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Electron Donating Properties of Thioanisole, *p*-Methylthioanisole & Diphenyl Sulphide

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The intermolecular charge transfer complexes formed between sulphides, viz. thioanisole, *p*-methylthioanisole, and diphenyl sulphide as donors and iodine as an acceptor have been studied spectrophotometrically and their stability constants (β_1) computed using graphical and iterative methods. The results obtained indicate that the complexes are of $n \rightarrow \sigma$ charge transfer types. The extent of conjugation of *n*-electrons with π-system affects significantly the stability of the resultant complex. The ionization potentials (I_D) of the donors have been computed.

THE charge transfer complexes of some organic sulphides have been studied and their stability constants computed using the approximate methods[1]. In the present study the electron donating properties of thioanisole, *p*-methylthioanisole, and diphenylsulphide were investigated through the formation of intermolecular charge transfer complexes with iodine. The stability constants were computed using the graphical and iterative techniques. The ionization potentials (I_D) of the donors were also calculated.

Materials and Methods

Purified cyclohexane, having no absorption in the near UV, was used as a solvent.

Thioanisole and *p*-methylthioanisole were prepared[2] and purified by distillation under reduced pressure. Diphenyl sulphide was prepared by adding solid sulphur to a mixture of benzene and $AlCl_3$ under reflux and stirring[3]. The product was purified by distillation under reduced pressure.

The UV spectra were scanned on a Beckman model DK spectrophotometer using fused silica cells of 1 ml capacity.

Calculations

When a solution of the organic sulphide is mixed with that of iodine, the equilibrium[1] is established.

$$\underset{(B)}{X_2S}+\underset{(A)}{I_2} = \underset{(BA)}{X_2S{\cdot}I_2} \qquad \ldots(1)$$

Following the Rossotti[4] notation, the equilibrium constant (β_1) is given by Eq. (2).

$$\beta_1=[BA]/[B][A] \qquad \ldots(2)$$

Using 1 cm path length, and assuming that Beer's law is obeyed, the absorbance (A_s) of a solution containing the species A and BA_n ($n>0$) is given by:

$$A_s = b \sum_0^N \epsilon_n \beta_n a^n + \epsilon_A a$$

or

$$A_s = [B]E + \epsilon_A a \qquad \ldots(3)$$

where ϵ_n is the extinction coefficient of species BA_n, a and b are the concentrations of free species A and B respectively at the equilibrium state, and [B] is the initial concentration of species B.

$$E = \sum_0^N \epsilon_n a^n \qquad \ldots(4)$$

Since $N = 1$, the Eqs. (3) and (4) lead to Eq. (5).

$$E = \frac{A_s - \epsilon_A a}{B} = \frac{\epsilon_0 + \epsilon_1 \beta_1 a}{1+\beta_1 a} \qquad \ldots(5)$$

where ϵ_0 is the extinction coefficient of species-B. Since ϵ_A and ϵ_0 can be obtained experimentally the value of β_1 can be calculated from the variation of absorbance with the total [A] and [B]. The equilibrium concentration of the species BA is related to the measured absorbance by:

$$[BA]= \Delta A_s/\Delta\epsilon \qquad \ldots(6)$$

where

$$\Delta A_s = A_s - \epsilon_A a - \epsilon_0 b \qquad \ldots(7)$$

and

$$\Delta\epsilon = \epsilon_1 - \epsilon_A - \epsilon_0 \qquad \ldots(8)$$

When the product $[A][B] \gg [BA]^2$, then

$$[BA] = [A][B]/(\beta_1^{-1} + [A] + [B]) \qquad \ldots(9)$$

and

$$[A][B]/\Delta A_s = ([A] + [B]/\Delta\epsilon + 1/\beta_1\Delta\epsilon \qquad \ldots(10)$$

Thus a plot of $[A][B]/\Delta A_s$ versus ([A]+[B]) should be linear with slope $1/\Delta\epsilon$ and intercept $1/\beta_1\Delta\epsilon$. Benesi and Hildebrand[5] used an approximate form

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of Eq. (10) for studying the intermolecular charge transfer complexes of iodine with organic donors. In the present work Eq. (10) has been used to compute, graphically, the stability constant β_1 for the 1 : 1 charge transfer complex and ϵ_1, its molar extinction coefficient.

Results and Discussion

Thioanisole-iodine System

The absorption spectra of iodine ($8{\cdot}1977\times10^{-4}M$) and thioanisole ($6{\cdot}8\times10^{-3}M$), and of mixtures of iodine at a fixed concentration ($8{\cdot}1977\times10^{-4}M$, with varying concentration of thioanisole ($6{\cdot}8\times10^{-3}$ to $0{\cdot}745\times10^{-3}M$) in cyclohexane are recorded in Fig. 1.

Iodine in cyclohexane shows a λ_{max} at 520 nm, but its absorption is very low in the region 410-290 nm. However, in the spectra of iodine-thioanisole solution, the iodine band at 520 nm undergoes a blue shift which descreases in intensity with increasing [thioanisole]. A new band appears at 329 nm, the intensity of which increases with increasing [thioanisole]. These results indicate that on mixing iodine and thioanisole a charge transfer complex is formed which exhibits a λ_{max} at 329 nm.

The blue shift of the visible iodine band, on mixing with an electron donor, has been interpreted by Mulliken[6] to be due to repulsive interaction between the two partners of the complex. In the present case, the charge transfer attraction is expected to originate from the interaction between σ_u MO of iodine, and most probably, the non-bonding orbitals on the sulphur atom of thioanisole. As a result energy of the σ_u MO of iodine will be raised and that of the non-bonding orbital of the donor will be lowered. Consequently, the visible band of iodine is blue shifted.

Eq. (10) was used to compute graphically the values of β_1 and ϵ_1 for the charge transfer complex of thioanisole and iodine. The plots of $[A][B]/\Delta A_s$ versus ([A]+[B]) at different wavelengths are linear (Fig. 2). From the slopes and intercepts of these plots values of the molar extinction coefficient and the stability constant of thioanisole-iodine complex were computed. The results are given in Table 1.

The values obtained for β_1 are very large for a π-charge transfer complex. The equilibrium constants[7,8] of some π-charge transfer complexes of benzene, toluene, xylene, and hexamethylbenzene vary between 0·13 and 1·35. This leads us to

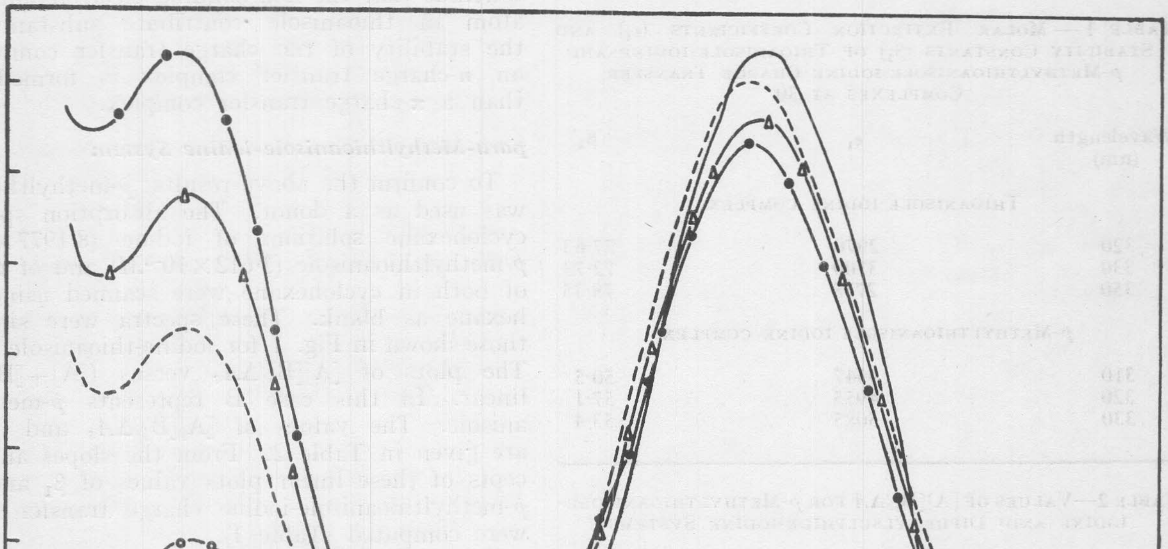

Fig. 1 — Absorption spectra of the mixtures of iodine and thioanisole and of iodine in cyclohexane at 30° {—, Pure I_2 ($8{\cdot}1977\times10^{-4}M$); —●—, I_2 ($8{\cdot}1977\times10^{-4}M$) — Thioanisole ($6{\cdot}8\times10^{-3}M$); —△—, I_2 ($8{\cdot}1977\times10^{-4}M$) — Thioanisole ($5{\cdot}2\times10^{-3}M$); - - -, I_2 ($8{\cdot}1977\times10^{-4}M$) — Thioanisole ($3{\cdot}7\times10^{-3}M$); —○—, I_2 ($8{\cdot}1977\times10^{-4}M$) — Thioanisole ($2{\cdot}23\times10^{-3}M$); —×—, I_2 ($8{\cdot}1977\times10^{-4}M$) — Thioanisole ($0{\cdot}745\times10^{-3}M$)}

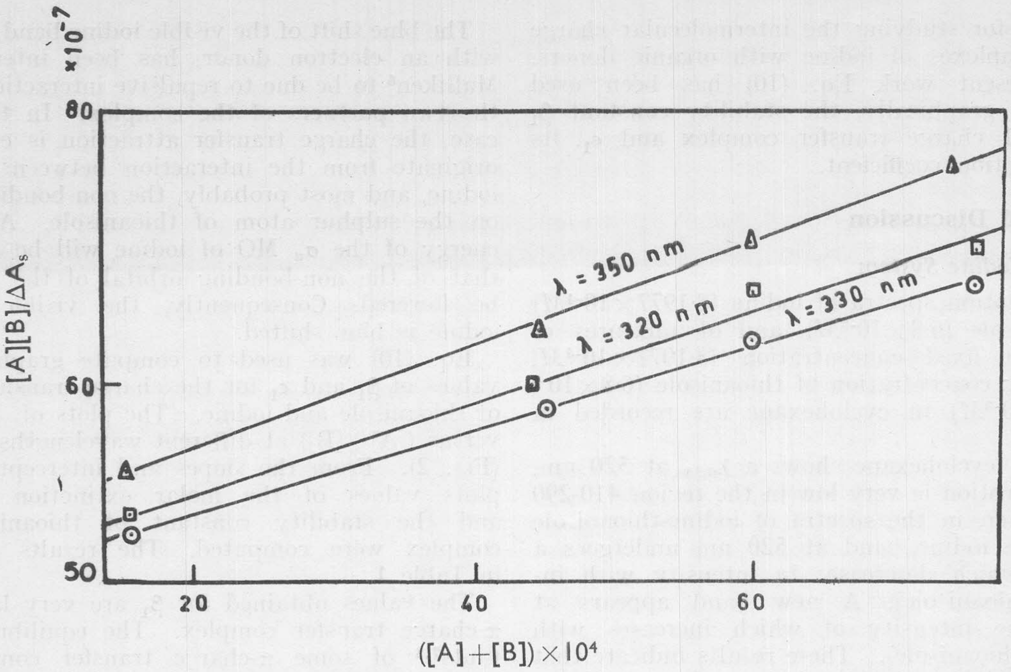

Fig. 2 — Plots of $[A][B]/\Delta A_s$ versus $([A]+[B])$ at different wavelengths for thioanisole-iodine system

TABLE 1 — MOLAR EXTINCTION COEFFICIENTS (ϵ_1) AND STABILITY CONSTANTS (β_1) OF THIOANISOLE-IODINE AND *p*-METHYLTHIOANISOLE-IODINE CHARGE TRANSFER COMPLEXES AT 30°

Wavelength (nm)	ϵ_1	β_1
	THIOANISOLE-IODINE COMPLEX	
320	2970	77·63
330	3100	72·73
350	2758	78·35
	p-METHYLTHIOANISOLE-IODINE COMPLEX	
310	4547	50·5
320	4955	57·1
330	5085	53·4

TABLE 2—VALUES OF $[A][B]/\Delta A$ FOR *p*-METHYLTHIOANISOLE-IODINE AND^s DIPHENYLSULPHIDE-IODINE SYSTEMS

$[A][B]\times10^7$	$([A][B]/\Delta A_s)\times10^7$ at			$([A]+[B])\times10^4$
	330 nm	320 nm	310 nm	
		p-METHYLTHIOANISOLE-IODINE SYSTEM		
3·2791	38·61	36·91	42·58	12·198
9·8373	40·91	39·84	44·37	20·198
16·3954	41·62	41·01	44·25	28·198
22·9536	39·11	38·92	42·00	36·198
29·5117	43·21	42·16	46·21	44·198
		DIPHENYL SULPHIDE-IODINE SYSTEM		
19·6745	—	2·445	2·623	32·198
59·0234	—	3·271	3·327	80·198
98·3724	—	2·953	3·028	128·198
154·4101	—	3·207	3·225	176·198

conclude that the non-bonding electrons on sulphur atom in thioanisole contribute substantially to the stability of the charge transfer complex and an *n*-charge transfer complex is formed rather than a π-charge transfer complex.

para-Methylthioanisole-iodine System

To confirm the above results, *p*-methylthioanisole was used as a donor. The absorption spectra of cyclohexane solutions of iodine ($8{\cdot}1977\times10^{-4}M$), *p*-methylthioanisole ($3{\cdot}612\times10^{-3}M$) and of mixtures of both in cyclohexane were scanned using cyclohexane as blank. These spectra were similar to those shown in Fig. 1 for iodine-thioanisole system. The plots of $[A][B]/\Delta A_s$ versus $([A]+[B])$ were linear. In this case B represents *p*-methylthioanisole. The values of $[A][B]/\Delta A_s$ and $([A][B])$ are given in Table 2. From the slopes and intercepts of these linear plots values of β_1 and ϵ_1 for *p*-methylthioanisole-iodine charge transfer complex were computed (Table 1).

The results indicate that β_1 for *p*-methylthioanisole-iodine complex is less than that for thioanisole-iodine complex. Although both the complexes belong to *n*-charge transfer type, yet the hyperconjugation effect of $-CH_3$ group is expected to increase the basic character of *p*-methylthioanisole in contrast to thioanisole. This anomaly will be discussed later.

Diphenylsulphide-iodine Systems

The effect of conjugation of the lone pair of electrons on the sulphur atom with the π-system on the stability of the charge transfer complex was investigated using diphenyl sulphide as donor. The extent of coplanarity in diphenyl sulphide is expected to be significant. As a result, the lone pair of electrons on the sulphur atom will be significantly delocalized. This will affect the stability of the resultant charge transfer complex. The absorption spectra of iodine ($8{\cdot}1977\times10^{-4}M$), diphenyl sulphide ($2{\cdot}16\times10^{-2}M$) and a set of diphenylsulphide-iodine mixtures at 30°C were recorded in cyclohexane as a solvent and as a blank. All mixtures had the same concentration of iodine ($8{\cdot}1977\times10^{-4}M$) but varying concentrations of diphenyl sulphide ($1{\cdot}68\times10^{-2}$-$0{\cdot}24\times10^{-2}M$). Features of the spectra were the same as those shown in Fig. 1. The plots of $[A][B]/\Delta A_s$ versus ($[A]+[B]$) were linear, where B represents diphenyl sulphide. The values of $[A][B]/\Delta A_s$ and ($[A]+[B]$) are given in Table 2.

From the slopes and intercepts of these linear plots the values of ϵ_1 and β_1 at 310 and 320 nm were calculated to be 2302, 17·8 and 2196, 19·9 respectively.

Computation of β_1 and ϵ_1 using iterative procedure — Eq. (10) is approximate in which the concentration of the charge transfer complex has been neglected with respect to that of the donor. The exact form is:

$$\frac{[A][B]}{\Delta A_s} = \frac{[A]+[B]}{\Delta\epsilon} + \frac{1}{\beta_1\Delta\epsilon} - \frac{x}{\Delta\epsilon} \qquad \ldots(11)$$

where x is the concentration of the charge transfer complex. The values of β_1 and ϵ_1 obtained graphically are approximate due to the neglect of the [complex] specially when the [donor] is not much more than that of the acceptor, and the approximations involved in drawing the linear plots. Generally, the results obtained graphically show an apparent dependence of β_1 and ϵ_1 on the donor and acceptor concentrations although the product $\beta_1\epsilon_1$ remains constant[9]. In some cases β_1 shows an apparent dependence on the wavelength of measurements[10] (Table 1). A number of explanations have been put forward for these anomalies.

To get more reliable values of β_1 and ϵ_1 several methods of numerical analysis can be applied to graphical results[11]. Surprisingly enough, the

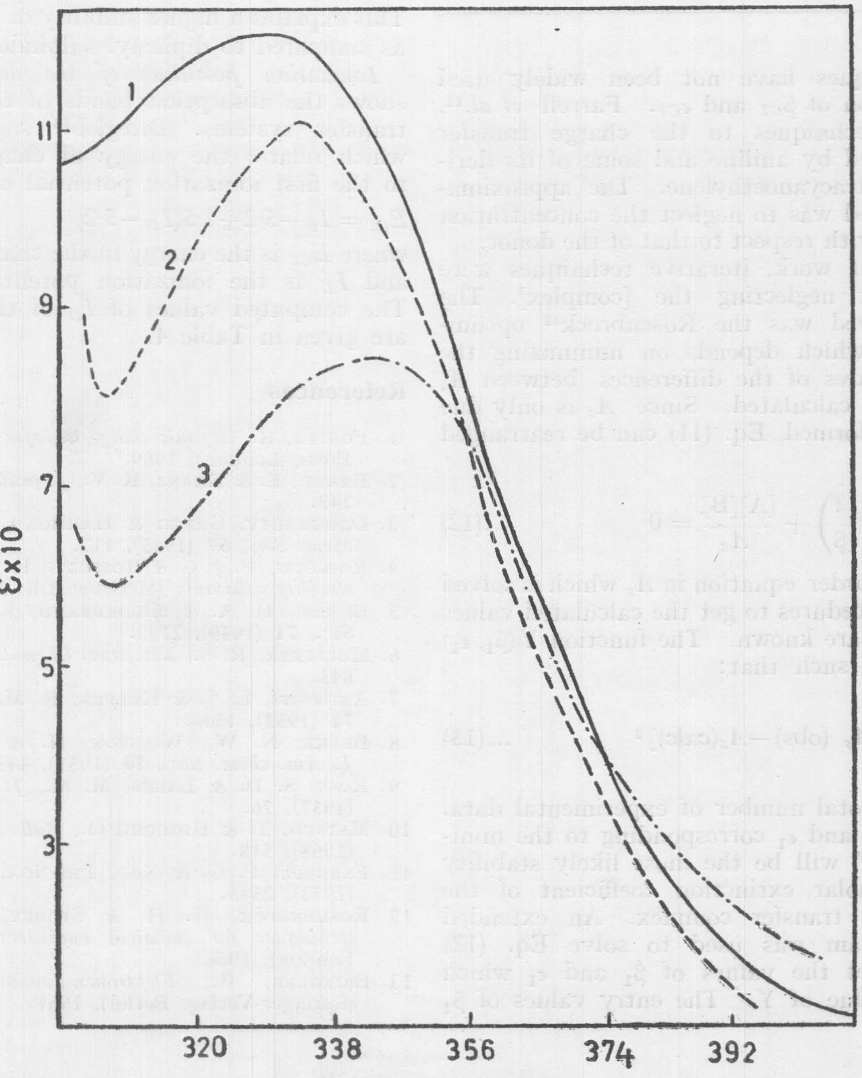

Fig. 3 — Charge transfer bands of different organic sulphide-iodine complexes [1, Thioanisole-I_2; 2, p-methylthioanisole-I_2; 3, diphenyl sulphide-I_2]

TABLE 3 — VALUES OF β_1 AND ϵ_1 OBTAINED FROM GRAPHICAL AND ITERATIVE METHODS FOR THE COMPLEX SULPHIDE-I_2 IN CYCLOHEXANE

Donor	Method	β_1	ϵ_1	$\Sigma[A_s$ (obs.) $-A_s$ (calc)]^2 $\times 10^3$
Thioanisole	Graphical	72·73	3100	2·88
	Rosenbrock	57·68	3648	
p-Methylthio-anisole	Graphical	57·1	4955	1·38
	Rosenbrock	66·81	4550	
Diphenyl-sulphide	Graphical	19·90	2196	1·64
	Rosenbrock	29·00	1545	

TABLE 4—IONIZATION POTENTIALS OF THE SULPHIDE DONORS

Donor	E_{CT} eV	I_D eV
Thioanisole	3·73	8·43
p-Methylthioanisole	3·70	8·40
Diphenylsulphide	3·60	8·32

iterative techniques have not been widely used for the evaluation of β_{CT} and ϵ_{CT}. Farrell *et al.*[11]. applied such techniques to the charge transfer complexes formed by aniline and some of its derivatives with tetracyanoethylene. The approximation they adopted was to neglect the concentration of the complex with respect to that of the donor.

In the present work, iterative techniques were applied without neglecting the [complex]. The procedure followed was the Rosenbrock[12] optimization method which depends on minimizing the sum of the squares of the differences between A_s observed and A_s calculated. Since A_s is only due to the complex formed, Eq. (11) can be rearranged to Eq. (12).

$$\frac{A_s}{\epsilon_1} - \left([A]+[B]+\frac{1}{\beta}\right) + \frac{[A][B]}{A_s} = 0 \qquad \ldots(12)$$

This is a second order equation in A_s which is solved by the usual procedures to get the calculated values of A_s if β and ϵ are known. The function $Y(\beta_1, \epsilon_1)$ may be defined such that:

$$Y(\beta_1, \epsilon_1) = \sum_{i=1}^{n}]A_s \text{ (obs)} - A_s\text{(calc)}]^2 \qquad \ldots(13)$$

where n is the total number of experimental data. The values of β_1 and ϵ_1 corresponding to the minimum value of Y will be the most likely stability constant and molar extinction coefficient of the resultant charge transfer complex. An extended precession program was used to solve Eq. (12) iteratively to get the values of β_1 and ϵ_1 which minimize the value of Y. The entry values of β_1 and ϵ_1 are the ones obtained from graphical method. The results of this treatment are given in Table 3.

The values of β_1 and ϵ_1 obtained by the Rosenbrock method differ from those obtained graphically but are of the same order of magnitude. The computed values are expected to be reliable as governed by the numerical values of Y. A significant observation is that β_1 and ϵ_1 increase in the order *p*-methylthioanisole > thioanisole > diphenyl sulphide, in agreement with the basicity of the donors. The results obtained graphically show some anomalies since thioanisole is found to be a stronger electron donor than *p*-methylthioanisole. The methyl group is expected to increase the basic character of thioanisole nucleus due to the hyperconjugation effect.

The values obtained for β_1 and ϵ_1 indicate that the resultant charge transfer complexes are of $n \rightarrow \sigma$ type. This means that the lone pair of electrons on the sulphur is slightly delocalized. The extent of the delocalization of lone pair of electrons on sulphur in diphenylsulphide is much more than that in anisole or *p*-methylthioanisole. This explains a higher stability of anisole-I_2 complex as compared to diphenyl sulphide-I_2 complex.

Ionization potential of the donor — Figure (3) shows the absorption bands of the studied charge transfer systems. Briegleb[13] suggested Eq. (14) which relates the energy of charge transfer band to the first ionization potential of the donor.

$$E_{CT} = I_D - 5{\cdot}2 + 1{\cdot}5(I_D - 5{\cdot}2) \qquad \ldots(14)$$

where E_{CT} is the energy of the charge transfer band, and I_D is the ionization potential of the donor. The computed values of I_D of the studied donors are given in Table 4.

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