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Spectrophotometric Study of the Reversible Iodine-thiocyanate Interaction

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The reversible iodine-thiocyanate interaction was studied spectrophotometrically. The very fast reversible process could be completely separated from the rapid, but relatively slower, irreversible reaction by means of the stopped-flow technique. It was found that the only product of the reversible iodine-thiocyanate interaction is the charge-transfer complex I_2SCN^-*, and* $I(SCN)_2^-$ *is not formed. The stability constant of* I_2SCN^- *at 25°C was found to be* 53.3 ± 6.5 *l.mol*$^{-1}$*, while its molar absorptivity at 302 nm was* $(4.62 \pm 0.20) \times 10^4$ *l.mol*$^{-1}$ *cm*$^{-1}$*.*

Introduction

During the study of the mechanism of the thiocyanate ion-catalysed iodine-azide reaction there arose the problem of the interaction between the iodine and the thiocyanate ion. The iodine-thiocyanate interaction consists of two processes. The formation of a charge-transfer complex (presumably of the type I_2X^-) must be considered in the first, reversible step. This very fast process is followed by an irreversible redox process, which is relatively slow compared with the former step, but is nevertheless still fairly fast.

The irreversible iodine-thiocyanate reaction was studied first by Griffith and McKeown,[1] who suggested the possibility of the formation of I_2SCN^- and ISCN as intermediates. In order to slow down the irreversible redox processes and to ensure a trouble-free study of the reversible iodine-thiocyanate interaction, Lewis and Skoog[2] used reduced temperatures (1-15°C) and worked in strongly acidic solution.

In the present work we were able to separate these two fast processes completely by using the stopped-flow technique, and hence we were able to study the reversible iodine-thiocyanate interaction independently of the irreversible redox processes.

Experimental Section

I_2 (sublimed from CaO and from KI) and KI (p.a.) were Reanal products. NaSCN (Reanal) was purified by repeated recrystallization from water and methanol. $NaClO_4$ was prepared from NaOH (Reanal) and $HClO_4$ (Apolda) by neutralization. The concentration of the NaSCN solution was determined by the Volhard method, and that of the iodine solution spectrophotometrically.

For the spectrophotometric measurements on a Hitachi-Perkin-Elmer 139 UV-VIS single-beam spectrophotometer was used, an attached fast-mixer being employed in the stopped-flow technique. A KI solution of iodine was mixed in the fast-mixing chamber with an equal volume of an NaNCS solution. The time required for the mixing of the two solutions and for the reaction mixture to reach the cell was 0.2 sec, about three-four orders of magnitude smaller than the half-time of the irreversible reaction. The composition of the reaction mixture flowing through the cell was determined by the reversible iodine-thiocyanate interaction; the disturbing effect of the irreversible reaction need not be considered 0.2 sec after the mixing of the components, because these equilibria are established in a much shorter time than this.

The measurements were made at 302 and 353 nm. At 353 nm I_3^- has an absorption maximum, and at 302-303 nm the charge-transfer complexes between I_2 and SCN^-, and in addition the equality $\varepsilon_{I_3^-}^{302} \cong \varepsilon_{I_3^-}^{353}$ permits the evaluation according to equations (7), (11), and (12).

Results and Discussion

The experimental results, and also the absorbance values *calculated* from the molar absorptivity and stability constant determined by us, are contained in Table I-III.

In a reaction mixture containing iodine, iodide and thiocyanate, we have assumed the equilibria (1) and (2):

$$I_2 + SCN^- \rightleftharpoons I_2SCN^- \quad (K_1) \tag{1}$$

$$I_2 + I^- \rightleftharpoons I_3^- \quad (K_2) \tag{2}$$

The calculations were carried out on the basis of the mass-balance:

$$T_{I_2} = [I_2] + [I_3^-] + [I_2SCN^-]$$

and equations (3) and (4):

$$\frac{A^{302}}{d} = \varepsilon_{I_3^-}^{302} \cdot [I_3^-] + \varepsilon_{I_2SCN^-}^{302} \cdot [I_2SCN^-] \tag{3}$$

$$\frac{A^{353}}{d} = \varepsilon_{I_3^-}^{353} \cdot [I_3^-] + \varepsilon_{I_2SCN^-}^{353} \cdot [I_2SCN^-] \tag{4}$$

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(1) R.O. Griffith and A. McTown, *Trans. Faraday Soc.*, *31*, 875 (1935)
(2) C. Lewis and D.A. Skoog, *J. Amer. Chem. Soc.*, *84*, 1101 (1962).

Table I. Measured and calculated absorbance of a solution of composition $T_{I_2}=4.91\times10^{-5}$ mol.l^{-1}, $T_{I^-}=2.5\times10^{-3}$ mol.l^{-1}, $T_{HClO_4}=2\times10^{-4}$ mol.l^{-1} as a function of T_{SCN^-} (I=0.11 mol.l^{-1} with NaClO$_4$ 25 °C).

T_{SCN^-} . 10^2 mol.l^{-1}	A^{302}_{measd}	A^{302}_{calcd}	A^{353}_{measd}	A^{353}_{calcd}
0.99	0.521	0.480	0.359	0.360
1.98	0.600	0.601	0.327	0.325
2.97	0.666	0.663	0.301	0.298
3.96	0.714	0.710	0.277	0.277
4.95	0.747	0.749	0.260	0.260
5.94	0.770	0.782	0.250	0.246
6.93	0.813	0.808	0.243	0.234
7.92	0.833	0.831	0.218	0.224
8.91	0.848	0.850	0.211	0.216
9.90	0.860	0.867	0.202	0.208

Table II. Measured and calculated absorbance of a solution of composition $T_{I_2}=5.01\times10^{-5}$ mol.l^{-1}, $T_{I^-}=5.0\times10^{-3}$ mol.l^{-1}, $T_{HClO_4}=2\times10^{-4}$ mol.l.$^{-1}$ as a function of T_{SCN^-} (I=0.11 mol.l^{-1} with NaClO$_4$, 25°C).

T_{SCN^-} . 10^2 mol.l^{-1}	A^{302}_{measd}	A^{302}_{calcd}	A^{353}_{measd}	A^{353}_{calcd}
0.99	0.569	0.572	0.458	0.467
1.98	0.623	0.624	0.431	0.433
2.97	0.649	0.668	0.406	0.404
3.96	0.696	0.704	0.377	0.381
4.95	0.727	0.735	0.359	0.361
5.94	0.757	0.763	0.343	0.343
6.93	0.777	0.787	0.324	0.328
7.92	0.798	0.807	0.314	0.315
8.91	0.823	0.825	0.296	0.303
9.90	0.833	0.842	0.288	0.292

Table III. Measured and calculated absorbance of a solution of composition $T_{I_2}=4.96\times10^{-5}$ mol.l^{-1}, $T_{I^-}=7.5\times10^{-3}$ mol.l^{-1}, $T_{HClO_4}=2\times10^{-4}$ mol.l^{-1}, as a function of T_{SCN^-} (I=0.11 mol.l^{-1} with NaClO$_4$, t=25°C).

T_{SCN^-} . 10^2mol.l^{-1}	A^{302}_{measd}	A^{302}_{calcd}	A^{353}_{measd}	A^{353}_{calcd}
0.99	0.577	0.566	0.507	0.508
1.98	0.617	0.623	0.474	0.479
2.97	0.639	0.657	0.454	0.454
3.96	0.664	0.682	0.428	0.433
4.95	0.691	0.711	0.407	0.414
5.94	0.706	0.734	0.396	0.397
6.93	0.733	0.754	0.380	0.381
7.92	0.750	0.773	0.360	0.367
8.91	0.765	0.789	0.347	0.355
9.90	0.779	0.804	0.327	0.343

(*T* is the total added concentration, *d* is the light pathlength of the cell. The absorbance of iodine at both wavelengths is negligibly small.) From the measurements made by Daniele,[3] for the reaction conditions we used $K_2 = 723$ l.mol^{-1}, which was confirmed by us. Considering that $T_{I_2} \ll T_{I^-} < T_{SCN^-}$, the experimental data obtained at 302 nm and at 353 nm are evaluated with equations (5) and (6), respectively:

$$\left\{\frac{A^{302}}{dT_{I_2}}\cdot(1+K_2T_{I^-})-\varepsilon^{302}_{I_3^-}\,.\,K_2T_{I^-}\right\}\cdot\frac{1}{T_{SCN^-}}=$$

$$=\varepsilon^{302}_{I_2SCN^-}\,.\,K_1-K_1\,.\,\frac{A^{302}}{dT_{I_2}} \qquad (5)$$

$$\left\{\frac{A^{353}}{dT_{I_2}}\cdot(1+K_2T_{I^-})-\varepsilon^{353}_{I_3^-}\,.\,K_2T_{I^-}\right\}\cdot\frac{1}{T_{SCN^-}}=$$

$$=\varepsilon^{353}_{I_2SCN^-}\cdot K_1-K_1\cdot\frac{A^{353}}{dT_{I_2}} \qquad (6)$$

The data obtained at the two wavelengths can be used simultaneously in equation (7):

$$A^{302}-A^{353}=(\varepsilon^{302}_{I_2SCN^-}-\varepsilon^{353}_{I_2SCN^-})\,.\,dT_{I_2}-$$

$$-\frac{(1+K_2T_{I^-})}{K_1}\cdot\frac{(A^{302}-A^{353})}{T_{SCN^-}} \qquad (7)$$

In all three cases the calculations were made using the least squares principle. The molar absorptivity and the stability constant calculated by us are given in Table IV together with the similar data from the literature. (The expression $\sigma = \pm\sqrt{\Delta^2/(n-1)}$ was used for he calculation of the spread.)

Lewis and Skoog[2] assumed equilibrium (1) in a solution containing iodine and thiocyanate. There is a good agreement, (Table IV) between our values and theirs for the stability constant and the molar absorptivity, in spite of the fact that they did not take into consideration the protonation of thiocyanate ion in their strongly acidic medium.[4-6] Because of the

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(3) G. Daniele, *Gazz. Chim. Ital.*, *90*, 1068 (1960).

(4) T.L. Crowell and M.G. Hankins, *J. Phys Chem.*, *73*, 1380 (1969)

Table IV. Stability constant and molar absorptivity values determined for the charge-transfer complex I_2SCN^-.

	calculated from (5)	calculated from (6)	calculated from (7)	results of Lewis and Skoog	results of Harwey
$K_1 l.mol^{-1}$	51.0±9.6	55.1±6.9	53.9±3.8	85 [a] (30—115) [b]	83±7 [c] (45±5)
$\varepsilon^{302}_{I_2SCN^-}$	$(4.62\pm0.20)\times10^4$	—	—	$(4.29\pm0.02)\times10^4$ [d]	$(4.2\pm0.4)\times10^4$
$\varepsilon^{353}_{I_2SCN^-}$	—	$(0.42\pm0.20)\times10^4$	—	—	—
$\varepsilon^{302}_{I_2SCN^-} - \varepsilon^{353}_{I_2SCN^-}$	—	—	$(4.10\pm0.11)\times10^4$	—	—

[a] Extrapolated to 25°C from K_1 values determined at 1-15°C; [b] Data measured at 25°C; [c] Measured at 7.9°C; [d] Measured at 303 nm.

irreversible reaction at 25°C they could determine only the approximate value of K_1.

The system studied by Harvey[7] contained iodine, iodide and thiocyanate in aqueous solution. In addition to the equilibria (1) and (2), he also assumed the equilibria (8), (9) and (10) in the iodine-thiocyanate interaction:

$$I_2+2SCN^- \rightleftharpoons I(SCN)_2^- + I^- \quad (K_8) \qquad (8)$$

$$I_2+2SCN^- \rightleftharpoons (SCN)_2+2I^- \quad (K_9) \qquad (9)$$

$$I_2+SCN^- \rightleftharpoons ISCN+I^- \quad (K_{10}) \qquad (10)$$

These latter three equilibria describe redox processes, similarly to the reaction given by Long and Skoog:[8]

$$I_2+4SCN^- = 2I(SCN)_2^- + 2e^-$$

Long and Skoog, however, also introduced strong oxidizing agents into the solution containing the iodine and thiocyanate (IO_3^-, H_2O_2, O_2+UV irradiation), whereas Harvey[7] did not. From Harvey's experimental results obtained at 7.9°C we calculated the stability constant of I_2SCN^- by using only equilibria (1) and (2), and neglecting reactions (8), (9), and (10) since these did not appear reasonable. We arrived at the same K_1 value (Table IV) as was obtained by Harvey from a consideration of all the equations. (If check calculations are carried out on the basis of only equilibria (2) and (8), then the data of Harvey do not satisfy the equation of the straight line derived similarly to above.) As a result, it can be concluded that under non-oxidizing conditions the assumption of processes (8), (9), and (10) is not justified, and equilibria (1) and (2) are sufficient for an explanation of the results. Harvey's data can be considered reliable for K_1 at 7.9°C, but in our opinion his measurements at 25°C yield an approximate value (Table IV), because the equilibrium studies are already disturbed by the irreversible decomposition of the I_2SCN^-.

By the simultaneous use of our experimental data for the two wavelengths, and by taking into account the relations $\varepsilon^{303}_{I_2SCN^-} \cong \varepsilon^{302}_{I(SCN)^-}$;[2,8] $\varepsilon^{353}_X = 0.09 \times \varepsilon^{302}_X$ [2] (where X is one of the complex species), and $\varepsilon^{302}_{I_3^-} \cong \varepsilon^{353}_{I_3^-}$, it can be shown unambiguously that the product of the reversible iodine-thiocyanate interaction is I_2SCN^- and not $I(SCN)_2^-$. If the equilibria in the system containing iodine, thiocyanate and iodide are correctly described by reactions (1) and (2), then equation (11) obtained by rearrangement of equations (3) and (4) must hold:

$$\frac{\dfrac{A^{302}}{A^{353}} - 1}{1-0.09\dfrac{A^{302}}{A^{353}}} = \frac{\varepsilon^{302}_{I_2SCN^-} \,.\, K_1}{\varepsilon^{353}_{I_3^-} \,.\, K_2} \cdot \frac{T_{SCN^-}}{T_{I^-}} \qquad (11)$$

From similar considerations, relation (12) is obtained from equilibria (2) and (8):

$$\frac{\dfrac{A^{302}}{A^{353}} - 1}{1-0.09\dfrac{A^{302}}{A^{353}}} = \frac{\varepsilon^{302}_{I(SCN)_2^-} \,.\, K_8}{\varepsilon^{353}_{I_3^-} \,.\, K_2} \cdot \frac{(T_{SCN^-})^2}{(T_{I^-})^2} \qquad (12)$$

The left hand sides of equations (11) and (12) were plotted as functions of (T_{SCN^-}/T_{I^-}) and of $(T_{SCN^-}/$

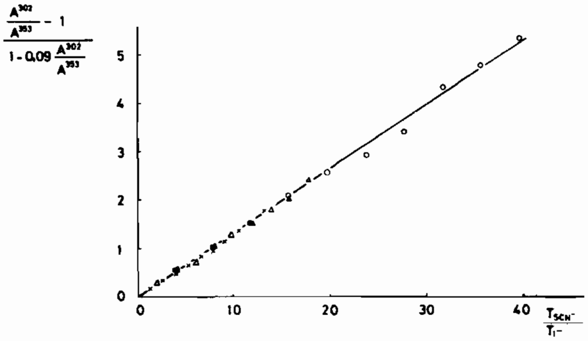

Figure 1. Plot of the experimental results according to equation (11).

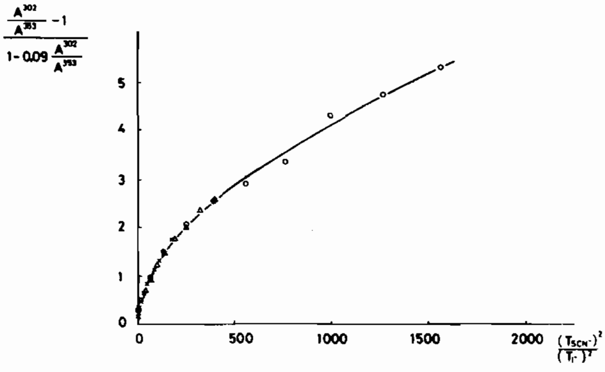

Figure 2. Plot of the experimental results according to equation (12).

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(5) T.D.B. Morgan, C. Stedman and P.A.E. Whincup: *J. Chem. Soc.*, 4893 (1965).
(6) I. Orsragh, *Diplom work*, Debrecen, 1970.
(7) J.A. Harvey, *Ph. D. Thesis*, Stanford University, 1965.
(8) C. Long and D.A. Skoog, *Inorg. Chem.*, 5, 206 (1966).

$T_{I^-})^2$ (Figures 1 and 2). The experimental data gave a straight line passing through the origin in the case of (11), (Figure 1), but not in the case of (12) (Figure 2).

It follows from all that has been said that the *only important product* of the reversible iodine-thiocyanate interaction is the charge-transfer complex I_2SCN^-. The stability constant of the complex at 25°C is $K_1 = 53.3 \pm 6.5$ $l.mol^{-1}$, and its molar absorptivity at 302 nm is $(4.62 \pm 0.20) \times 10^4$ $l.mol^{-1}$ cm^{-1}.