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Weak Complexes of S and Se: Interaction and Complex Formation of Iodide Ions with Some Arenesulfonyl Chlorides

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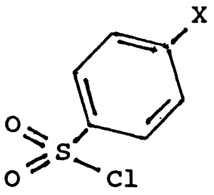
Mixtures of arylsulfonyl compounds with iodide ions were investigated in acetonitrile. They gave rise to 1 : 1 yellow coloured complex species which absorbed at 286 and 360 nm. The appearance of the yellow species is time dependent and is first order in [I^-] and in [sulfur compound] and has an E_a^* ranging from 10–20 kcal. When mixtures were left for longer periods an equilibrium was reached and the formation constants for benzenesulfonyl chloride, *p*-methoxy, *p*-toluene, 4-bromo and 4-chloro were determined with iodide ions over range of temperatures (5°–35°C). The thermodynamic parameters of the complex species agree with those of charge transfer complexes. Chloride and bromide ions react with the yellow species to give the original reactants.

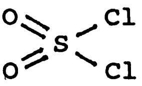
INTRODUCTION

The tendency for complex formation between sulfur bearing compounds and iodide ions was established for the following sulfur compounds: SO_2, $SOCl_2$, $SOBr_2$ and SO_2Cl_2. They form weak charge transfer complexes and their standard enthalpies and free energies of formation vary between 2–5 kcal/mol[1].

The arysulfonyl compounds selected for this work have the general formula (I), which bears resemblance to that of sulfonyl chloride (II).



(I)



(II)

The substituent groups (X) represent varying values of Hammett's σ_{p-x} constant, Table 1.

The present work aims to probe possibilities of complex formation and/or interaction between derivatives of Table 1 and I^- ions.

TABLE 1

SUBSTITUENT GROUP (X) AND σ_{p-x} VALUES

	I_a	I_b	I_c	I_d	I_e
X	$-OCH_3$	$-CH_3$	H	$-Br$	$-Cl$
σ_{p-x}	-0.27	-0.17	0	$+0.23$	$+0.23$

RESULTS AND DISCUSSION

Table 2 shows the initial rates for the appearance of the yellow species when derivatives of Table 1 are mixed with I^- ions.

TABLE 2

Derivatives	I_a	I_b	I_c	I_d	I_e
10^7 R mol/L_{min}	2.2	3.2	6.5	14.4	16.5

Mixtures of the above compounds with iodide ions in acetonitrile showed the following features:

1. Their reaction profiles with iodide ions are similar. Peaks for the reactants in the region 230–250 nm (I^- absorbs at 247 nm in MeCN) of the spectrum disappear gradually with time. At the same time the peaks of the yellow species emerge at 286 and at 360 nm. A single isobestic point exists at 265 nm as shown in Fig. 1 (a) and (b).
2. Absorbance peaks for reactants and for the yellow species reach a constant value and remain unchanged for a long time which may be a further indication for the existence of a state of equilibrium between the yellow species and the reactants for the compounds investigated.

Job's method of continuous variation[2] was used to find the stoichiometry of the yellow species. Mixtures of the sulfur compounds and iodide ions were prepared in acetonitrile. Mole fractions of reactants were varied between 0.9 and 0.1. Table 3 includes the absorbances of different mixtures at 360 nm.

TABLE 3

ABSORBANCES OF MIXTURES OF I_b, I_c AND I_d WITH I^- IN MeCN

Mole fraction for I^-	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1
Compd. I_b	0.068		0.192	0.197		0.181			0.061
Compd. I_c		0.055	0.096		0.100	0.072		0.063	
Compd. I_d	0.190		0.355		0.440		0.330		0.120

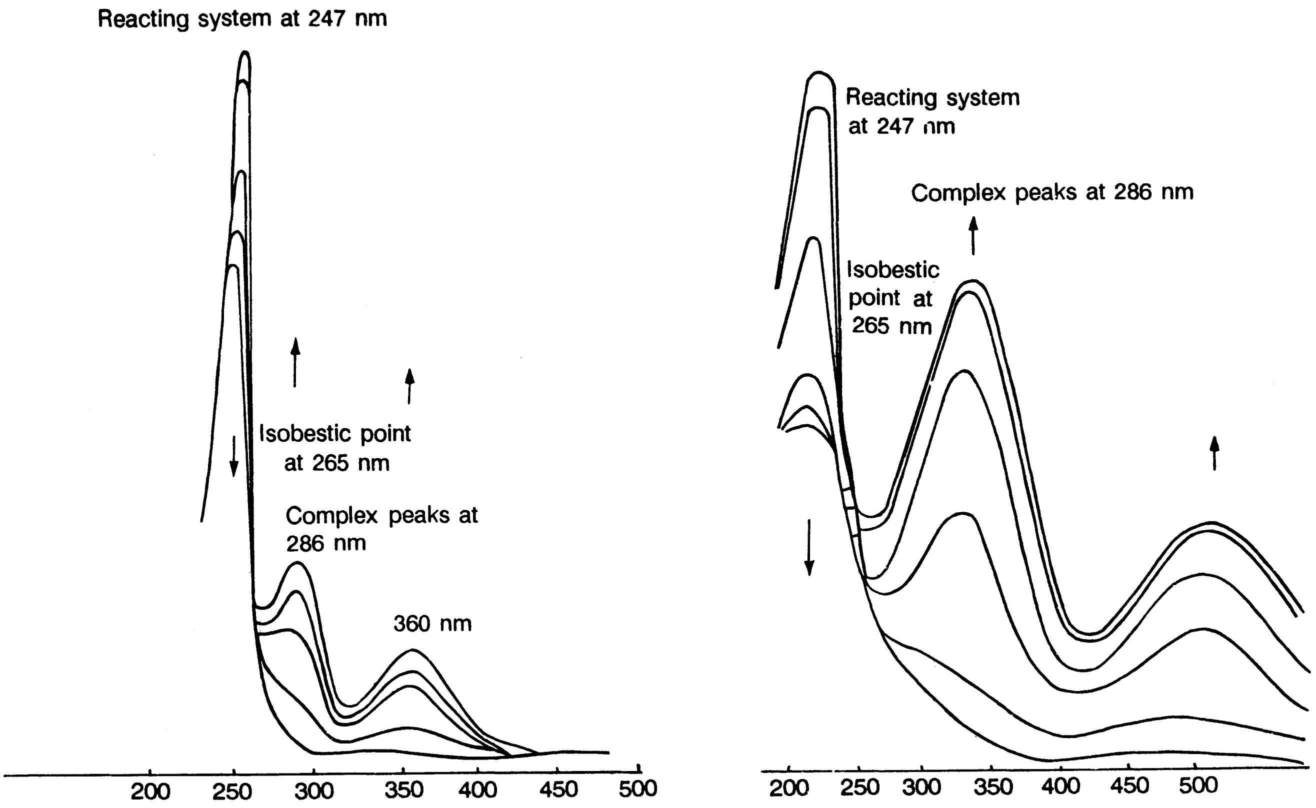
The absorbance data in Table 3 show that a maximum appears for the 0.5 mole fraction mixture which confirms the 1:1 nature of the yellow species.

This behaviour is similar to that found for the complex species between the iodide ions and inorganic sulfur compounds[1].

By analogy we may consider the yellow species from interaction of the aromatic compounds and iodide ions a 1:1 complex species.

Stability Constants for the Complex Species of Compounds I_a–I_e and Their Thermodynamic Parameters

Mixtures of I_a–I_e with iodide ions were prepared in acetonitrile. The



(a) Time interval 2 days

(b) Time interval 1 day

Fig. 1 Profile for (a) $S_B + I^-$ reaction, (b) $S_H + I^-$ reaction concentration of iodide ions was always greater than that of the sulfur compounds. For all mixtures investigated, the concentration of I_a–I_e was in the order 2–5 × 10^{-5} and the ratio $[I^-]/[S]$ was varied a wide range in which $[I^-] >> [S]$ to ensure the existence of one species, a 1:1 species, in the system[3–5] Mixtures were kept at room temperature and in absence of light. Their spectra were recorded at 360 and 286 nm until constant absorbance was reached. The treatment of spectral data was done graphically by Benesi-Hildebrand[6] and Scott-Foster[7] equations to calculate the formation constant K_c of the complex species. The calculation method was carried out by determining $[\text{Complex}]_e$ at equilibrium and also $[S]_e$ & $[I^-]_e$ from the E_c value for the complex species evaluated graphically. The formation constant was thus calculated for each experimental solution by equation

$$K_c = [\text{Complex}]_e/[S]_e[I^-]_e$$

The K_c data for *p*-toluenesulfonyl chloride-iodide system calculated from absorbance at 360 nm and over the temperature range 5–25°C is given in Table 4.

TABLE 4
EQUILBRIUM DATA AND THERMODYNAMIC PARAMETERS FOR THE *p*-TOLUENESULFONYL CHLORIDE-IODIDE SYSTEM

Solution:	1	2	3	4	5	6	7
10^5(S) mol L^{-1}	2.0	2.0	2.0	2.0	2.0	2.0	2.0
$10^3(I^-)$ mol L^{-1}	8.0	12.0	20.0	24.0	32.0	40.0	48.0
Absorbance at 360 nm:							
5°C	0.410	0.480	0.555	0.585	0.600	0.618	
15°C	0.380	0.440	0.520	0.569	0.575	0.625	0.648
20°C	0.346	0.423	0.510	0.553	0.564	0.602	0.610
25°C	0.310	0.380	0.478	0.546	0.546	0.590	0.619

$E_c = 3.7 \times 10^4$ L mol^{-1} cm^{-1}

Formation Constants:

K_c (L mol^{-1})

	Law of Mass Action								Graphical			
								Mean	B–H	S–F	Mean	K_c
At 5°C	155.5	153.9	150.0	157.3	133.3	126.6	Mean	146.1	155.2	163.2	Mean	154.8 ± 5.7
At 15°C	132.2	122.3	118.2	137.5	109.0	135.8	146.5	128.7	135.0	139.0		134.3 ± 3.6
At 20°C	109.9	111.3	110.9	123.4	100.0	109.1	97.3	108.9	110.0	115.0		111.3 ± 3.1
At 25°C	84.2	93.6	91.3		87.9	95.7	85.2	87.3	88.5	91.0		88.9 ± 1.3

Thermodynamic Constants:

$\Delta G_f^0 = -2.641$ kcal/mol; $\Delta H_f^0 = -4.219$ kcal/mol; $\Delta S_f^0 = -5.3$ cal $K^{-1}mol^{-1}$

Table 5 summarises all K_c data evaluated by both methods graphically and calculation at 25°C and the thermodynamic constants for the formation of the different species.

In most cases difference in K_c values between the graphical and calculation methods does not exceed ±3% and this may be taken as the limit of experimental error.

TABLE 5
SUMMARY OF K_c^* DATA AND THERMODYNAMIC CONSTANTS OF THE $S_{compound}$- I^- SPECIES IN ACETONITRILE AT 25°C

Species	I_a	I_b	I_c	I_d	I_e
K_c (Graphical)	53.9	88.9	252.4	639.0	777.0
K_c (Calculation)	53.9	87.3	258.5	629.0	789.0
$-\Delta G_f°$ kcal/mol	2.36	2.64	3.28	3.83	3.94
$-\Delta H_f°$ kcal/mol	4.59	4.22	3.62	3.46	3.46
$-\Delta S_f°$ cal/K/mol	7.48	5.30	1.15	–1.2	–1.6
σ_{p-x}	–0.27	–0.17	0	+0.23	+0.23

*L mol^{-1}

Discussion of the K_c Data

A. The Nature of the Complex Species

The formation constants values given in Table 5 are higher than those reported for the inorganic sulfur compounds[1] indicating stronger coordination.

Compounds I_a–I_e exhibit inuictive and mesomeric effects which give rise to a residual charge δ+ on the sulfur atom. This makes it a suitable acceptor site for coordination with I^- ligands[8–11]. The K_c values suggest strongest coordination for –Cl and weakest coordination for $-OCH_3$ and an intermediate value for the unsubstitued derivative (H). The diversity of K_c values for the different complex species (Table 5) confirms the equilibrium shown by Eq. (1).

$$I^- + S \rightleftarrows SI^- \qquad (1)$$

A plot of $\Delta G_f°$ against the Hammett's function σ_{p-x} is linear as is expected from the effects of the substituent groups –Cl, –Br, $-CH_3$ and $-OCH_3$ on the coordinating power of the sulfur atom with I^- ligands[12]. Fig. 2 shows such linear free energy relation with slope = 3.

B. The Charge Transfer Nature of the Complex Species

A study of the temperature effects on the absorbance for the complex species shows analogies between the inorganic and organic complex species with I^- ions.

Table 5 includes the standard enthalpies of formation for the organic complex species. The values fall between 2–5 kcal/mol which are of the same order of magnitude as those reported for the inorganic sulfur complex species[1], and which are considered as charge transfer complexes[13–16].

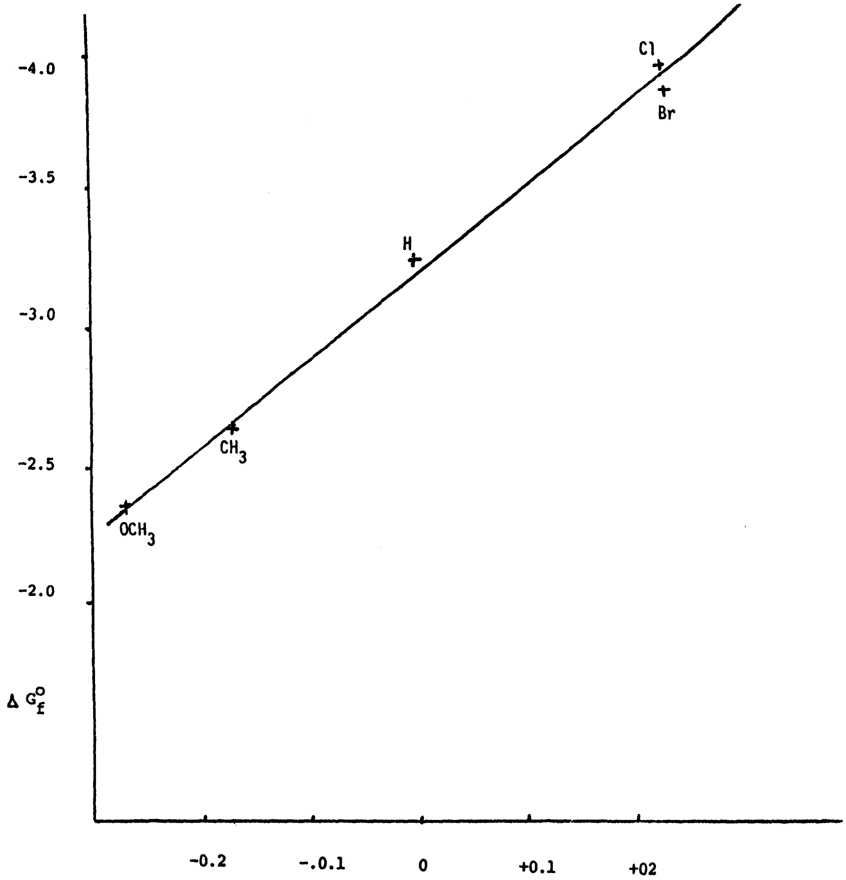


Fig. 2 Linear free energy relationship between ΔG_f^o for complex species and Hammett's σ_{P-X} for substitutions

Free energies of formation, ΔG_f°, being small and negative are characteristics of weak complexes that can only be detected in solution. They are easily affected by heat and by the addition of other ligands, such as Cl^- or Br^-, with higher donor numbers[1, 16]. Entropies of formation, ΔS_f°, as expected, are small and are mostly with negative values.

C. An Order for [S] and [I^-] in Eq. (1): Reaction Activation Energy E_0^*

The time dependent emergence of the complex peaks was made use of at 286 and 360 nm to establish the rate law for Eq. (1). Mixtures of I_c with iodide ions were used. The concentration of one reactant was kept constant while that of the other reactant was increased.

The E_c value was used to find the concentration of the complex species at different times and R was calculated in mol/L_{min}. Table 6 includes rate data at 298 K.

TABLE 6
DEPENDENCE OF REACTION RATE OF $I_c + I^-$ ON $[I_c]$ AND $[I^-]$ IN ACETONITRILE AT 298 K

	(a) $[I^-] = 1.94 \times 10^{-2}\ ML^{-1}$			
$10^4[I_c]\ ML^{-1}$	1.94	3.88	5.82	7.76
$10^7\ R\ mol/L_{min}$	2.25	4.62	6.86	9.53
	(b) $[I_c] = 1.33 \times 10^{-2}\ ML^{-1}$			
$10^4[I^-]\ ML^{-1}$	5.0	7.5	10.0	12.5
$10^7\ R\ mol/L_{min}$	2.25	4.36	4.95	6.18

The rate data in Table 6 fall on a straight line which passes through the origin confirming first order dependence for each reactant and giving a second order rate law: $R = k[S][I^-]$ which supports the stoichiometry of equation 1.

Similar experiments have shown that the other sulfur compounds follow the same rate law.

Table (7) includes the $E_0^{\neq}$ data for all the compounds studied in the present work over the temperature range 278–308 K at a unified concentration of $[I^-] = 0.01\ ML^{-1}$ and $[S] = 0.002\ ML^{-1}$.

TABLE 7
ACTIVATION ENERGY $E_a^{\neq}$/HAMMETT FUNCTION $\sigma_{p\text{-}x}$ CORRELATIONS FOR $I_{a-e} + I^-$ REACTION

Derivative (X)	$-OCH_3$	CH_3	H	Cl	Br
$E_a^{\neq}$ kcal	15.97	15.02	14.01	13.27	12.67
$\frac{E_a^{\neq}(X)}{E_0^{\neq}(H)}$	0.0567	0.0302	0.000	–0.0236	–0.0435

Comparison of the data in Table 7 shows that the compounds investigated exhibit parallel gradation between their rates (Table 2) and their activation energies. Slower derivatives needed higher energies. The unsubstituted is half way in this series.

EXPERIMENTAL

Absorbances were recorded by a Hewlett Packard 8451A Diode Array spectrophotometer with matched thermostatted S–Q cells. Chemicals from Aldrich, solutions prepared by standard analytical procedures. Reaction mixtures were kept in sealed flasks, in absence of light for several weeks to ensure attainment of equilibrium. Duplication was a standard procedure.

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