Charge-transfer Complexes of Imidazole-2-thiones with Iodine

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The charge-transfer complexes between various alkyl- and aryl-substituted imidazole-2-thiones and iodine in methylene dichloride and carbon tetrachloride were studied spectrophotometrically in the u.v.–visible region. Spectral data, the formation constants, and thermodynamic functions ΔH°, ΔG°, and ΔS° have been determined and the effect of substituents on them discussed. The spectroscopic results suggest the presence of both thiol and thione tautomers involved in complex formation.

Compounds with a thioamide group, like thioacetamide, thioureas, thiocarbanilides, and some heterocyclic thiones, form 1 : 1 charge-transfer complexes with iodine in apolar solvents.[1,2] These *n*-donor–σ-acceptor complexes are of high thermodynamic stability and their formation constants and enthalpies of formation locate them among the strongest complexes of this type. Recently, the spectroscopic and equilibrium data on the charge-transfer complex of 1-methylimidazole-2-thione with iodine in carbon tetrachloride have been reported.[3] The present study was undertaken to determine the spectroscopic and thermodynamic characteristics of iodine complexes with imidazole-2-thione and its alkyl and aryl derivatives in order to establish the influence of the substituents on stability of the complexes. The following imidazolethiones were used as electron donors in this study: imidazole-2-thione (IT), 1-methylimidazole-2-thione (1-MeIT), 1,3-dimethylimidazole-2-thione (1,3-Me_2IT), 4,5-dimethylimidazole-2-thione (4,5-Me_2IT), 1,4,5-trimethylimidazole-2-thione (1,4,5-Me_3IT), and 4,5-diphenylimidazole-2-thione (4,5-Ph_2IT).

Experimental

1-MeIT and 4,5-Ph_2IT were commercial products of Aldrich. Imidazole-2-thione was synthesized according to Akabori[4] and 4,5-Me_2IT and 1,4,5-Me_3IT were prepared as described by Sandstrom.[5] 1,3-Me_2IT was obtained from *N*-methylimidazole by its conversion into dimethylimidazolium iodide and treatment with sulphur in methanolic potassium carbonate. Analytical-grade iodine was resublimed twice under reduced pressure. Carbon tetrachloride, analytical grade, was distilled through a 40 cm Dufton column over phosphorus pentaoxide. Reagent grade methylene dichloride was washed with concentrated sulphuric acid, aqueous sodium carbonate, and water. After predrying with anhydrous sodium sulphate it was fractionally distilled over Drierite. When distilled over P_2O_5, methylene dichloride caused considerable iodine consumption and gradual fading of complex absorption.

Stock solutions of iodine and donors sufficiently soluble in given solvent, *i.e.* 1-MeIT and 1,3-Me_2IT in carbon tetrachloride and IT, 1-MeIT, 1,3-Me_2IT, and 1,4,5-Me_3IT in methylene dichloride, were prepared by weighing. 4,5-Me_2IT and 4,5-Ph_2IT, because of their much smaller solubility in methylene dichloride, were prepared as saturated solutions the concentration of which was determined spectrophotometrically after dilution with ethanol using the previously estimated absorption coefficients of those compounds in ethanol.

All spectra and quantitative spectrophotometric measurements were made on a Specord M-40 (C. Zeiss, Jena) spectrophotometer. Precise estimation of $\lambda_{max.}$ and calculation of fourth derivatives of complex spectra were performed using an internal microcomputer with the aid of a Data Handling I program cassette. The temperature of solutions before and during measurements was maintained to within 0.1 °C using a constant-temperature circulating bath with an external refrigerating unit for operation below ambient temperature. During measurements at 5 °C the cell compartment was flushed with dry nitrogen gas.

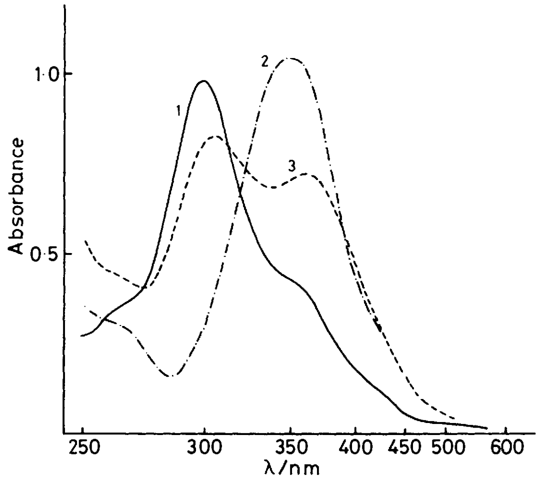

Figure 1. Absorption spectra of imidazolethione–iodine complexes in CH_2Cl_2: 1, [IT] 4.68 × 10^{-5}M; 2, [1,3-Me_2IT] 4.53 × 10^{-5}M; 3, [1,4,5-Me_3IT] 3.87 × 10^{-5}M. Iodine concentration was in all cases 6.0 × 10^{-5}M

Results and Discussion

Electronic Spectra of Imidazolethione.—Spectra of iodine complexes in methylene dichloride were taken in the wavelength range 240—650 nm. Typical examples are shown in Figure 1. A strong charge-transfer (CT) band is observed at *ca.* 300 nm for all compounds studied except 1,3-Me_2IT, for which the CT band appears at 349.6 nm. The exact λ values of CT band maxima collected in the Table show that substitution of methyl groups into the imidazole ring increases the wavelength of the band maximum. This bathochromic shift, being in good agreement with earlier observations on substituted benzene–I_2 systems,[6] can be attributed to the inductive effect of alkyl groups increasing the electron-donating ability of the sulphur atom. The negative inductive effect of two aryl groups in 4,5-Ph_2IT is responsible for decreasing the wavelength of its CT band maximum, compared with that of the unsubstituted imidazolethione.

The charge-transfer band of 1,3-Me_2IT complex is shifted markedly toward the longer wavelength ($\lambda_{max.}$ *ca.* 350 nm) and cannot be explained simply by the inductive effect of two methyl groups. A similar observation was reported by Rao[2] for alkylthioureas: complexes of mono- and di-alkylthioureas with

Table. Spectroscopic and thermodynamic data on imidazole-2-thione–iodine complexes in methylene dichloride and carbon tetrachloride

	Donor		Complex						
	$\lambda_{max.}$	ε	λ_{CT}[a]	$h\nu_{CT}$		$K_{c298\,K}$	$-\Delta H^{\circ}$	$-\Delta S^{\circ}$	$-\Delta G^{\circ}_{298\,K}$
Donor	nm	l mol^{-1} cm^{-1}	nm	eV	A_{CT}[b]$/A_{350}$	l mol^{-1}	kcal mol^{-1}	cal mol^{-1} K^{-1}	kcal mol^{-1}
				Carbon tetrachloride					
1-MeIT	275.6	13 300	303.4	4.08	2.85	16 740 ± 638	8.6	9.6	5.8
1,3-Me_2IT	272.3	13 700	351.0	3.53		27 096 ± 315	9.6	12.0	6.0
				Methylene dichloride					
IT	270.5	13 500	299.4	4.14	2.79	49 480 ± 196	9.2	9.2	6.4
1-MeIT	269.7	14 850	303.8	4.08	1.79	84 730 ± 417	9.6	9.7	6.7
1,3-Me_2IT	266.8	15 400	349.7	3.54		106 905 ± 510	9.9	10.3	6.9
4,5-Me_2IT	280.5	16 100	302.3	4.10	2.46	73 525 ± 805	9.5	9.7	6.6
1,4,5-Me_3IT	276.8	14 300	305.3	4.06	1.30	112 453 ± 795	9.9	10.2	6.9
4,5-Ph_2IT	287.7	15 500	294.5	4.18	2.47	12 635 ± 475	8.2	8.8	5.6

[a] Subscript CT refers to main charge-transfer band. [b] Ratio of the main CT band absorbance to that of the band located at 350 nm.

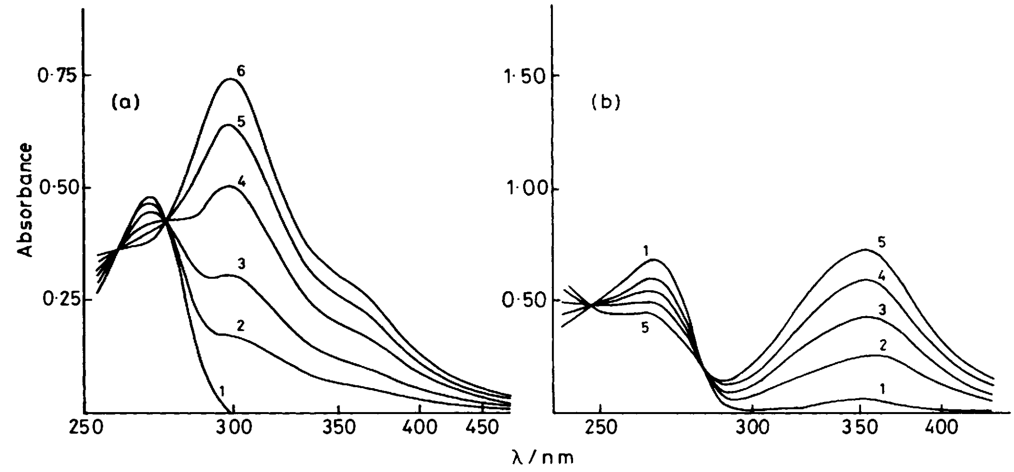

Figure 2. Effect of varying iodine concentration on absorption spectra of imidazolethione–iodine complexes in CH_2Cl_2. (a) [IT] 3.88 × 10^{-5}M. Iodine concentration: 1, 0.0, 2, 0.6 × 10^{-5}M; 3, 1.2 × 10^{-5}M; 4, 2.4 × 10^{-5}M; 5, 3.6 × 10^{-5}M; 6, 4.8 × 10^{-5}M. (b) [1,3-Me_2IT] 4.0 × 10^{-5}M. Iodine concentration: 1, 0.0; 2, 0.8 × 10^{-5}M; 3, 1.6 × 10^{-5}M; 4, 3.2 × 10^{-5}M; 5, 4.0 × 10^{-5}M

iodine showed the maximum of the CT band at 300—305 nm whereas for tetramethylthiourea complex this maximum appeared at 334 nm. It has to be emphasized that 1,3-Me_2IT exists only as the thione whereas the remaining compounds may form thiol–thione tautomers. Charge-transfer bands of those two forms may be located at two different wavelengths, namely *ca.* 300 and *ca.* 350 nm. This assumption is supported by the appearance of an additional absorption band of different intensity, seen as a maximum (for 1,4,5-Me_3IT in CH_2Cl_2) or shoulder overlapping the main CT band at λ *ca.* 350 nm in spectra of those imidazolethiones for which the tautomeric exchange is possible. The spectra were resolved into component bands by a computer-assisted method,[7] and the ratio $A_{CT}:A_{350}$ of their $\lambda_{max.}$ absorbances calculated (Table). These data show that the ratio of two tautomers depends not only on the structure of a given imidazolethione but also on the polarity of solvent (the less polar the solvent, the more shifted the equilibrium towards the thiol form). However, the full picture needs detailed studies on tautomeric equilibria of these compounds in different solvents. The lack of tautomeric-constant data prevents an estimate of ε for the main CT bands as well as for the overlapping (*ca.* 350 nm) ones. ε_{CT} Values calculated for 1,3-Me_2IT complexes are 31 850 and 30 100 l mol^{-1} cm^{-1} in carbon tetrachloride and methylene dichloride, respectively. The suggestion made by Raby *et al.*[4] that the tri-iodide ion, formed during the transformation of the outer complex into the inner one, is responsible for the peak at *ca.* 350 nm could not be accepted for two reasons: (i) the spectrum of I_3^- has two maxima at 292 and 360 nm with an absorbance ratio $A_{292}:A_{360}$ equal to 1.83.[8] If the suggestion is to be valid the absorption-peak ratio of imidazolethione complexes should not be lower than this value; in the case of 1,4,5-Me_3IT in CH_2Cl_2, however, it is *ca.* 1.30. (ii) No absorption band characteristic of I_3^- is observed at *ca.* 290 nm in spectra of the complex of 1,3-Me_2IT. If we assumed I_3^- to be formed in other imidazolethione–I_2 systems there would be no reason to disregard this assumption in the case of 1,3-Me_2IT, the more so as the formation constants of those complexes are of comparable magnitude.

The spectra of solutions with constant donor (IT and 1,3-Me_2IT) concentration and varying concentration of iodine are shown in Figure 2. The development of the CT band and the simultaneous decrease in the intensity of the donor absorption band are clearly seen together with two isosbestic points. The

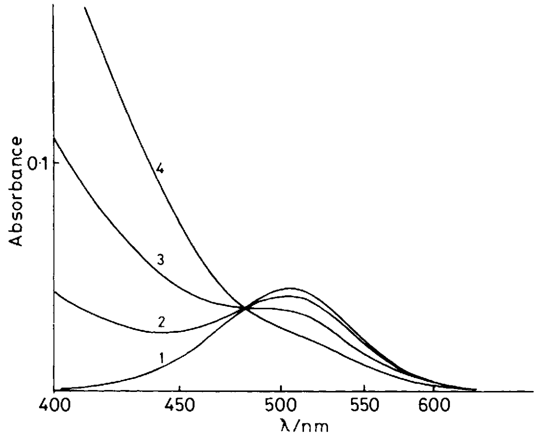

Figure 3. Effect of varying donor concentration on visible absorption spectra of imidazole-2-thione–iodine complex in CH_2Cl_2. $[I_2]$ 6.0×10^{-5}M. Concentration of IT: 1, 0.0; 2, 2.34×10^{-5}M; 3, 4.68×10^{-5}M; 4, 9.36×10^{-5}M

blue-shifted band of complexed iodine is located at *ca.* 430 nm (431.8 nm for IT as shown by higher order derivative spectrophotometry) and can be seen as a more or less pronounced shoulder on the CT band. For solutions of constant iodine concentration and different concentrations of donor a set of spectra were obtained in the visual region with an isosbestic point observed between free and complexed iodine bands (Figure 3).

The stoicheiometry of imidazolethione–I_2 complexes was established by Job's method of continuous variation and by the mole ratio method as 1:1. The single isosbestic point located between free and complexed iodine bands lends additional support for the estimated ratio.

Formation constants, K_c, were determined by measuring the absorbance for series of five solutions with varying concentration of imidazolethione and constant iodine concentration. Since the CT band at the wavelength of its maximum absorption overlaps in part the band of uncomplexed donor (except 1,3-Me_2IT where no overlap takes place) the readings were made at three different wavelengths (425, 430, and 435 nm) in the region of the blue-shifted iodine band. The latter overlaps the end portion of the CT band but since the absorption of both is linearly related to complex concentration, they do not need to be separated. For the calculation of formation constants the modification (1) of the Benesi–Hildebrand equation proposed by Lang[1] was used. In equation (1) [D] is the initial concentration of donor, $[I_2]$ is the initial

$$\frac{[D][I_2]}{ABS} = \left([D] + [I_2] - \frac{ABS}{\varepsilon}\right)\frac{1}{\varepsilon} + \frac{1}{K_c\varepsilon} \qquad (1)$$

concentration of iodine, ABS is the measured absorbance, and ε is the molecular absorption coefficient at a given wavelength. The iterative procedure of solving the equation for ε by the least-squares method was repeated until the two successive ε values differ by less than unity. In order to estimate the thermodynamic parameters the equilibrium measurements were carried out at three different temperatures: 5, 15, and 25 °C in methylene dichloride and 15, 25, and 35 °C in carbon tetrachloride solutions. Calculated formation constants and thermodynamic parameters of imidazolethione–iodine complexes in both solvents are shown in the Table. Since formation constants were determined from shifted iodine bands and since the two imidazolethione tautomers will complex to different extents with iodine, those constants give only information on the overall complexing of iodine by both tautomers and do not show the contribution of individual forms to complex formation. However, it is seen clearly that the alkyl groups in the imidazole ring, increasing the electron-donating ability of the sulphur atom, also increase the stability of the complex. The effect of the number and location of alkyl substituents as well as the decreasing effect of aryl groups on complex formation indicate the inductive nature of their influence. Formation constants are considerably higher in methylene dichloride than in carbon tetrachloride and show the highly polar character of the complexes. The increase in K_c values when changing to more polar solvents has also been observed with other very strong complexes[9–11] as a result of solvent stabilization of the complex dipole.

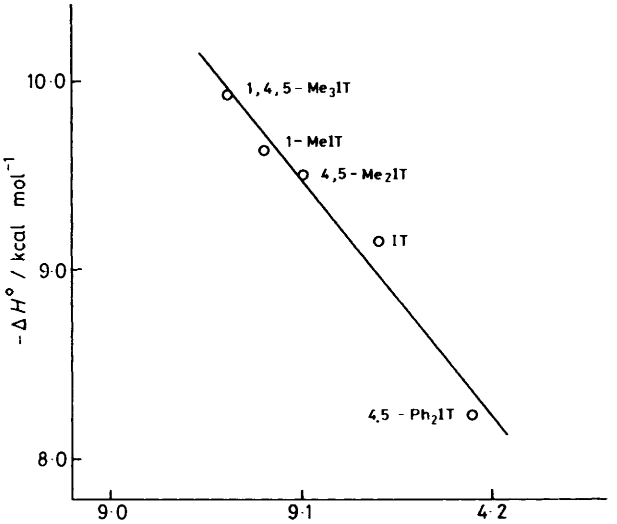

Figure 4. Plot of the frequency of the CT band maximum against the enthalpy of formation of imidazolethione–iodine complexes in methylene dichloride

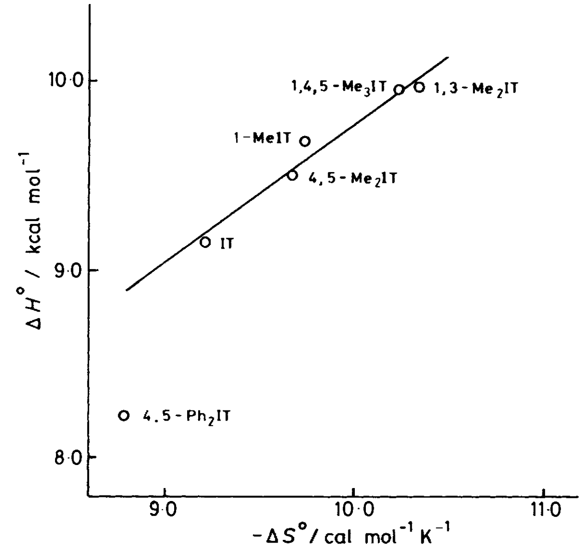

Figure 5. Relation between ΔH° and ΔS° for the imidazolethione–iodine complexes in methylene dichloride

The relationship between the enthalpy of formation of a complex and the frequency of a charge-transfer band, $h\nu_{CT}$, is, as expected, a regularly increasing function of those two parameters, being almost linear for the limited range of studied donors (Figure 4). The linearity of a relationship between ΔH° and ΔS° is not so satisfactory unless we ignore the point for 4,5-Ph_2IT which is evidently out of line (Figure 5). Nevertheless, there is a definite tendency for ΔH° to increase with increasing ΔS°. It should be pointed out that the ratio of the thiol–thione tautomers may depend on the temperature and that such a dependence of formation constants may be different for two tautomers. Hence, the observed temperature dependence of the estimated overall formation constants reflects in a rather complicated way the enthalpy changes associated with tautomer equilibrium and with the charge-transfer-complex equilibria between each of the two tautomers and iodine. A full interpretation of these relationships requires data on tautomeric equilibria and details about the contribution of both tautomers to complex formation.

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