893. The Ionisation Constant of Thiocyanic Acid

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The ionisation of thiocyanic acid in aqueous solution at 25° has been studied by a solvent extraction method. By working at constant ionic strength partition coefficients for covalent thiocyanic acid have been obtained, and these used to calculate classical ionisation constants. By an extrapolation procedure the thermodynamic pK_a has been estimated to be $-1{\cdot}84$. The results have been confirmed by studies of the ultraviolet spectra under the same conditions. Uncertainties in the H_- acidity function make it difficult to obtain an accurate ionisation constant but the results suggest a lower pK_a, $-1{\cdot}38$. Studies of the light absorption of the complex formed between ferric and thiocyanate ions in moderately concentrated perchloric acid lead to the same conclusions. This is confirmed by results on the hydrolysis of nitrosyl thiocyanate.

IN the course of a kinetic study of the mechanism of the oxidation of the thiocyanate ion by nitric and nitrous acids evidence was obtained that the reaction occurred through covalent thiocyanic acid. It was necessary to have a value for the ionisation constant to calculate the appropriate rate constants. It is sometimes stated that thiocyanic acid is at least as strong as hydrochloric acid, which implies that the pK_a is less than about -7. These statements are usually based on the fact that measurements of the pH or of the electrical conductivity show no detectable formation of covalent thiocyanic acid when an alkali metal thiocyanate is added to a solution of hydrochloric acid. All that can be deduced from this type of evidence is that the pK_a is less than some particular value. Gorman and Connell [1] have shown that it is not a weak acid, and from their results it would appear that the pK_a is less than about three. Calculations on the equilibrium

$$H^+ + HNO_2 + NCS^- \rightleftharpoons NONCS + H_2O \qquad (1)$$

in a Paper by two of the present authors [2] imply that the pK_a is less than about -1, though this was not originally explicitly stated Edwards [3] quotes a value of approximately $-0{\cdot}7$, but does not give any indication of his source. There do not appear to be any reliable values in the literature. The usual position of thiocyanate in the halogen and pseudo-halogen series between bromide and iodide would lead one to expect [4] a pK_a of about -9, but this would correspond to such a low concentration of covalent thiocyanic acid in our solutions that the frequency of encounter with the oxidising agent would not be enough to account for the observed rate. The pK_a values for hydrobromic, hydrochloric, nitric, hydrofluoric, and thiocyanic acids have been measured in ethanol,[5] and for the first four acids there are pK_a values in water [5] (the value for hydrobromic acid is rather approximate). By an interpolation procedure one can estimate that the pK_a for thiocyanic acid in water is about -2, though this is subject to an uncertainty of at least ± 1 unit. We have studied the ionisation by a solvent extraction method, and also by direct spectrophotometry in the ultraviolet. We also report the results of a study of the ferric ion–thiocyanate ion equilibrium and of the nitrous acid–nitrosyl thiocyanate equilibrium, both at high acidities, which confirm our conclusions.

EXPERIMENTAL

Solvent Extraction Studies.—Solutions of perchloric acid, sodium perchlorate, and sodium thiocyanate were extracted with carbon tetrachloride at 25° ± 1°. The length of time for which the solutions were shaken was varied threefold, but no differences in the apparent

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[1] M. Gorman and J. Connell, *J. Amer. Chem. Soc.*, 1947, **69**, 2064.
[2] G. Stedman and P. A. E. Whincup, *J.*, 1963, 5796.
[3] J. O. Edwards, " Inorganic Reaction Mechanisms," Benjamin, New York, 1964, p. 54.
[4] R. P. Bell, " The Proton in Chemistry," Methuen, London, 1959, p. 91.
[5] Chem. Soc. Special Publ., No. 17, London, 1964.

partition coefficients were observed, showing that there was equilibrium between the two phases. An aliquot portion of the separated organic layer was added to a known volume of dilute sodium hydroxide and re-extracted. Finally a portion of the aqueous phase was acidified, and the thiocyanate concentration determined by addition to a solution of a ferric salt in perchloric acid. Measurements were made on the band at 465 mμ using standard solutions of thiocyanate for calibration. Beer's Law was obeyed.

Ultraviolet Spectrophotometry.—Measurements were made with 1 cm. silica cells, using a Unicam S.P. 800 instrument. Ionisation ratios were calculated from the results at one wavelength by the usual formula

$$[\mathrm{NCS}^-]/[\mathrm{HNCS}] = (\varepsilon_1 - \varepsilon)/(\varepsilon - \varepsilon_2);$$

ε_1, ε_2, and ε are the molar extinction coefficients for thiocyanic acid, the thiocyanate ion, and the solution in question, respectively. The main difficulty in applying this is the existence of solvent effects, and several procedures have been suggested [6] for dealing with it. We found that at high acid concentrations a plot of ε against $[\mathrm{H}^+]$ was linear, and nearly horizontal. Values of ε_1 at lower acid concentrations were obtained by a linear extrapolation. A similar procedure could not be used to obtain ε_2 because it was difficult to distinguish between the effects due to a small amount of protonation and those due to solvent shifts. Instead measurements were made of the effect of large concentrations of neutral salts, lithium and sodium perchlorates, on the spectrum of sodium thiocyanate. The effects were similar, and it was assumed that these results could be used to predict the effect of ionic strength on the spectrum of the thiocyanate ion. Such corrections need to be checked. We found that the ionisation ratios calculated in this way from the results at several wavelengths were in agreement, and were consistent with ionisation ratios obtained from solvent extraction studies. For results in sulphuric acid the ionic strength at a given molarity was calculated, and the solvent effect taken from the sodium perchlorate results at the same ionic strength.

Ferric Ion–Thiocyanate Ion Equilibrium.—Measurements were made at room temperature, using a Unicam S.P. 800. The solutions were made up, and the band at 465 mμ was recorded at several times as the intensity of the colour faded. The optical densities were extrapolated to the time of mixing.

RESULTS AND DISCUSSION

Solvent Extraction Studies in Concentrated Perchloric Acid.—It is known that in the presence of mineral acids, thiocyanates can be extracted from aqueous solution into organic solvents, and Lewis and Skoog [7] showed that for extractions with ether $[\mathrm{HNCS}]_{\mathrm{eth}}/a_{\mathrm{H}^+}a_{\mathrm{NCS}^-}$ was a constant. This clearly means that monomeric covalent thiocyanic acid was extracted into the organic layer, but as they did not have a value for the partition coefficient they could not calculate an ionisation constant. In a preliminary set of experiments 0·003M solutions of sodium thiocyanate in perchloric acid of various concentrations up to 8M were extracted with carbon tetrachloride. The concentration of thiocyanate in the organic layer increased rapidly with acid concentration up to 6M, and then increased only slowly. Presumably the thiocyanate was nearly fully protonated at 6M-acid; however, as the curve did not level off it was not possible to obtain an accurate value for the partition coefficient of thiocyanic acid. A second set of experiments was carried out with solutions containing a constant total concentration of sodium perchlorate and perchloric acid, but with varying relative amounts. The results are summarised in Table 1. It is well known that extraction studies of this type are often complicated by the formation of dimers and trimers in the organic phase. As can be seen from Table 1 our results were independent of the thiocyanate concentration; in another group of experiments the thiocyanate concentration was varied eightfold, with no change in the apparent partition coefficient. Pullin and his co-workers [8] found that at much higher concentrations of thiocyanic acid in carbon tetrachloride, 0·02M, the infrared spectra indicated negligible self-association, and so no difficulty would be expected at the much lower concentrations that we used.

[6] D. S. Noyes and M. J. Jorgenson, *J. Amer. Chem. Soc.*, 1962, **84**, 4312.

[7] C. Lewis and D. A. Skoog, *J. Amer. Chem. Soc.*, 1962, **84**, 1101.

[8] T. M. Barakat, N. Legge, and A. D. E. Pullin, *Trans. Faraday Soc.*, 1963, **59**, 1764, 1773.

Above 3·2M acid a constant proportion of the thiocyanate was extracted, and a similar levelling off was observed for solutions of formal ionic strength 6·4 and 5·6M. These results may be simply interpreted as showing that in the levelling off region the thiocyanate ion is fully protonated. This also means that the partition coefficient for covalent thiocyanic acid is independent of the relative amounts of sodium perchlorate and perchloric acid at constant ionic strength. The thermodynamic partition coefficient K_D may be written as

TABLE 1

Solvent extractions in concentrated perchloric acid at 25°

Ionic strength 7·2M

	$[H^+]$ (M)	0·4	0·8	1·6	2·0	2·4	2·8	3·2	4·0	4·8	6·4
a	$10^4[HNCS]_2$ (M)	2·55	5·47	8·62	9·96	10·35	10·7	10·9	11·0	11·0	11·0
b	$10^4[HNCS]_2$ (M)	—	11·9	17·1	20·8	—	—	21·7	22·0	22·0	21·7
c	$10^4[HNCS]_2$ (M)	8·04	17·4	29·3	—	—	—	38·2	38·2	38·2	38·2

Ionic strength 6·4M

	$[H^+]$ (M)	4·8	5·6	6·4
a	$10^4[HNCS]_2$ (M)	10·1	10·5	10·5

Ionic strength 5·6M

	$[H^+]$ (M)	4·0	4·8	5·0	5·6
a	$10^4[HNCS]_2$ (M)	9·44	9·71	9·77	9·83

In all experiments 50 ml. of the aqueous phase and 35 ml. of carbon tetrachloride were used. Initial concentrations of sodium thiocyanate in the aqueous layer were: *a*, $3 \cdot 10^{-3}$M; *b*, $6 \cdot 10^{-3}$M; *c*, 10^{-2}M.

$$K_D = a_1/a_2 = ([HNCS]_1/[HNCS]_2)\,.\,(f_1/f_2) = P\,.\,f_1/f_2 \qquad (2)$$

where a refers to activity, f to activity coefficient, and the subscripts 1 and 2 to the aqueous and organic phases, respectively. For an immiscible solvent such as carbon tetrachloride, f_2 may be taken as unity whatever the concentrations in the aqueous phase. A constant value of P thus implies a constant value of f_1. The activity coefficient of non-electrolytes vary relatively slightly with ionic strength in aqueous solution, and so the apparent constancy of f_1 is not unreasonable. The partition coefficients P calculated from the levelled off parts of the curves are 2·03, 2·16, and 2·35 for 7·2, 6·4, and 5·6M ionic strengths, respectively. These values can be used to calculate the classical ionisation constant K^* defined by the equation $K^* = [H^+][NCS^-]/[HNCS]$, which is related to the thermodynamic ionisation constant K_a by the relation $K_a{}^* = K^* f_{H^+} f_{NCS^-}/f_1$. K^* is not a constant. At a constant formal ionic strength of 7·2M the mean values are 1·92, 1·20, 0·63, and 0·28 at perchloric acid concentrations of 0·4, 0·8, 1·6, and 2·0M, respectively. The drift in these values is not surprising. The activity coefficients of ions are a much more sensitive function of ionic strength than those of neutral molecules, and are only independent of the nature of the ions at ionic strengths less than about 0·1M. Substantial differences probably exist in solutions as concentrated as 7·2M. The problem has been discussed by Stokes and Robinson,[9] and there is no reliable way of predicting the activity coefficients in the present case. One possible method seemed to be to extrapolate the K^* values to 7·2M-perchloric acid, and then to use the known mean ion activity coefficient for perchloric acid as an approximation to $f_{H^+} f_{NCS^-}$. However, this leads to a value of about 0·06 for K_a, and were thiocyanic acid as weak as this it would certainly have been detected by Gorman and Connell. The error does not seem to lie in the K^* values, for these are in good agreement with those from the spectrophotometric study. Part may lie in the use of the mean ion activity coefficient as an approximation to $f_{H^+} f_{NCS^-}$, but we think that a much greater source of error is the extrapolation from 2- to 7·2M-perchloric acid, which may not be linear. It does not seem possible to obtain reliable thermodynamic ionisation constants from the classical ionisation constants.

Solvent Extraction Studies in More Dilute Perchloric Acid (*Less than* 2M).—A more satisfactory procedure is to carry out the solvent extraction in more dilute perchloric acid. The results of a study of equilibrium (1) at various ionic strengths suggested that up to about 2M ionic strength the activity coefficients $f_{H^+} f_{NCS^-}$ for dilute solutions of sodium

[9] R. H. Stokes and R. A. Robinson, " Electrolyte Solutions," Butterworths, London, 1959, p. 445.

thiocyanate in mixtures of sodium perchlorate and perchloric acid can apparently be estimated fairly accurately from the known mean ion activity coefficients for perchloric acid, sodium perchlorate, and sodium thiocyanate.[2] If the partition coefficient P can be estimated for these lower ionic strengths by an extrapolation method, it is possible to obtain a reliable thermodynamic ionisation constant. The activity coefficients of non-electrolytes[10] obey the relation $\log f = C_1 . I$, where I is the ionic strength and C_1 is a constant which in many cases is in the range 0·05—0·2. If this relationship is assumed to hold up to ionic strengths as high as 7·2M then a plot of log P against I should enable an extrapolation to be made to lower ionic strengths, and K_D and f_1 to be estimated. The three points for 7·2, 6·4, and 5·6M ionic strength lie on a straight line of slope 0·041. It is not possible to obtain additional points at higher ionic strengths because the solutions are unstable, while at lower ionic strengths conversion to thiocyanic acid is not complete. The value for C_1 seems reasonable and suggests that this procedure is justified. The results are summarised in Table 2. At these low acidities only a small proportion of the thiocyanate ion is protonated, so quite a large error in the extrapolated value of P will not make a serious error in the thiocyanate ion concentration. Errors in the extrapolation of log P against I will affect the absolute value of K_a, but as the range of ionic strengths covered is only from 0·4 to 1·8M the internal consistency of a group of values will not be much affected.

TABLE 2

Solvent extractions in dilute perchloric acid, 25°

$[H^+]$	I	$[NCS^-]$	$10^5[HNCS]_2$	K^*	K_a	$[H^+]$	I	$[NCS^-]$	$10^5[HNCS]_2$	K^*	K_a
0·4	0·4	0·04	3·0	139	87	1·2	1·8	0·01	6·40	55	67
0·4	0·8	0·04	3·9	110	80	1·8	1·8	0·006	5·22	60	73
0·4	1·6	0·04	7·9	59	65	1·8	1·8	0·01	9·29	56	68
0·8	1·8	0·01	4·23	47	68	1·8	1·8	0·03	26·3	59	73

In all experiments 50 ml. of the aqueous phase and 40 ml. of carbon tetrachloride were used.

The values in the last column of Table 2 are reasonably constant, and are clearly much more consistent than the classical ionisation constants K^*. There may be a drift towards higher K_a values at low ionic strengths, but the experimental errors were distinctly larger at low acidities. In a separate experiment at 0·2M ionic strength, designed to give increased accuracy, a value of 53 was obtained for K_a, inconsistent with such a drift. If there is a real trend in the K_a values it might be due both to errors in the extrapolation procedure used to estimate P and f_1, and to the assumptions made in estimating the $f_{H^+}f_{NCS^-}$ term. From these and other values we taken a mean figure of 70 mole l.$^{-1}$ for K_a. It is difficult to estimate the possible error, but we think that it is less than ± 30.

We have extended the extraction studies to solvents other than carbon tetrachloride, and find that the partition coefficients at 25° are n-hexane 3·87, chloroform 0·60, mesitylene 0·50, benzene 0·39, and di-n-butyl ether 0·050 for an ionic strength of 7·2M. This is the same order as has been observed by Cutmore and Hallam[11] for hydrogen bonding effects between compounds with an N–H bond and the solvent. The only exception is that the positions of benzene and mesitylene are inverted. These workers measured the shift in the stretching frequency relative to the frequency in the vapour phase and found values of $\Delta\nu/\nu$ of n-hexane 6·8, carbon tetrachloride 8·5, chloroform 12·5, benzene 20·4, mesitylene 25·8, and di-n-butyl ether 52·7. There seems little point in attempting a more detailed comparison because the partition coefficients refer to solvent saturated with water, whereas the infrared results refer to the dry solvent.

Spectrophotometric Study of the Ionisation of Thiocyanic Acid.—To confirm the solvent extraction studies by an alternative method we investigated the ultraviolet spectra of solutions of sodium thiocyanate in perchloric acid and sodium perchlorate. The first experiments were done under similar conditions to those used in the solvent extraction

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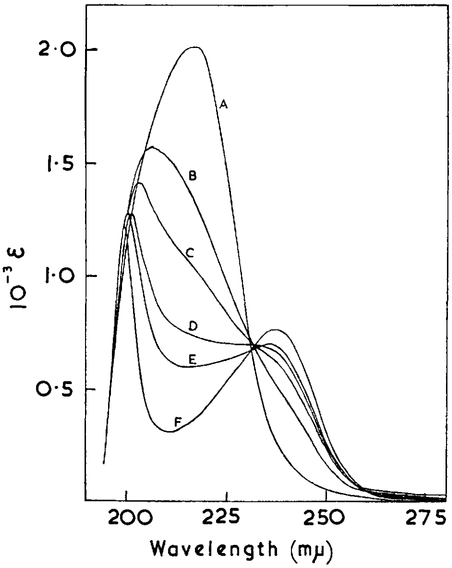
[10] F. A. Long and W. F. McDevitt, *Chem. Rev.*, 1952, **51**, 119.

[11] E. A. Cutmore and H. E. Hallam, *Trans. Faraday Soc.*, 1962, **58**, 40.

work at 7·2M ionic strength. At low acidities the spectra were characterised by a peak at 217 mμ, with $\varepsilon = 2010$, presumably due to the thiocyanate ion. As the perchloric acid content of the medium was increased this disappeared and was replaced by a spectrum with a sharp peak at 200 mμ, $\varepsilon = 1290$, and a broader peak at 235 mμ, $\varepsilon = 700$. This change in the spectrum was complete at about 4M-perchloric acid; further increases in the perchloric acid concentration produced smaller changes in the position of these maxima and in the extinction coefficients. Beer's Law was obeyed. Typical spectra are shown in the Figure. We take the large changes in the spectra below 4M-acid to be due to conversion of the thiocyanate ion to thiocyanic acid, while the smaller changes at higher acidities are thought to be medium effects. The spectra in the Figure show that although there is not a sharply defined isosbestic point medium effects seem to be rather small. Calculations of the ionisation ratio have been made at 220 and 235 mμ, where large changes in optical density occurred. The values of K^* so obtained at 0·4, 0·8, and 1·6M-perchloric acid are 1·62, 1·35, and 0·68 (235 mμ) and 1·62, 1·35, and 0·93 (220 mμ) which may be compared with the solvent extraction results of 1·92, 1·20, and 0·68. The agreement is sufficiently good to confirm that both methods are giving essentially correct results, though the existence of medium effects makes the results based on the ultraviolet spectra a little less certain. To obtain a value for K_a we would need to have values of the H_- acidity function in solutions of sodium perchlorate and perchloric acid. There does not seem to be data available covering our range of acidities.



Effect of perchloric acid concentration on the spectrum of sodium thiocyanate. Ionic strength 7·2M

[$HClO_4$] (M) A, 0; B, 1·6; C, 2·4; D, 3·2; E, 4·0; F, 7·2.

Measurements in Perchloric and Sulphuric Acids.—We extended our measurements to solutions in perchloric and sulphuric acids because a limited amount of work on the H_- acidity function has been reported for these acids. Inspection of the spectrum suggested that there might be medium effects involved as well as the changes due to protonation of the thiocyanate ion. We therefore also investigated the spectra of solutions of sodium thiocyanate in lithium and sodium perchlorate solutions. Below 215 mμ the spectra depended markedly on the ionic strength, whereas above this wavelength the effects were very much smaller. It has been suggested that part of the apparent "medium" effect below 215 mμ may be due to stray light.[†] We have restricted our calculations of the ionisation ratio to wavelengths of 215 mμ or greater where such effects seem to be small. Results for perchloric acid are in Table 3.

[†] We are indebted to a referee for this point.

TABLE 3

Ionisation ratios for solutions of sodium thiocyanate in perchloric acid

$[HClO_4]$ M	2·4	3·2	4·0	4·8	5·6
215 mμ	5·5	2·2	0·99	0·42	0·14
220 ,,	4·9	1·9	0·84	0·36	0·15
225 ,,	4·8	1·9	0·76	0·32	—
230 ,,	—	1·9	0·84	0·33	—
Mean	5·1	2·0	0·86	0·36	0·145

The ionisation ratios seem to be independent of the wavelength, so we think that our procedure for correcting for medium effects, described in the Experimental section, is satisfactory. A plot of log $[NCS^-]/[HNCS]$ against H_- should be linear with unit slope. Unfortunately it is now clear that the original postulate of Hammett that the ratio $a_{H^+}f_B/f_{BH^+}$ is independent of the nature of the neutral base B only holds accurately for a series of structurally related indicators. Thus different acidity functions are needed to describe the protonation of amines, of amides, of olefins, and of indoles.[12] It seems likely that there will be a similar series of H_- acidity functions for the protonation of negatively charged bases. Cox and McTigue [13] have deduced an acidity function from kinetic results for the protonation of carboxylate ions. Fuller [14] has measured the H_- function using a variety of indicators, and Boyd [15] has studied the problem using cyanocarbons as indicators; there are substantial differences. A plot of the logarithm of the ionisation ratio against H_- gives a slope of 0·72 for Boyd's data, 0·81 for McTigue's data, and 0·98 for Fuller's data. It is clear that a pK_a value calculated from the first two plots will not be a " true " thermodynamic constant, whereas it might be thought that a value from the third one, with unit slope, will be so. This will only be necessarily true if all the different H_- functions, which are asymptotic to a common curve at low acid concentrations, diverge at higher concentrations, and do not intersect. If such intersections occur, then two different H_- functions might be parallel ones of acid concentration over a limited range. Plots of the logarithm of the ionisation ratio against H_- might have similar slopes but yield different pK_a values because of differences in the absolute value of H_-. This does not seem to occur for the protonation of neutral bases in the limited number of cases that have been studied, but the acidity functions of McTigue and Fuller do intersect. This may be associated with the fact that McTigue's function was derived from kinetic results, whereas the other was obtained from direct spectrophotometric measurements. If we take the apparent pK_a as the value of H_- at 50% protonation then the values are −1·37 (Fuller), −1·37 (McTigue), and −2·16 (Boyd). From the slope of the logarithm of the ionisation ratio against H_- it is likely that this last value is too negative. The deviations are similar to those observed for the protonation of amides [16] when H_0 values based on aniline-type indicators were used. A comparison of the H_0 and H_A acidity functions suggest, by analogy, that the pK_a based on Boyd's data may be 0·2 to 0·3 unit too negative. This would give a value of about −1·9, corresponding to $K_a = 90$, compared with $K_a = 23$ from Fuller's results. A corrected value based on McTigue's acidity function would be lower still. It is difficult to decide if there is any real inconsistency between the figure of $K_a = 70$ by solvent extraction and the results described above. There is no structural similarity between the thiocyanate ion and any of the indicators used by Fuller, even though the slope of the logarithm plot is close to the theoretical value of one. We have carried out similar studies in sulphuric acid, with almost identical results.

Another way of obtaining K_a is to extrapolate K^* to zero ionic strength. This has been done by Symons [17] and his co-workers in a study of the protonation of a number of

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[12] R. L. Hinman and J. Lang, *J. Amer. Chem. Soc.*, 1964, **86**, 3796.

[13] B. G. Cox and P. T. McTigue, *J.*, 1964, 3893.

[14] M. W. Fuller, private communication.

[15] R. H. Boyd, *J. Amer. Chem. Soc.*, 1961, **83**, 4288.

[16] K. Yates, J. B. Stevens, and A. R. Katritzky, *Canad. J. Chem.*, 1964, **42**, 1957.

[17] N. Bailey, A. Carrington, K. A. K. Lott, and M. C. R. Symons, *J.*, 1960, 290.

anions of oxy-acids of the transition metals in perchloric acid, by plotting ($\log [BH^+]/[B] - \log [H^+]$) against the molarity of perchloric acid. They comment that this appears to work satisfactorily for neutral bases. A similar extrapolation on the data in Table 3 gives $K_a = 85$. Now the mean ion activity coefficients for many salts and acids decrease from one in dilute solution to a minimum, and then increase again with increasing ionic strength. The minimum often occurs in the region 0·5—1M ionic strength. Extrapolation of chemical ionisation constants for solutions on the high ionic strength side of the minimum could easily give an incorrect value for K_a. The reason why the procedure works fairly well for neutral bases may be that in the activity coefficient term correcting classical to thermodynamic ionisation constants, $f_{H^+}f_B/f_{BH^+}$, there is a partial cancellation of the activity coefficients of the two singly positively charged ions. Such a cancellation would not in general be expected to occur for the term $f_{H^+}f_{NCS^-}/f_{HNCS}$. The variation of many mean-ion activity coefficients can be represented fairly well by the expression

$$-\log f_i = 0{\cdot}5\,\frac{Z_i^2 I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} + C_i I \tag{3}$$

C_i is an empirical constant, obtained by fitting the experimentally determined mean ion activity coefficients to equation (3). For the ionisation of the thiocyanic acid it follows that

$$\log K_a = \log K^* - (I^{\frac{1}{2}}/1 + I^{\frac{1}{2}}) - (C_1 + C_{H^+} + C_{NCS^-})I$$

A plot of $\log K^* - [I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}]$ against molarity of perchloric acid gave a straight line, and extrapolation to zero ionic strength gave $K_a = 25$. Other modifications of this treatment are possible. The term $1 + I^{\frac{1}{2}}$ could be replaced by $1 + BI^{\frac{1}{2}}$, where B contains a term allowing for ionic size, but as the results referred to concentrated ionic solutions for which no satisfactory quantitative theory of activity coefficients exists there seems little point in using such refinements.

The ultraviolet spectra thus confirm the general conclusions reached from the solvent extraction studies, and where a direct comparison is possible the classical ionisation constants are in good agreement. The thermodynamic ionisation constants are somewhat different, but in view of the uncertainties associated with the correction for medium effects, the use of the H_- acidity function, and the procedure for extrapolating to zero ionic strength, we consider that pK_a value of —1·84 from the solvent extraction to be more reliable than the value of —1·4 from the ultraviolet spectra.

The Ferric Ion–Thiocyanate Ion Equilibrium at High Acidities.—The results described above show that the thiocyanate ion is fully protonated in moderately concentrated perchloric and sulphuric acids. This should affect the rates of reaction and equilibria involving the thiocyanate ion. We have studied the most familiar case, the formation of a complex between ferric and thiocyanate ions. A number of these are known, $Fe(H_2O)_5NCS^{2+}$, $Fe(H_2O)_4(NCS)_2{}^+$, etc., which absorb strongly at about 465 mμ. The equilibrium constants for their formation have been measured by many workers,[5] by a variety of techniques. The values seem to be rather sensitive to the ionic strength. There do not appear to be any detailed studies at acidities greater than 1·8M-perchloric acid, where the degree of protonation of the thiocyanate ion is small. We have extended these measurements to higher acid concentrations where a substantial fraction of the thiocyanate was converted to thiocyanic acid, hoping that this would be reflected in a lower concentration of complex, and a decreased light absorption.

We worked with low concentrations of both ferric and thiocyanate ions so that the only complex that needed to be considered was $Fe(H_2O)_5NCS^{2+}$. The concentrations were low enough for equilibrium (4) to lie well over to the left hand side.

$$\mathrm{Fe(H_2O)_6{}^{3+} + NCS^- \rightleftharpoons Fe(H_2)O_5NCS^{2+} + H_2O} \tag{4}$$

This is important, because if the equilibrium lies mainly to the right, then even if the thiocyanate ion is partly protonated there will be only a small change in the concentration of the ferric thiocyanate complex. There are at least two possible serious complications. Perchlorate ions are thought to form complexes with the ferric ion,[18] and although these do not absorb appreciably in the visible light range, our solutions may contain mixed complexes of the type $Fe(H_2O)_y(ClO_4)_{5-y}NCS^{y-3}$, which probably would absorb strongly at 465 mμ. The other complication is that the activity coefficients of doubly and triply charged ions are very sensitive to changes in the ionic strength, and might also vary with the nature of the ions in the medium at a given ionic strength. A further difficulty is that the activity of water will vary with the relative amounts of perchloric acid and sodium perchlorate, and this will affect equilibrium (4). We used solutions containing a constant total concentration of sodium perchlorate and perchloric acid, but with varying relative amounts. This should minimise, though it will probably not eliminate, these effects. Vasilev[19] has measured the classical equilibrium constant K_1 for equilibrium (4) in the presence of a number of salts, up to quite high ionic strengths. $K_1 = [FeNCS^{2+}]/[Fe^{3+}][NCS^-]$. He finds that K_1 is not very sensitive to changes in ionic strength, or to changes in the nature of the electrolyte above about 0·5M. This is confirmed by the work of Yatsimirskii and Tetyashkino.[20] The results for solutions of lithium nitrate and sodium nitrite are very similar. As the variation of the mean ion activity coefficient for lithium salts Li^+X^- usually parallels that of the strong acid H^+X^- very much more closely than any other salt M^+X^-, this suggests that in our medium of sodium perchlorate and perchloric acid of constant total ionic strength, changes in the relative amounts of the two components will not have much effect upon K_1. As nitrate should be as good a complexing agent as perchlorate, complications due to the formation of mixed complexes should also show up in these results. It seems that the assumption that K_1 may be treated as a constant at a given ionic strength is reasonably satisfactory.

Two sets of experiments were carried out, one at 6·75M and one at 4·44M ionic strength. The extinction coefficient of the ferric thiocyanate complex was obtained by carrying out a set of measurements at a fixed medium composition and a fixed thiocyanate concentration, with a varying concentration of excess ferric ion. A plot of $1/D$ against $1/[Fe^{3+}]$ was linear, and could be extrapolated to $1/[Fe^{3+}] = 0$ to give the limiting optical density for complete complexing of the thiocyanate ion. D is the optical density. At 3·91M-perchloric acid and 2·88M-sodium perchlorate the maximum in the visible spectrum was at 465 mμ, with $\varepsilon = 5310$, while for 0·61M-perchloric acid and 3·83M-sodium perchlorate the peak was at 457 mμ, $\varepsilon = 4720$. It was assumed that these extinction coefficients could be used for other medium compositions, at the same ionic strength. The results of the other experiments are summarised in Table 4.

TABLE 4

The ferric ion–thiocyanate ion equilibrium at high acidities

	Ionic strength 4·44M					Ionic strength 6·75M				
$[H^+]$ M	0·61	1·57	2·53	3·48	4·44	3·41	3·89	4·85	5·80	6·75
D	0·57	0·52	0·49	0·44	0·39	0·70	0·62	0·52	0·42	0·34
$[H^+]$X D	0·35	0·82	1·24	1·53	1·73	2·48	2·41	2·51	2·44	2·30
K^*	8·7	8·7	8·3	8·4	7·0					

$[Fe^{3+}]$ 7·48 × 10^{-4}M; [NaNCS] 7·58 × 10^{-4}M; 1 cm. cells in all cases.

Assuming that equilibrium (4) and the ionisation of thiocyanic acid are the only equilibria involved, and that K_1 and K^* may be treated as constants at constant ionic strength, it can readily be shown that

$$\frac{[Fe^{3+}]([NCS^-] + [HNCS])}{[FeNCS^{2+}]} = \frac{1}{K_1} + \frac{[H^+]}{K_1K^*} \qquad (5)$$

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[18] K. W. Sykes, *J.*, 1959, 2473.

[19] V. P. Vasilev, *Zhur. neorg. Khim.*, 1962, **7**, 1788.

[20] K. B. Yatsimirskii and V. D. Tetyushkina, *Zhur. neorg. Khim.*, 1957, **2**, 320.

From the known initial concentration, the optical density D, and the measured extinction coefficient for the ferric thiocyanate complex, all the concentrations in equilibrium (4) can be evaluated. The solvent extraction and the ultraviolet work showed that for the acidities used in the experiments at 6·75M ionic strength thiocyanic acid is only slightly ionised. This means that $[H^+]/K^*$ is much greater than one, and the concentration of the ferric thiocyanate complex should be inversely proportional to the hydrogen ion concentration. Inspection of the results in Table 4 shows that this is approximately correct, as shown by the constancy of $[H^+]XD$, though the acid concentration only varies by a factor of two. For the experiments at 4·44M ionic strength the thiocyanic acid is largely ionised, and so the concentration of the complex should vary only slightly with acid concentration. Again the results in Table 4 confirm this. A plot of equation (5) gives a reasonable straight line, and from the slope and intercept we calculate that $K^* = 8$ and $K_1 = 340$. The K^* values from the ultraviolet measurements are 4·0 and 1·7 for 4·0M and 4·8M perchloric acid, respectively. It has previously been shown that at constant ionic strength K^* increases as the perchloric acid content of the medium decreases, and so the agreement may be rather better than appears from these figures. There are many values of K_1 available in the literature.[5] The nearest to our experimental conditions is a figure of $K_1 = 330$ for 4·5M-sodium perchlorate by Vasilev.[19] It is also possible to calculate a value for K^* for the results at 6·75M ionic strength. By extrapolation of Vasilev's data K_1 can be estimated, while the slope of a plot of equation (5) gives $1/K_1K^*$. This gives $K^* = 0{\cdot}16$ for $[H^+] = 2{\cdot}5$M (mean value), which compares with $K^* = 0{\cdot}28$ for $[H^+] = 2{\cdot}0$M, at 7·2M ionic strength. It is obvious that with the assumptions made the values of K^* will be approximate figures only. The agreement with the ultraviolet and solvent extraction results is very satisfactory, and it appears that the effect of acidity upon the ferric ion–thiocyanate ion equilibrium is just what would be expected.

Equilibrium between Nitrosyl Thiocyanate and Nitrous and Thiocyanic Acids.—The position of equilibrium in reaction (1) should be influenced by protonation of the thiocyanate ion. In an earlier study[2] the thermodynamic equilibrium constant for reaction (1), K_2, was measured for solutions containing up to 2M-perchloric acid. This work has recently been extended to 6M-acid in order to be able to interpret some kinetic results. Provided that the ionisation of thiocyanic acid and reaction (1) are the only equilibria involved it can be shown that

$$K_2 = \frac{[\mathrm{NONCS}]}{([\mathrm{nit}] - [\mathrm{NONCS}])} = \frac{a_{\mathrm{H_2O}}\,(1 + \alpha)}{([\mathrm{T}] - [\mathrm{NONCS}])\,K_a f_1}$$

This assumes that the activity coefficients of molecular nitrous acid and nitrosyl thiocyanate approximately cancel, $[\mathrm{nit}] = [\mathrm{HNO_2}] + [\mathrm{NONCS}]$. $[\mathrm{T}] = [\mathrm{NONCS}] + [\mathrm{HNCS}] + [\mathrm{NCS^-}]$. $\alpha = [\mathrm{NCS^-}]/[\mathrm{HNCS}]$. The concentration of nitrosyl thiocyanate was obtained from the optical density at 460 mμ, the extinction coefficients being obtained by an extrapolation procedure, as has been described previously. The total concentration of nitrite and thiocyanate, [nit] and [T], respectively, were known from the amounts added initially; α was obtained from the ultraviolet spectra, f_1 from the solvent extraction work, and K_2 from the previous work. This is essentially a method of calculating the activity coefficient term $f_{\mathrm{H^+}}f_{\mathrm{NCS^-}}$, though it is convenient to do the calculation so as to give a value of K_a, which can be compared with the

TABLE 5

Equilibrium between nitrosyl thiocyanate and nitrous and thiocyanic acids at 25°

$[H^+]$	10^3[nit]	10^3[NaNCS]	10^3[NONCS]	α	K_a
3	1	8	0·86	0·30	60
3	1	4	0·75	0·30	62
4	1	2	0·80	0·46	100
5	1	1·2	0·81	0·78	180
5	1	1·6	0·81	0·78	150

other results. The measurements were made on solution containing concentrations similar to those used in the kinetic studies, and were not well suited to giving very accurate K_a values. A large fraction of the nitrite is present as nitrosyl thiocyanate, and errors in the concentration clearly have a cumulative effect on the ratio [NONCS]/([nit] − [NONCS])([T] − [NONCS]). We consider that the K_a values in Table 5 are good enough to confirm our general picture. The experimental accuracy falls off at high acid concentrations, and we do not attribute any significance to the rather higher values in 5M-acid.

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