the sulphoxides may be compared with those of the sulphides which have been extensively studied in recent years. Firstly, the sulphides are stronger donors than the sulphoxides. Moreover, diethyl sul-

phide²³⁻²⁵ seems more basic than dimethyl sulphide,²⁶ even if thermodynamic data for the latter have not been reported. The basicities of the saturated, cyclic sulphides^{15,25,27} towards iodine are comparable to diethyl sulphide. However, the thioanisoles²⁸ are much weaker donors than diethyl sulphide because of the electron attracting phenyl group. The substituents seem to have a comparable effect on the relative basicities of the sulphides and the sulfoxides towards iodine.

The *CT* absorption band was situated at 285 and 290 $m\mu$ for MPSO and DPSO, respectively, compared to 272 $m\mu$ for DMSO. The ionization potentials for MPSO and DPSO should therefore be lower than for DMSO. The extinction coefficients at the *CT*-peak or the oscillator strength for the *CT*-band could only be roughly estimated for MPSO and DPSO. However, the intensities are undoubtedly lower and the half intensity widths smaller for MPSO and DPSO compared to DMSO,¹ in agreement with their lower basicities.

Financial support from *Nansen-fondet—Axel Auberts fond* is gratefully acknowledged.

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Received February 12, 1964.