1105. *The Equilibrium Constant for the Formation of Nitrosyl Thiocyanate in Aqueous Solution.*

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The formation of nitrosyl thiocyanate from nitrous acid and thiocyanic acid in aqueous solution has been studied quantitatively by spectrophotometric methods, and the equilibrium constant has been measured over a range of ionic strengths and temperatures. Nitrosyl thiocyanate absorbs at 4600 Å, with an extinction coefficient of 100.

Recent work has shown that the thiocyanate ion catalyses a number of reactions of nitrous acid through the formation of nitrosyl thiocyanate, which can act as a nitrosating agent.[1,2] In this respect it resembles the nitrosyl halides.[3]

$$H^+ + HNO_2 + SCN^- \rightleftharpoons NOSCN + H_2O \qquad (1)$$

It is necessary to know the equilibrium constant for reaction (1) in order to interpret the catalytic effect of nitrosyl thiocyanate. The importance of this has been shown by Ridd[3] in the case of nitrosyl bromide and chloride. Nitrosyl thiocyanate can be isolated at low temperatures, and is red.[4] Aqueous solutions at 25° containing sufficiently large concentrations of nitrous acid, thiocyanate, and hydroxonium ions are red, and absorb at

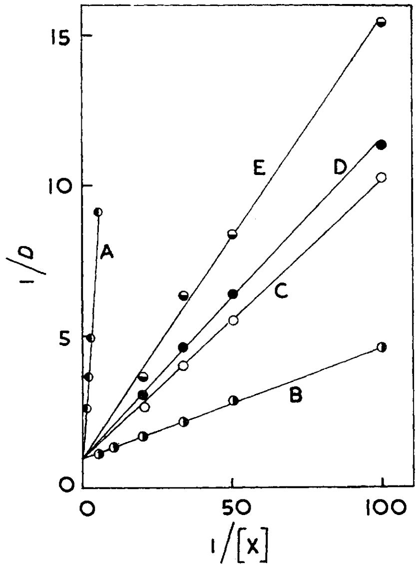
[1] Stedman and Hughes, *J.*, 1963, 2824.
[2] Bunton and Stedman, *J.*, 1959, 568.
[3] Ridd, *Quart. Rev.*, 1961, **15**, 418.
[4] Addison and Lewis, *Quart. Rev.*, 1955, **9**, 115.

4600 Å. By measuring the optical density at this wavelength over a range of conditions we have shown that the light absorption is due to nitrosyl thiocyanate, and have obtained values for K_1 for reaction (1). The solutions were slightly unstable, but measuring the optical densities at several times and extrapolating to the time of mixing gave reproducible values.

Provided that measurements are made at constant ionic strength, a classical equilibrium constant for reaction (1) can be defined in terms of concentrations, $K_1 = [\mathrm{NOSCN}]/[\mathrm{H^+}][\mathrm{HNO_2}][\mathrm{SCN^-}]$. If the total concentration of nitrous acid species is $[\mathrm{nit}] = [\mathrm{HNO_2}] + [\mathrm{NOSCN}]$, l is the path length, ε the extinction coefficient of nitrosyl thiocyanate at 4600 Å, and D the optical density, then

$$\frac{1}{D} = \frac{1}{l\varepsilon\,[\mathrm{nit}]} + \frac{1}{l\varepsilon[\mathrm{nit}]K_1[\mathrm{H^+}][\mathrm{SCN^-}]}. \tag{2}$$

This assumes that all the light absorption at 4600 Å is due to nitrosyl thiocyanate, and that molecular nitrous acid is the only other " nitrite " species present in appreciable concentration. The only species that needs to be considered under our conditions is dinitrogen trioxide. The equilibrium constant $[\mathrm{N_2O_3}]/[\mathrm{HNO_2}]^2$ has been measured;[5] under the present conditions less than 0·1% of the nitrite is present as dinitrogen trioxide. The extinction coefficient of dinitrogen trioxide in aqueous solution at 4600 Å is ~6, much less than the value for nitrosyl thiocyanate. We confirmed that the light absorption was due to one species only, by showing that the ratios of the optical densities at 4200, 4600, and 5000 Å were independent of acidity.



Variation of optical density with thiocyanate and hydronium ion concentrations at 20°.

(A) $[\mathrm{X}] = [\mathrm{H^+}][\mathrm{SCN^-}] = 0{\cdot}02\,\mathrm{M}$. $I = 1{\cdot}2$.
(B) $[\mathrm{X}] = [\mathrm{SCN^-}][\mathrm{HClO_4}] = 1{\cdot}00\,\mathrm{M}$. $I = 1{\cdot}0$.
(C) $[\mathrm{X}] = [\mathrm{SCN^-}][\mathrm{H_2SO_4}] = 0{\cdot}50\,\mathrm{M}$. $[\mathrm{NaHSO_4}] = 0{\cdot}40\,\mathrm{M}$.
(D) $[\mathrm{X}] = [\mathrm{SCN^-}][\mathrm{H_2SO_4}] = 0{\cdot}50\,\mathrm{M}$.
(E) $[\mathrm{X}] = [\mathrm{SCN^-}][\mathrm{H_2SO_4}] = 0{\cdot}40\,\mathrm{M}$. $[\mathrm{NaHSO_4}] = 0{\cdot}20\,\mathrm{M}$ (at 25°).

The results fit equation (2) quite well. In one group of experiments it was shown that D is strictly proportional to [nit] over the range $2{\cdot}5$—$12{\cdot}5 \times 10^{-3}\,\mathrm{M}$. Several groups of experiments were carried out in which all concentrations used within one group were kept constant, and only the concentration of thiocyanate ion was varied. Plots of $1/D$ against $1/[\mathrm{SCN^-}]$ give good straight lines, which have a common intercept corresponding to complete conversion of nitrous acid into nitrosyl thiocyanate. In other experiments only the concentration of hydroxonium ion was varied, and a plot of $1/D$ against $1/[\mathrm{H^+}]$ gives a good straight line with the same intercept as before. Some of these results are shown in the Figure. From the intercept of these, and other similar graphs, it is estimated that ε

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[5] Bunton and Stedman, *J.*, 1958, 2440.

is 100 ± 5 mole^{-1} l. cm.$^{-1}$. By using this value for ε, values of the equilibrium constant K_1 were calculated from the known composition of the solution and the measured optical density. The measurements were extended to cover a range of ionic strengths and temperatures.

To obtain a thermodynamic equilibrium constant for reaction (1) it is necessary to correct for activity coefficient effects. If K_1' is the thermodynamic equilibrium constant, then $K_1' = K_1 = K_1 a_{H_2O} f_{NOSCN}/f_{HNO_2} f_{H^+} f_{SCN^-}$, where a respresents activity and f the activity coefficient. In our solutions the activity of water is close to unity, and the ratio f_{NOSCN}/f_{HNO_2} should be close to one. Values for the term $f_{H^+} f_{SCN^-}$ are more difficult to obtain. Stokes and Robinson[6] have summarised values of $f\pm$ for solutions of perchloric acid, sodium perchlorate, and sodium thiocyanate.

We have assumed that

$$f_{H^+} f_{SCN^-} = (f\pm)^2_{HClO_4} (f\pm)^2_{NaSCN}/(f\pm)^2_{NaClO_4}. \qquad (3)$$

This is admittedly an approximation, for activity coefficients vary with the nature of the ions in the medium, as well as with the formal ionic strength. In this case, however, it seems to be a reasonable approximation. The compounds concerned are all 1 : 1 electrolytes, and in the concentration range in which we are interested (0·4—1·2M) the $f\pm$ values are similar and do not vary much; $HClO_4$ 0·766—0·858; NaSCN 0·720—0·716; $NaClO_4$ 0·683—0·622. The best justification lies in the constancy of the K_1' values compared with the K_1 values, as can be seen in the Table.

Equilibrium constants for the formation of nitrosyl thiocyanate at 20°.

$[H^+]$	$[SCN^-]$	I	D	K_1	K_1'
0·4	0·02	0·42	0·144	21·0	32·3
0·4	0·02	0·82	0·162	24·2	31·1
0·4	0·02	1·02	0·188	28·6	32·7
0·4	0·02	1·42	0·225	36·3	32·0
0·2	0·02	1·22	0·109	30·6	30·8
0·6	0·02	1·22	0·269	31·8	32·0
1·2	0·02	1·22	0·415	31·2	31·4
1·0	0·01	1·01	0·215	28·9	33·2
1·0	0·05	1·05	0·568	27·0	29·9

K_1 and K_1' in mole^{-2} l.^{2}. I = ionic strength. $[\text{nit}]_0 = 0{\cdot}0025$M. l = 4 cm. ε = 100 mole^{-1} l. cm.$^{-1}$. All solutions in $HClO_4$.

A plot of $\log_e K_1'$ against $1/T$ is linear, with $\Delta H = -2{\cdot}9$ kcal mole^{-1}.

These results may be compared with those of Schmid and Hallaba[7] for nitrosyl chloride and bromide.[8] At 0°, K_1' for nitrosyl chloride is $5{\cdot}6 \times 10^{-4}$, and for nitrosyl bromide $2{\cdot}2 \times 10^{-2}$, compared with 46·3 for nitrosyl thiocyanate. Thus thiocyanate falls in its usual place in the halogen and pseudohalogen sequence. The ΔH values do not fit this pattern. For nitrosyl chloride $\Delta H = 4{\cdot}3$, for nitrosyl bromide 5·4, and for nitrosyl thiocyanate $-2{\cdot}9$ kcal. mole^{-1}.

Results in Sulphuric Acid.—In addition to the tabulated results for solutions in perchloric acid, many experiments were carried out with solutions made up with sulphuric acid and sodium hydrogen sulphate. Provided that the composition of the medium is kept constant, plots of $1/D$ against $1/[SCN^-]$ give excellent straight lines with the same intercept as is obtained for the perchloric acid experiments, as can be seen from the Figure. The equilibrium constants obtained from the slopes of these plots are lower than the values in Table 1. There are difficulties in calculating K_1 and K_1': what values should be used for the concentration of hydroxonium ions and for $f_{H^+} f_{SCN^-}$? Sulphuric acid ionises to give appreciable concentrations of both sulphate and hydrogen sulphate ions in the concentration range used in the present work. For solutions in sulphuric acid, the hydroxonium ion concentration can be calculated fairly accurately from Raman data; for solutions containing both sulphuric acid and sodium hydrogen sulphate it can be calculated by a series of successive approximations. The real difficulty lies in the estimation of

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[6] Stokes and Robinson, "Electrolyte Solutions," Butterworths, London, 1959, p. 491.

[7] Schmid and Hallaba, *Monatsh.*, 1956, **87**, 568.

[8] Schmid, *Monatsh.*, 1957, **88**, 631.

$f_{\mathrm{H}^+}f_{\mathrm{SCN}^-}$. The large amount of ionisation to sulphate ion shows that the activity coefficient of the sulphate ion must be very low, and so a mean ion activity coefficient for sulphuric acid is probably very different from $(f_{\mathrm{H}^+}f_{\mathrm{SCN}^-})^{\frac{1}{2}}$. The formal ionic strength can be calculated from the concentrations of hydroxonium, sulphate, and hydrogen sulphate ions obtained from Raman data, and this can be used to calculate activity coefficients by means of equation (3). For 0·5M-sulphuric acid at 20°, $f_{\mathrm{H}^+}f_{\mathrm{SCN}^-}$ calculated by this method is $(0{\cdot}88)^2$. In this solution $K_1 = 14{\cdot}3$ mole^{-2} l.^{2}, and hence $K_1' = 18{\cdot}5$. This is much lower than the mean value of 32·0 from the Table. We have not found a satisfactory method of calculating $f_{\mathrm{H}^+}f_{\mathrm{SCN}^-}$ for solutions in sulphuric acid, and for this reason have not used any of these results for the calculation of K_1'.

Experimental.—*Materials.* Materials were of "AnalaR" grade, except sodium thiocyanate.

Procedure. The solutions were made up in two flasks, the first holding sodium nitrite solution and the second containing all the other components. The contents of both vessels were brought to the desired temperature in a thermostat-bath. A known volume of nitrite was pipetted into a known volume of the other solution, and the time of mixing was noted. A clean, dry 4-cm. cell was filled with solution, and the optical density at 4600 Å measured at half-minute intervals for several minutes. In most cases the optical density decreased only slowly with time, about 1% per min., and it was easy to extrapolate the measured optical densities to the time of mixing.

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