Weak Complexes of Sulphur and Selenium. Part II.[1] Complex Species of SO_2, $SOCl_2$, and SO_2Cl_2 with the Thiocyanate Ligand

By **Saad Wasif,*** Department of Chemistry, Faculty of Science, University of Libya, Tripoli, Libya
S. B. Salama, Department of Chemistry, Faculty of Science, University of Khartoum, Sudan

The formation of 1 : 1 complex species between SO_2, $SOCl_2$, and SO_2Cl_2 with the SCN^- ligand is reported in dilute solutions. Their thermodynamic constants point to a weak association of a charge-transfer type. The nature of the complex species is discussed in relation to polarisability and basicity of the SCN^- ligand.

SEVERAL studies were reported on the interaction of the SCN^- ligand with SO_2, $SOCl_2$, and SO_2Cl_2 acceptors. Charge-transfer species between SCN^- and SO_2 have been reported both in solution and in the solid state. Lippincott and Welch[2] pointed out that the spectra of $SCN,4SO_2$ indicate a charge-transfer interaction. Others studied the $NaSCN,SO_2$,[3] $KSCN,SO_2$,[3] $CsSCN,SO_2$,[4] and $RbSCN,SO_2$[5] systems. An interaction energy of *ca.* 9·56 kcal mol^{-1} was reported for all systems.

Foote and Fleischer[3] determined an enthalpy of dissociation for $KSCN,4SO_2$ from vapour-pressure relations in the two-component system to be 9·77 kcal mol^{-1} which, when compared with the enthalpy of vaporisation of SO_2 (5·95 kcal mol^{-1}) gives *ca.* 3·82 kcal mol^{-1} for the enthalpy of interaction in the charge-transfer species (1 cal = 4·184 J). Jander and Mesech[6] studied the interaction of NH_4SCN with $SOCl_2$ and reported the formation of thionyl thiocyanate species $SO(SCN)_2$. Dixon[7] reported the same species from mercuric thiocyanate and thionyl chloride in various solvents. Forbes and Anderson[8] prepared sulphur monothiocyanate $S_2(SCN)_{2x}$, thionyl thiocyanate $SO(SCN)_{2x}$, and sulphuryl thiocyanate $SO_2(SCN)_{2x}$ by refluxing S_2Cl_2, $SOCl_2$, and SO_2Cl_2 with AgSCN in benzene.

To explore the nature of these species we restricted this study to dilute solutions in which one complex species was detectable which had the general formula X,SCN^- ($X = SO_2$, $SOCl_2$, or SO_2Cl_2), *i.e.*, 1 : 1 type. This made our correlations favourable as species of similar general formulae could be compared and differences and gradations in stabilities noticed.

EXPERIMENTAL

Detection of the Complex Species.—Table 1 includes the absorbance peaks of equimolar mixtures of SO_2, $SOCl_2$, and SO_2Cl_2 with KSCN in acetonitrile. Similar peaks were obtained in dimethyl sulphoxide. The same peaks were obtained when tetraethylammonium and trimethylsulphonium thiocyanate were used in place of KSCN. This confirmed that the new spectra resulted from the interaction of the SCN^- ligand with SO_2, $SOCl_2$, and SO_2Cl_2.

Stoicheiometry of the Complex Species.—Job's[9] method was adopted. The data for SO_2,SCN^- in Table 2 show that the complex species is of 1 : 1 type in our conditions. Complex species with $SOCl_2$ and SO_2Cl_2 give similar results.

TABLE 1

Absorption spectra of mixtures of SCN^- with SO_2, $SOCl_2$, and SO_2Cl_2 in acetonitrile

	Absorption peaks, $\lambda_{max.}$/nm		
	Donor	Acceptor	Mixture
SO_2,SCN^-	210	280	345
$SOCl_2,SCN^-$	210	280	350
SO_2Cl_2,SCN^-	210	275	350

TABLE 2

Stoicheiometry of SO_2,SCN^- species by Job's method

$[SO_2] = 0{\cdot}003$M [KSCN] = 0·003M

Mixtures	1	2	3	4	5
Volume of SO_2 soln./ml	0·5	1·0	1·25	1·5	2·0
Volume of KSCN soln./ml	2·0	1·5	1·25	1·0	0·5
Volume of acetonitrile/ml	2·5	2·5	2·5	2·5	2·5
Mol fraction of SO_2	0·2	0·4	0·5	0·6	0·8
d_{obs}	0·05	0·08	0·10	0·07	0·04

No attempt was made to determine the true molecular formula by Asmus's method[10] as this was found unnecessary.

Evaluation of Stability Constants of Complex Species.—The complex species are formed between a polar molecule (such as SO_2) and a pseudohalide ion and this required that all the spectra be studied in a polar solvent. Other solvents can be used but acetonitrile was preferred so that our results could be compared with those for halide ions with the same acceptors which were also studied in acetonitrile.

All the complex species had $\lambda_{max.}$ 345—350 nm. Over this spectral range the SCN^- ligand had no absorbance but sulphur compounds had, and the spectral data were treated graphically by the Ketelar[11] equation (1), where E_a = the

$$\frac{1}{E_a - E_A} = \frac{1}{K_c[SCN]_0(E_c - E_A)} + \frac{1}{E_c - E_A} \quad (1)$$

observed extinction of the experimental solution and equals $d_{obs}/[\text{S compound}]_0$; E_A = the extinction of the sulphur compound at $\lambda_{max.}$ of the complex; E_c = the

---

[1] Part I, A. Salama, S. B. Salama, M. Sobeir, and Saad Wasif, *J. Chem. Soc.* (*A*), 1971, 1112.

[2] E. R. Lippincott and F. E. Welch, *Spectrochim. Acta*, 1961, **17**, 123.

[3] E. R. Foote and Fleischer, *J. Amer. Chem. Soc.*, 1932, **54**, 3902.

[4] G. Jander and H. Mesech, *Z. phys. Chem.*, 1938, **183**, *A*, 121, 137.

[5] F. Ephriam and J. Kornblum, *Ber.*, 1916, **49**, 2007.

[6] G. Jander, ' Die Chemie in Wasseranlichen Losungmitteln,' Springer-Verlag, Berlin, 1949.

[7] E. A. Dixon, *J. Chem. Soc.*, 1901, **79**, 541.

[8] G. D. Forbes and H. H. Anderson, *J. Amer. Chem. Soc.*, 1943, **65**, 2271.

[9] P. Job, *Ann. Chim.*, 1928, **10**, 113.

[10] E. Asmus, *Analyt. Chem.*, 1960, **178**, 104.

[11] J. A. A. Ketelar, C. van de Stoppe, A. Goudsmit, and W. Dzcubas, *Rec. Trav. chim.*, 1952, **71**, 1104.

extinction of the complex species (all E values in l mol^{-1} cm^{-1}); K_c = the stability constant/l mol^{-1}, and $[\mathrm{SCN}^-]_0$ = the initial concentration of the SCN$^-$ ligand in mol l^{-1}.

TABLE 3

Evaluation of K_c for SO_2Cl_2,SCN$^-$ species in acetonitrile at 15 and 25 °C

Solution	1	2	3
$10^5[SO_2Cl_2]_0$/M	9·661	9·661	9·661
$10^3[SCN^-]_0$/M	4·704	7·056	9·408
d_{obs} at 15 °C	0·108	0·120	0·130
d_{obs} at 25 °C	0·097	0·110	0·120

E_c = 1663 l mol^{-1} cm^{-1}
K_c = 409·6 (15 °C), 299·2 (25 °C) l mol^{-1} (graphically)

10^5C_c/mol l^{-1} (15 °C)	6·439	7·111	7·683
K_c/l mol^{-1} (15 °C)	413·1	399·2	415·9
10^5C_c(mol l^{-1} (25 °C)	5·650	6·476	7·111
K_c/l mol^{-1} (25 °C)	303·2	290·8	298·6

$E(SO_2Cl_2)$ = 88 l mol^{-1} cm^{-1} at 350 nm or d = 0·008 for 9·661 × 10^{-5}M-solution

TABLE 4

Evaluation of K_c for $SOCl_2$,SCN$^-$ species in acetonitrile at 15, 25, and 35 °C

Solution	1	2	3	4
$10^4[SOCl_2]_0$/M	4·435	4·436	4·436	4·435
$10^3[SCN^-]_0$/M	2·000	4·000	6·000	8·000
d_{obs} at 15 °C	—	0·360	0·455	0·550
d_{obs} at 25 °C	0·250	0·320	0·412	0·500
d_{obs} at 35 °C	0·220	0·270	0·360	0·410

E_c = 2911 l mol^{-1} cm^{-1}
K_c = 89·8 (15 °C), 76·1 (25 °C), and 59·3 (35 °C) l mol^{-1} (graphically)

10^4C_c/(mol l^{-1} (15 °C)	—	1·176	1·544	1·841
K_c/l mol^{-1} (15 °C)		92·9	91·3	90·8
10^4C_c/mol l^{-1} (25 °C)	—	1·036	1·358	1·666
K_c/l mol^{-1} (25 °C)		78·2	75·3	76·9
10^4C_c/mol l^{-1} (35 °C)		0·861	1·176	1·351
K_c/l mol^{-1} (35 °C)		61·5	61·3	55·7

$E(SO_2Cl_2)$ = 54 l mol^{-1} cm^{-1} at 350 nm
or d = 0·024 for a 4·436 × 10^{-4}M-solution

TABLE 5

Evaluation of K_c for SO_2,SCN$^-$ species in acetonitrile at 15, 25, and 35 °C

Solution	1	2	3	4
$10^3[SO_2]_0$/M	2·599	2·599	2·599	2·599
$10^3[SCN^-]_0$/M	2·000	4·000	6·000	8·000
d_{obs} at 15 °C	0·330	0·510	0·670	0·820
d_{obs} at 25 °C	0·278	0·448	0·600	0·743
d_{obs} at 35 °C	—	0·390	0·525	0·655

E_c = 874 l mol^{-1} cm^{-1}
K_c = 71·8 (15 °C), 59·7 (25 °C) and 50·0 (35 °C) l mol^{-1} (graphically)

10^4C_c/mol l^{-1} (15 °C)	—	5·748	7·586	9·311
K_c/l mol^{-1} (15 °C)		82·9	78·7	77·9
10^4C_c/mol l^{-1} (25 °C)	—	5·035	6·782	8·426
K_c/l mol^{-1} (25 °C)	—	68·7	66·3	67·1
10^4C_c/(mol l^{-1} (35 °C)	—	4·368	5·920	7·415
K_c/l mol^{-1} (35 °C)	—	56·7	54·6	55·0

$E(SO_2)$ = 4 l mol^{-1} cm^{-1} at 345 nm
or d = 0·01 for a 2·599 × 10^{-3}M-solution.

Equation (1) implies that the plot of $1/(E_a - E_A)$ against $1/[SCN^-]_0$ is a straight line with intercept $1/(E_c - E_A)$ and slope $1/K_c(E_c - E_A)$. Tables 3—5 include the data. Equation (2) was also used [1] to compute K_c for the same

$$K_c = C_c/[A]_{eqb}[D]_{eqb} \qquad (2)$$

complex species and the data are in Tables 3—5. Here C_c, $[A]_{eqb}$, and $[D]_{eqb}$ are the equilibrium *molar concentrations* of the complex species, the acceptor, and the donor and $[A]_{eqb} = [A]_0 - C_c$ and $[D]_{eqb} = [D]_0 - C_c$. Table 6 summarises all the mean K_c data by the two methods at different temperatures. For $SOCl_2$,SCN$^-$ and SO_2Cl_2-SCN$^-$ the error limit did not exceed ±1% [by equations (1) and (2)] but in SO_2,SCN$^-$ it was ±2%. The constancy of K_c [by equation (2)] is further evidence that all the complex species investigated under our conditions were of 1 : 1 type.

TABLE 6

Summary of K_c data for SCN$^-$ complex species

	K_c/l mol^{-1}*		
	15 °C	25 °C	35 °C
SO_2,SCN$^-$	77·8 ± 1·5	65·4 ± 1·5	54·1 ± 1·0
$SOCl_2$,SCN$^-$	91·2 ± 0·4	76·6 ± 0·4	59·4 ± 0·9
SO_2Cl_2,SCN$^-$	409·4 ± 2·6	297·9 ± 1·8	—

* A mean value is taken for data from equations (1) and (2).

The data in Table 6 were used to determine $\Delta G°$, $\Delta S°$, and $\Delta H°$ (Table 7) for the formation of the complexes and they point to a weak association of a charge-transfer type.

TABLE 7

Thermodynamic constants of the complex species in acetonitrile

	$-\Delta G°$ kcal mol^{-1}	$-\Delta H°$ kcal mol^{-1}	$-\Delta S°$ cal mol^{-1} K^{-1}
SO_2,SCN$^-$	2·4	3·3	2·7
$SOCl_2$,SCN$^-$	2·6	3·5	3·1
SO_2Cl_2,SCN$^-$	3·5	2·7	−2·5

Purification of materials, spectral measurements, and preparation of solutions were as before.[1] Most solutions were prepared immediately before the spectra were measured.

DISCUSSION

The complex species of the SCN$^-$ ligand with SO_2, $SOCl_2$, and SO_2Cl_2 are similar to those with halide ions under similar conditions.[1] Their stabilities will be discussed in relation to the complex species with halide ions, whose nature has been discussed.[1] All data are in Table 8. We summarise the factors thought responsible for the order of stabilities among halide ion complexes as: (1) The formation of the complex occurs as a result of Lewis acid–base interaction; (2) Cl$^-$, Br$^-$, and I$^-$ ions are three Lewis bases of varying strengths; (3) SO_2, $SOCl_2$, and SO_2Cl_2 molecules may be considered three

TABLE 8

Stability constants/l mol^{-1} in acetonitrile at 25 °C

X$^-$ =	Cl$^-$	Br$^-$	I$^-$	SCN$^-$
SO_2,X$^-$	372	160	38	65
$SOCl_2$,X$^-$	362	241	150	77
SO_2Cl_2,X$^-$	10	41	77	298

Lewis acids of increasing acceptor character; and (4), along with acid–base characters of the donors and acceptors, we find that the polarity of SO_2Cl_2 plays a very important role with the highly polarisable I^- ligand.

The Nature of the SCN^- *Complexes and the Role of Polarisability in Stabilising Them.*—Like halide ions, the SCN^- ligand is a soft Lewis base and the formation of the complex species can be attributed to acid–base interaction between acceptor and donor. The nature of this association can be understood from the gradation in stability constants shown in Table 8. We first consider the SO_2Cl_2,X^- species. Although acid–base interaction is responsible for their formation the sudden increase in stability from SO_2Cl_2,I^- to SO_2Cl_2,SCN^- indicates a progressive increase in ion–dipole (donor–acceptor) interaction owing to the greater polarisability of SCN^- than I^-. Other factors which might account for this sudden change, such as solvation, are not supported by our thermodynamic data.

For SO_2,X^- complexes the order of K_c for the halide ligands is attributed mainly to back-donation [1] and the high stability constants of SO_2,Cl^- and SO_2,Br^- are evidence of its role. The lower stability constant of SO_2,I^- shows a minor role for back-donation and a larger one for polarisability. A higher K_c for SO_2,SCN^- than for SO_2,I^- is evidence that SCN^- is more polarisable than the I^- ligand which promotes stronger ion–dipole interaction.

K_c for the $SOCl_2,X^-$ species decreases for Cl^- and Br^- complexes (relative to SO_2,X^-) and increases for I^- and SCN^- ligands. This trend suggests that polarisability plays an increasingly greater part in stabilising the species $SOCl_2,I^-$ and $SOCl_2,SCN^-$. The order of stability $SO_2Cl_2,SCN^- \gg SOCl_2,SCN^- > SO_2,SCN^-$ shows a maximum interaction with SO_2Cl_2. The high dipole moment of SO_2Cl_2 (1·86 D) helps stronger ion–dipole interaction with the highly polarisable SCN^- ligand and thus accounts for the high stability constant of SO_2Cl_2,SCN^-. Polarisability is thus the main factor influencing K_c.

[3/549 *Received*, 15*th March*, 1973]