[CONTRIBUTION FROM DEPARTMENT OF INORGANIC AND PHYSICAL CHEMISTRY, THE UNIVERSITY, LEEDS, ENGLAND]

Electron Transfer and Other Processes Involved in the Spontaneous Bleaching of Acidified Aqueous Solutions of Ferric Thiocyanate

BY R. H. BETTS[1] AND F. S. DAINTON

RECEIVED JUNE 11, 1953

The kinetics of the thermal auto-reduction of ferric thiocyanate in aqueous solutions of perchloric acid have been investigated at four temperatures between 14.8 and 29.9°. The reaction was followed by measurement of the ferrous ion formed. The results suggest that both $FeSCN^{++}$ and $Fe(SCN)_2^+$ react with thiocyanate ion to form ferrous ion; $(SCN)_2^-$ is an intermediate in each case. Ferrous ion retards the reaction by competing with ferric ion for $(SCN)_2^-$. A detailed kinetic scheme is given in equations 2 to 9. For the conditions $(H^+) = 0.967$ *M*, $(SCN^-) = 0.005–0.1$ *M*, $(Fe^{III}) = 0.5–10 \times 10^{-3}$ *M* $(Fe^{++})_0 = 0–3 \times 10^{-4}$ *M*, $\mu = 1.28$, the observed rate law is: $d(Fe^{2+})/dt = 2(Fe^{III})[k_1K_1(SCN^-)^2 + k_2K_1K_2(SCN^-)^3]/[1 + K_1(SCN^-) + K_1K_2(SCN^-)^2][1 + k_3(Fe^{++})/k_4(Fe^{III})]^{-1}$; at 25°, $k_1 = 1.8 \times 10^{-5}$ liter/mole sec., $k_2 = 1.4 \times 10^{-4}$ liter/mole sec. The corresponding energies of activation are 26.2 and 27 ± 3 kcal./mole, respectively. The ratio k_3/k_4 has a value of 3.5 ± 1.0, independent of temperature. The association constant K_1 of $Fe(SCN)^{++}$, measured spectrophotometrically, has a value of 114 at 25°, $\mu = 1.28$; extrapolation to zero ionic strength gives $\Delta H_1^0 = -1.6$ kcal./mole, $\Delta F_1^\circ = -4.0$ kcal./mole, and $\Delta S_1^0 = +8$ e.u. A value of 20 ± 5 for the association constant K_2 of $Fe(SCN)_2^+$, independent of temperature, was deduced from the kinetic data. The stoichiometry of the reaction is consistent with the suggestion that $(SCN)_2$ is formed, and that it hydrolyzes rapidly to thiocyanate, cyanide and sulfate.

Introduction

Numerous investigations of the ionic association of ferric ion with thiocyanate ion have appeared in recent years.[2–11] The existence of the ion $FeSCN^{++}$[12] is well established, and several reasonably concordant values of its association constant have been published.[3,7,11] However, the nature of the ions or molecules present in solution for large values of the ratio $(SCN^-)/(Fe^{III})$ is less well understood. Qualitative evidence depending on a variety of experimental methods including spectrophotometric measurements,[5,6,10,11] migration of the red color in an electric field,[7,9,10] and extraction of ferric thiocyanate from aqueous solutions by organic solvent,[7] points to the formation of complexes containing up to four or more thiocyanate ions per ferric ion at higher concentrations of thiocyanate. The only quantitative studies in this region of concentration appear to be those of Babko[10] and MacDonald, *et al.*,[7] and these are not in close agreement. Nevertheless the available evidence does suggest that anionic complexes are present above 0.5 *M* SCN^-, and that below 0.1 *M* (for $(Fe^{III}) << (SCN^-)$) virtually no complex ions exist other than $FeSCN^{++}$ and $Fe(SCN)_2^+$.

Another aspect of this system which has received less attention is the thermal and photochemical bleaching of the red color. Several investigators[6,7] have made passing references to these phenomena, and it is generally recognized that these effects are a potential source of error in the colorimetric determination of ferric by the thiocyanate method. Møller[8] has suggested that fading is due to reduction of ferric ion by thiocyanate ion, with formation of ferrous ion and thiocyanogen. Such a spontaneous reaction would be expected to occur to an appreciable extent since chemical evidence suggests that the standard oxidation–reduction potential of the couple Fe^{++}/Fe^{+++} is about the same as that of $2(SCN^-)/(SCN)_2$, namely, −0 .77 v.[13]

In the present work, we describe experiments relating to the kinetics of the thermal bleaching of ferric thiocyanate in aqueous solutions of perchloric acid. The expression "thermal bleaching" in this context refers to the reduction of ferric ion to ferrous ion by thiocyanate ion in the dark, with a consequent diminution of the red color of the solution. We have followed the kinetics of the process by measurement of the rate of formation of ferrous ion, rather than by the stoichiometrically equivalent, but less precise and less sensitive method of measurement of the rate of disappearance of ferric ion. Apart from a few qualitative trials at concentrations up to 0.30 *M* thiocyanate, all the experiments reported here have been made with concentrations in the range 0.005–0.10 *M* for thiocyanate ion and 0.0005–0.01 *M* for ferric ion. For these conditions, the variety of complex ions should not be so great as to complicate unduly the interpretation of the results.

In addition, we have measured by spectrophotometric techniques the association constant of $FeSCN^{++}$, and its variation with temperature.

In this paper, we shall assume that HSCN is a strong acid.[13] This assumption is supported by at least one observation in the literature[11] regarding the neutral reaction of an aqueous solution of potassium thiocyanate; we have corroborated this behavior for the sodium salt. In addition, kinetic experiments of the kind described below showed only 10% increase in the rate of formation of ferrous ion when the acidity of the solution was reduced by one-half. Such small effects do not suggest that HSCN is a weak acid.

---

[1] Chemistry Division, Atomic Energy of Canada, Ltd., Chalk River, Ontario, Canada.

[2] H. E. Bent and C. L. French, THIS JOURNAL, **63**, 568 (1941).

[3] S. M. Edmonds and N. Birnbaum, *ibid.*, **63**, 1471 (1941).

[4] O. E. Lanford and S. J. Kiehl, *ibid.*, **64**, 291 (1942).

[5] R. K. Gould and W. C. Vosburgh, *ibid.*, **64**, 1630 (1942).

[6] S. E. Polchlopek and J. H. Smith, *ibid.*, **71**, 3280 (1949).

[7] J. Y. MacDonald, K. M. Mitchell and A. T. S. Mitchell, *J. Chem. Soc.*, 1574 (1951).

[8] M. Møller, *Kem. Maanesblaad*, **18**, 38 (1937); *C. A.*, **33**, 9179 (1939).

[9] H. I. Schlesinger, THIS JOURNAL, **63**, 1765 (1941).

[10] A. K. Babko, *Compt. rend. acad. sci. U.R.S.S.*, **52**, 37 (1946); *C. A.*, **33**, 9179 (1939).

[11] H. S. Frank and R. L. Oswalt, THIS JOURNAL, **69**, 1321 (1947).

[12] Throughout this paper we shall write ionic aggregates with their *net* charge, *e.g.*, $FeSCN^{++}$, rather than $Fe^{+++}\cdot SCN^-$. This is for convenience only, and should not be taken to imply a special distribution of charge in the complex ion.

[13] W. M. Latimer, "Oxidation Potentials," 2nd edition, Prentice-Hall, Inc., New York, N. Y., 1952, pp. 138, 223.

Experimental

Reagents.—All solutions were prepared and all experiments were made with doubly distilled water.

A stock aqueous solution of ferric perchlorate was prepared from A.R. (analytical reagent) $FeCl_3$ by repeated precipitation of ferric hydroxide from perchloric acid solution with ammonia. The final precipitate was washed thoroughly with water to free it from excess ammonium hydroxide, and then redissolved in perchloric acid. The stock solution was free of ammonium salts, and gave negative tests for chloride and sulfate ions. Its iron content was determined by reduction of aliquot portions to the ferrous form, followed by titration with standard potassium permanganate.

A.R. 72% perchloric acid was further purified by distillation at 100°, 0.5–1.0 mm., in a Pyrex still.

Sodium thiocyanate was purified by three recrystallizations from water, and standardized argentometrically.

A solution of sodium perchlorate, which was used to adjust the ionic strength of various solutions, was prepared by exact neutralization of pure sodium carbonate with perchloric acid.

Solutions of ferrous salts were prepared by dissolving A.R. ferrous ammonium sulfate in 1.0 *M* perchloric acid, and were standardized by titration with potassium permanganate. We found, in agreement with Carter and Davidson,[14] that such solutions are stable toward oxidation by air; ferrous concentrations as low as 2×10^{-5} *M* are less than 0.2% oxidized at 25° in three days.

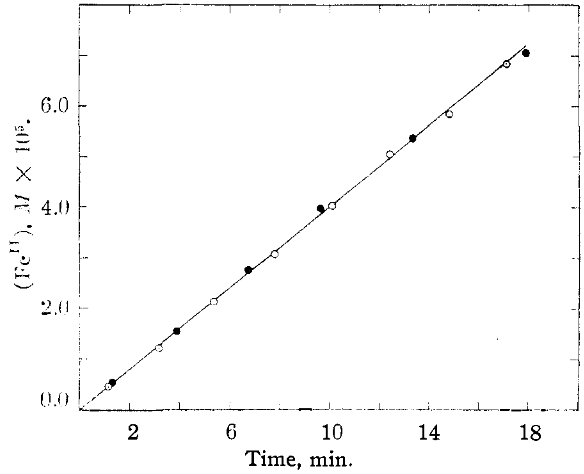

Fig. 1.—Typical results for duplicate measurements of initial rate of formation of Fe^{II}: 0.00230 *M* (Fe^{III}), 0.0784 *M* (SCN^-), 0.967 *M* $(HClO_4)$; $T = 29.89°$.

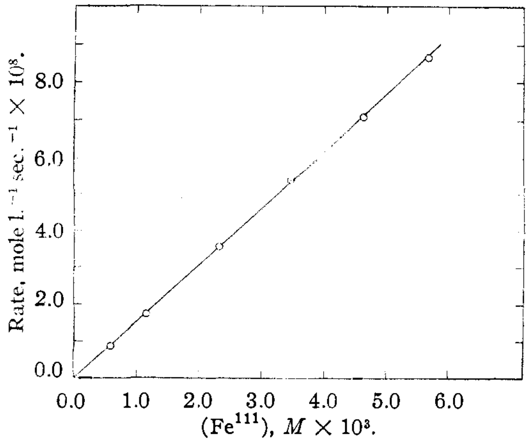

Fig. 2.—Effect of variation of (Fe^{III}) on initial rate of formation of Fe^{II} for $(SCN^-)_0 = 0.0784$ *M*, $(HClO_4) = 0.967$ *M*, $T = 25.00°$.

All other reagents used were C.P. materials which were not further purified.

Experimental Methods and Results

All kinetic and equilibrium measurements were made at an ionic strength of 1.28 ± 0.01 and with 0.967 *M* perchloric acid. Temperature control was precise to ±0.005° in the kinetic experiments, and to ±0.1° in the experiments relating to the formation constant of $FeSCN^{++}$.

Procedure in Kinetic Experiments.—Solutions containing the required amounts of all reagents, except ferric perchlorate, were measured into a 25-ml. volumetric flask, diluted nearly to the calibration mark with water, and then placed in a thermostated water-bath in the dark. After thermal equilibrium had been reached, the required amount of ferric solution was added by micro-pipet, the solution brought to exactly 25.0 ml. with water, and the contents of the flask thoroughly mixed. Zero time was measured from this point. Aliquot portions were removed thereafter at measured times, and run into a solution which quenched the reaction, and which, after dilution, permitted analysis of the ferrous content.

This quenching mixture contained sufficient ammonium fluoride to discharge completely the red color of the ferric thiocyanate present. In addition, sufficient ammonium acetate was present to raise the *p*H of the final solution to 4.0. The third component was *o*-phenanthroline, which reacted with ferrous ion to form the colored complex $[Fe(o\text{-phen})_3]^{++}$. Estimation of the ferrous concentration was made by measurement of the optical density of such a solution at 512 mμ using a Unicam SP 350 spectrophotometer. The analytical method was calibrated by addition of known amounts of ferrous ion to solution identical with those analyzed in the kinetic experiments. A small blank was observed which depended on the concentration of ferric ion in the sample.

Measurements of the Initial Rate.—Early in this work we observed that the presence of ferrous ion retarded the reduction of the remaining ferric ion (see below). Consequently the method of initial rates was used to investigate the kinetics of the process. A typical measurement of ferrous ion concentration *versus* time is given in Fig. 1 in which the results for duplicate experiments are shown. From the slope of such lines, the rate of reduction of ferric ion was measured for a variety of conditions. These results are summarized in Table I and Fig. 2.

TABLE I

INITIAL RATES OF FORMATION OF FERROUS ION

$Fe^{III} = 0.00230$ *M* for all experiments; $\mu = 1.28$; $(HClO_4) = 0.967$ *M*; rate, mole/liter/sec. $\times 10^8$.

(SCN^-), *M*	*T*, °C. → 14.82°	20.00°	25.00°	29.89°
0.0157	0.041	0.089	0.193	0.41
.0314	.151	.323	0.71	1.54
.0470	.298	.68	1.45	3.02
.0626	.47	1.07	2.25	4.92
.0784	.70	1.55	3.05	6.6
.0940	.87	1.93	3.96	8.7
.1097	...	...	4.9	..
.125	...	...	5.9	..
.141	...	...	6.6	..
.157	...	...	7.4	..

For the majority of experiments, the initial rate could be characterized with sufficient precision before not more than 1 to 1.5% of the original ferric ion had been reduced. Under these conditions, corrections to the observed rate caused by depletion of the reactants, or by accumulation of ferrous ion, were negligible. In a few cases, *e.g.*, when the initial concentration of ferric ion was low, and its percentage reduction correspondingly greater at the end of the experiment, the observed values of the initial rate were corrected for these two effects by means of equation 20. Such corrections never amounted to more than 5% of the total rate. The reproducibility in measurements of the rates in duplicate experiments was ±2%.

Retardation by Ferrous Ion.—This effect was demonstrated most simply by addition of ferrous ion to the reaction

---

[14] P. R. Carter and N. Davidson, *J. Phys. Chem.*, **56**, 877 (1952).

TABLE II

VALUES OF RETARDATION CONSTANT k_5 (EQ. 20 IN TEXT)

$(\mathrm{Fe^{III}})$, $M \times 10^4$	$(\mathrm{SCN^-})$, M	$(\mathrm{Fe^{++}})_0$, $M \times 10^4$	k_5
	A Added ferrous ion		
23.0	0.077	0.8	3.5
23.0	.077	1.82	3.5
23.0	.308	2.30	3.0
23.0	.094	1.60	2.5[a]
23.0	.078	0.64	3.0[b]
23.0	.078	0.25	3.5[b]
23.0	.078	1.27	2.5[b]
	B No added ferrous ion		
23.0	0.308	..	4.0
23.0	.134	..	4.5
23.0	.077	..	3.5
23.0	.031	..	3.0
11.5	.308	..	4.0
5.76	.308	..	3.5

All results at 25.0°, except [a] 14.8°, [b] 29.89°.

mixture at the start of the reaction. Figure 3 gives a typical example of this effect. The low concentration of bisulfate ion ($\sim 7 \times 10^{-4}$ M) added with ferrous ion from the stock solution was shown in separate experiments to have no measurable effect on the process.

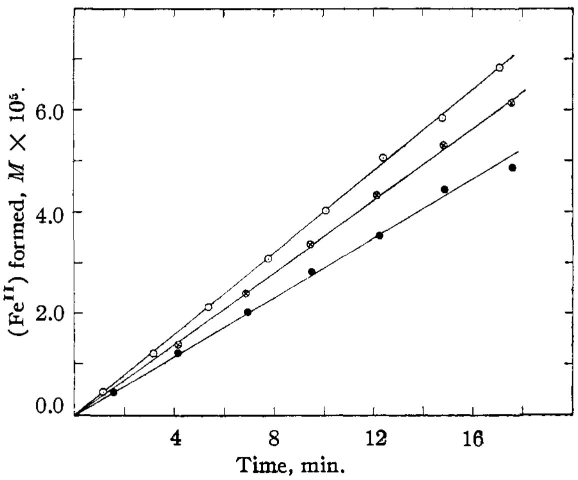

Fig. 3.—Effect of added ferrous ion on initial rate of reduction of ferric ion, 0.00230 M $(\mathrm{Fe^{III}})$, 0.0784 M $(\mathrm{SCN^-})$, 29.89°: ⊙, no added ferrous ion; ⊗, 0.000127 M $(\mathrm{Fe^{II}})_0$; ●, 0.000255 M $(\mathrm{Fe^{II}})_0$.

The auto-retardation is apparent in reaction carried to an appreciable extent of reduction. Thus in Fig. 4, the upper line represents the course of the reaction as predicted from initial rate measurements, on the basis that the reaction is of first order with respect to ferric ion (see Discussion below regarding order of reaction for ferric ion). In this experiment, the concentration of thiocyanate ion remains virtually unchanged over the whole interval of time shown in Fig. 4. The lower line in Fig. 4 represents experimental results, and provides clear evidence of retardation by the products. The magnitude of this retardation is that to be expected from the amount of ferrous ion produced and the known effect of added ferrous ion on the *initial* rate (Fig. 3). This retardation by ferrous ion can be expressed quantitatively by a constant k_5 (for definition see equation 20), and in Table II it is evident that the values of k_5 are identical whether determined from experiments in which (a) ferrous ion was deliberately added or (b) the ferrous ion present is that merely generated in the course of the reaction.

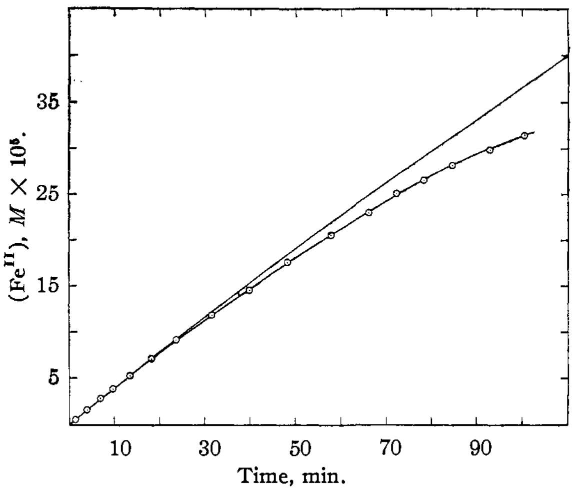

Fig. 4.—Retardation of reaction by ferrous ion: upper line, course of reaction calculated for no retardation; lower line, observed behavior; $(\mathrm{Fe^{III}})_0$ = 0.00230 M $(\mathrm{SCN^-})_0$ = 0.0784 M, T = 29.89°.

Association Constant of FeSCN+++.—Measurements were made at three temperatures of the optical density at 460 mμ of three solutions containing a large excess of ferric ion over thiocyanate ion. For these conditions, the possibility of formation of complexes containing more than one thiocyanate per ferric ion is remote, and it is permissible to assume that $\mathrm{FeSCN^{++}}$ is the only species which absorbs light at 460 mμ. The association constant (neglecting activity coefficients) is defined by: $K_1 = (\mathrm{FeSCN^{++}})/(\mathrm{Fe^{+++}})(\mathrm{SCN^-})$. For a 1-cm. cell, the optical density D is given by $D = EC$, where E and C are, respectively, the molar extinction coefficient and molar concentration of the complex ion $\mathrm{FeSCN^{++}}$. If the total concentration of ferric ion is a, and that of thiocyanate ion is b, and if $a >> b$, then to a very good approximation

$$K_1 = \frac{D}{a(bE - D)} \qquad (1)$$

Values of the nine observed optical densities when substituted into equation 1 gave a series of simultaneous equations which were solved to give a range of values of E, all lying between 4950 and 5050. Since it is unlikely that the extinction coefficient of such species is appreciably affected by variations in the temperature between 11° and 29°, an average value of E = 5000 ± 50, independent of temperature, was used to re-calculate values of K_1. These values are shown in Table III.

TABLE III

ASSOCIATION CONSTANT OF $\mathrm{FeSCN^{++}}$ AT DIFFERENT TEMPERATURES, $\mu = 1.28$

$(\mathrm{Fe^{III}})$, M $\times 10^3$	$(\mathrm{SCN^-})$, M $\times 10^5$	11.4°	18.8°	28.5°
1.16	8.0	129.9	121.2	111.7
2.32	8.0	129.6	120.1	110.2
5.80	8.0	130.0	119.9	109.9
Average values		129.8 ± 0.2	120.4 ± 0.5	110.6 ± 0.7

The log K_1 *vs.* $1/T$ plot is a good straight line, and corresponds to the values $\Delta H = -1.6$ kcal./mole, K_1 at 25° = 114, and $\Delta F°_{25°} = -2.8$ kcal./mole. If we use the extrapolation to zero ionic strength suggested by Rabinowitch and Stockmayer[15] for the analogous $\mathrm{FeCl^{++}}$ system in perchloric acid solution, $K°_1$ at $\mu = 0$, 25°, is 865. $\Delta F°_{25°}$ ($\mu = 0$) is then -4.0 kcal./mole. Using this value, together with ΔH equals -1.6 kcal./mole, we calculate $\Delta S°$ to be +8 e.u. we have assumed here that ΔH is independent of the ionic strength. Precisely the same results are obtained for $\Delta S°$ and $\Delta H°$ by extrapolation to zero ionic strength of *each* value of K_1 shown in Table III, followed by calculation of the entropy change from the relation $\delta \Delta F_{\mu=0}/\delta T = -S_{\mu=0}$, and $\Delta H°$ from the relation $\Delta H° = \Delta F° + T\Delta S°$.

---

(15) E. Rabinowitch and W. H. Stockmayer, THIS JOURNAL, **64**, 335 (1942).

Other values reported in the literature for the association constant of $FeSCN^{++}$ in perchloric media are given in Table IV. The indicated uncertainties in column 3 are those given in the original papers. The values of K°_1 shown in this Table are remarkably concordant. A further agreement between the present work and that already cited is found in the values of the extinction coefficient of $FeSCN^{++}$ at 460 mμ. Earlier values for this quantity are 4946 ± 40,[7] 4512 ± 90[11] and our value is 5000 ± 50.

TABLE IV

VALUES OF THE ASSOCIATION CONSTANT FOR $FeSCN^{++}$ IN PERCHLORATE MEDIA

	μ	K_1[c]	K°_1 at $\mu = 0$[d]
Present work	1.28	114 ± 0.4	865
MacDonald, *et al.*[7]	1.8	115 ± 1.0[a]	730
MacDonald, *et al.*[7]	1.0	120 ± 6[a]	970
Edmonds and Birnbaum[3]	1.0	127 ± 9	1020
Frank and Oswalt[11]	0.5	138 ± 2	890[b]

[a] Values adjusted from 18 to 25°, using $\Delta H_1 = -1.6$ kcal./mole. [b] Extrapolated to $\mu = 0$ in reference 11. [c] First three values at 25°, others uncertain. [d] Extrapolation to $\mu = 0$ by the Rabinowitch–Stockmayer equation.[15]

Discussion

The following mechanism describes adequately the foregoing experimental results

$$Fe^{+++} + SCN^- \rightleftarrows FeSCN^{++} \tag{2}$$

$$K_1 = (FeSCN^{++})/(Fe^{+++})(SCN^-) \tag{3}$$

$$FeSCN^{++} + SCN^- \rightleftarrows Fe(SCN)_2{}^+ \tag{4}$$

$$K_2 = (Fe(SCN)_2{}^+)/(FeSCN^{++})(SCN^-) \tag{5}$$

$$FeSCN^{++} + SCN^- \xrightarrow[k_1]{} Fe^{++} + (SCN)_2{}^- \tag{6}$$

$$Fe(SCN)_2{}^+ + SCN^- \xrightarrow[k_2]{} Fe^{++} + (SCN)_2{}^- + SCN^- \tag{7}$$

rate controlling

$$Fe^{++} + (SCN)_2{}^- \xrightarrow[k_3]{} Fe\,(III) + 2SCN^- \tag{8}$$

$$Fe\,(III) + (SCN)_2{}^- \xrightarrow[k_4]{} Fe^{++} + (SCN)_2 \tag{9}$$

fast

$$(SCN)_2 + H_2O \longrightarrow \text{Products} \tag{9a}$$

The essential features of the scheme are: (i) reversible equilibria involving the complex ions $FeSCN^{++}$ and $Fe(SCN)_2{}^+$, (ii) formation of the ion-radical[16] $(SCN)_2{}^-$ by reaction of either of these complex ions with thiocyanate ion in rate-controlling steps, and (iii) fast and competitive reactions between $(SCN)_2{}^-$ and either ferrous ion or all species of trivalent iron present. We shall reserve for later discussion the possible fate of the thiocyanogen molecules postulated above. In equations 2 to 9 and subsequently, a distinction is made between Fe^{+++} and Fe^{III}, the former being fully hydrated ferric ion, and the latter representing all forms of trivalent iron present.

In the above scheme equation 4 and 6 have been written separately, although the kinetic laws observed would be satisfied by a unimolecular decomposition of $Fe(SCN)_2{}^+$ at a concentration determined by the mobile equilibrium between $FeSCN^{++}$ and SCN^- shown in equation 4. Likewise, the term (SCN^-) appears on both sides of equation 7, and might therefore seem unrealistic in this respect (but compare $p\text{-}H_2 + H \rightarrow o\text{-}H_2 + H$). We imply in equation 7 that the activated complex contains three thiocyanate ions, and the reaction might, for example, proceed by $Fe(SCN)_2{}^+ + SCN^- \rightleftarrows X^* \rightarrow FeSCN^+ + (SCN)^-{}_2$, followed immediately by dissociation of $FeSCN^+$ to Fe^{++} and SCN^-. Such a scheme would also satisfy the kinetic laws observed. At present, no means exist of distinguishing kinetically between these and other equivalent processes.

Putting $d(SCN)_2{}^-/dt = 0$, the above mechanism leads to equation 10 for the steady rate of formation of ferrous ion

$$R = \frac{d(Fe^{++})}{dt} = 2\,[k_1(FeSCN^{++})(SCN^-) + k_2(Fe(SCN)_2{}^+)(SCN^-)]\left[1 + \frac{k_3(Fe^{++})}{k_4(Fe^{III})}\right]^{-1} \tag{10}$$

The association constants K_1 and K_2 may be introduced into equation 10 by the relations

$$(FeSCN^{++}) = \frac{K_1\,(Fe^{III})(SCN^-)}{1 + K_1(SCN^-) + K_1K_2(SCN^-)^2} \tag{11}$$

and

$$(Fe(SCN)_2{}^+) = \frac{K_1K_2(Fe^{III})(SCN^-)^2}{1 + K_1(SCN^-) + K_1K_2(SCN^-)^2} \tag{12}$$

Equations 11 and 12 follow from the assumption that Fe^{+++}, $FeSCN^{++}$ and $Fe(SCN)_2{}^+$ are the only important species of trivalent iron present below 0.1 *M* SCN^- ($FeOH^{++}$ may be neglected for the acidity used in these experiments[15]). Substitution of equations 11 and 12 into equation 10 and rearrangement gives

$$R\left[\frac{1 + K_1(SCN^-) + K_1K_2(SCN^-)^2}{2(Fe^{III})(SCN^-)^2}\right] = \frac{k_1K_1 + k_2K_1K_2(SCN^-)}{1 + \frac{k_3(Fe^{++})}{k_4(Fe^{III})}} \tag{13}$$

We consider first the application of equation 13 to the kinetic data for fixed (Fe^{III}) and variable concentration of thiocyanate ion (Table I), and then for fixed total concentration of thiocyanate ion, and variable (Fe^{III}) (Fig. 2), all in the absence of ferrous ion. Equation 13 then reduces to

$$R\left[\frac{1 + K_1(SCN^-) + K_1K_2(SCN^-)^2}{2(Fe^{III})(SCN^-)^2}\right] = k_1K_1 + k_2K_1K_2(SCN^-) \tag{14}$$

If we denote by $f(K_1, K_2, SCN^-)$ the quantity

$$\frac{1 + K_1(SCN^-) + K_1K_2(SCN^-)^2}{2(Fe^{III})(SCN^-)^2} \tag{15}$$

Equation (14) may be written

$$Rf(K_1K_2, SCN^-) = k_1K_1 + k_2K_1K_2(SCN^-) \tag{16}$$

A plot of the term on the left-hand side of equation 16 *versus* the concentration of thiocyanate ion should give a straight line, from the intercept and slope of which k_1 and k_2 may be determined. (If the equivalent first-order processes referred to above are assumed in place of the second-order processes given in equation 6 and 7, then the intercept would be given by $k_1'K_1K_2$, and the slope by $k_2'K_1K_2K_3$. k_1' and k_2' are the first-order rate constants for decomposition of $Fe(SCN)_2{}^+$ and $Fe(SCN)_3$, and K_3 is the formation constant of $Fe(SCN)_3$. Values of K_2 and K_3 could not then be separated by kinetic means from the first order rate constants. This uncer-

---

(16) It is pertinent to note that the ion-radicals $I_2{}^-$ and $Br_2{}^-$ have been postulated to account for the retardation by products in the reduction of ferric ion by iodide ion (ref. 22), and in the oxidation of ferrous ion by bromine (ref. 14).

tainty is inherent in the interpretation, on purely kinetic grounds, of any system of this kind.)

To use equation 16 in this way, it is necssary first to know the value of K_2 and its variation with temperature. In addition, allowance must be made for the fact that the equilibrium concentration of thiocyanate ion (and not the total concentration) is required in this equation.

It is possible of course to proceed by trial and error, and to calculate $f(K_1, K_2, \mathrm{SCN}^-)$ for a wide range of values of K_2, and determine which value of K_2 gives the best straight line when applied to equation 16. This is in essence the procedure we have used, although we were guided in our choice of K_2 by the following considerations. The value of the ratio K_1/K_2 for the corresponding ferric + chloride system at an ionic strength of 1.0 is 3.3.[15] No certainty exists that it will be the same for the present system at $\mu = 1.28$, since apart from specific effects, the dependence of K_1 on ionic strength will be different from that of K_2. If we use this as a rough guide, K_2 at 25° is then about 30. MacDonald, *et al.*,[7] found K_2 to be 56 at 18° for an ionic strength of 1.8, and stated that a value of 30 at this ionic strength is to be expected by considerations of the type suggested by Bjerrum.[17] Although Babko's results[10] are not of direct applicability, the ratio of K_1/K_2 which he states for an unspecific temperature and ionic strength is in accord with MacDonald's data.[7] K_2 for the present system may therefore reasonably be expected to lie between 15 and 50.

With respect to the possible variation of K_2 with temperature, we have found that the optical density at 460 mμ changes by -0.7% per degree (corresponding roughly to $\Delta H_1 = -1.6$ kcal./mole for K_1) when FeSCN^{++} is the principal colored species present. The temperature coefficient becomes less negative at higher concentrations of thiocyanate ion. and is -0.3% per degree at 0.06 M SCN^-. For the latter conditions, a considerable proportion of $\mathrm{Fe}^{\mathrm{III}}$ is in the form $\mathrm{Fe(SCN)_2}^+$. Such measurements cannot be used to evaluate the temperature coefficient of K_2, since the extinction coefficients of $\mathrm{Fe(SCN)_2}^+$ are not known. However, this result suggests that ΔH_2 is less negative than ΔH_1, and may well be zero. Variation of K_2 with temperature may therefore be neglected for the present purpose. This conclusion agrees with the suggestion of Rabinowitch and Stockmayer,[15] who give reasons for expecting that the temperature coefficient of K_2 for complexes of this sort should not be greatly different from that of K_1.

The calculation referred to earlier of the equilibrium concentration of thiocyanate ion from the known total concentration present was made by means of the relation

$$(\mathrm{SCN}^-) = (\mathrm{SCN}^-)_0 - (\mathrm{Fe}^{\mathrm{III}}) \left[\frac{K_1(\mathrm{SCN}^-) + 2K_1K_2(\mathrm{SCN}^-)^2}{1 + K_1(\mathrm{SCN}^-) + K_1K_2(\mathrm{SCN}^-)^2}\right] \quad (17)$$

The validity of equation 17 depends on the assumption that Fe^{+++}, FeSCN^{++} and $\mathrm{Fe(SCN)_2}^+$ are the important species of trivalent ion present. The possibility of complexing of ferrous ion by thiocyanate does not affect this calculation, since it was applied only to cases for which the concentration of ferrous ion was negligible.

Figure 5 shows some representative results of the application of equation 16 to the kinetic data at 14.8° (Table I). In this figure, a plot of $Rf(K_1, K_2, \mathrm{SCN}^-)$ is made *versus* the equilibrium concentration of thiocyanate ion, for the postulated values of K_2 shown. The results for $K_2 = 50$ give six points through which a smooth curve may be drawn, but which is concave upward. For $K_2 = 10$ the reverse behavior is noted. $K_2 = 20$ on the other hand, gives a series of points through which a satisfactory straight line can be drawn, with a positive intercept.

Two possibilities must be considered in the interpretation of Fig. 5, and of similar plots for the results at the other temperature shown in Table I. (i) The rate function $Rf(K_1, K_2, \mathrm{SCN}^-)$ may give a straight line passing through the origin, indicating that the rate constant k_1 in equation 16 is zero. (ii) a straight line with a positive intercept equal to k_1K_1 may be found, indicating that both FeSCN^{++} and $\mathrm{Fe(SCN)_2}^+$ take part in the reaction. In the former case, the results for the rate functions calculated from the kinetic data for other temperatures given in Table I should also pass through the origin, with the same value of K_2. In the latter case, the positive intercept should increase as the temperature is raised, in the proportions governed by the energy of activation associated with k_1 (and the temperature coefficient of K_1).

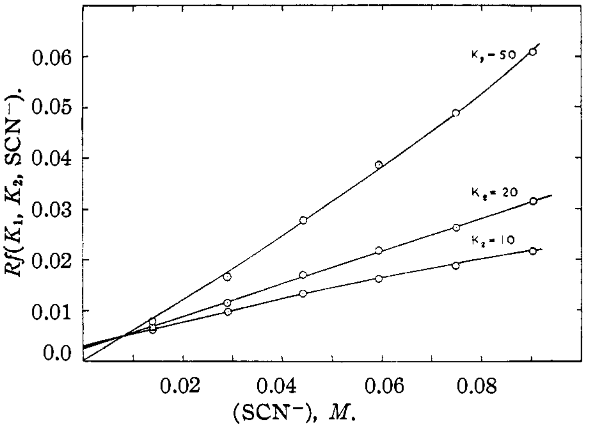

Fig. 5.—An example of application of equation 16 to kinetic data; $T = 25.00°$.

Application of these criteria to all of the results in Table I led to the conclusion that the best fit to the data was obtained by $K_2 = 20$, for all temperatures, with an intercept which increased with temperature. The results of such calculations are give in Fig. 6. Values of K_2 as large as 25, and as small as 15, gave almost equally good straight lines, all with positive intercepts. Above or below this range of values for K_2, the calculations gave plots which were not straight lines within the limits of error of the rate measurements. We therefore conclude that both $\mathrm{FeSCN_2}^{++}$ and $\mathrm{Fe(SCN)_2}^+$ take part in the reaction, and that the association constant K_2 has a value of 20 ± 5, independent of temperature.

---

[17] N. Bjerrum, *Z. physik. Chem.*, **106**, 214 (1923).

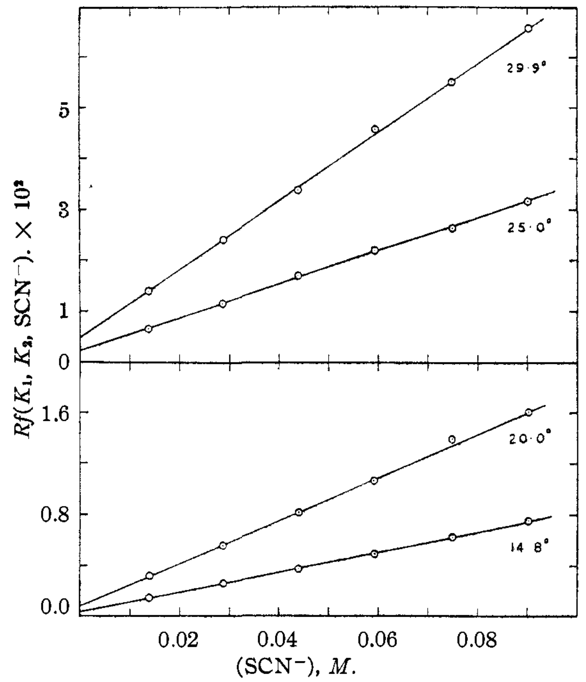

Fig. 6.—Application of equation 16 to kinetic data, for $K_2 = 20$.

Table V gives the values of the rate constants k_1 and k_2, calculated from the intercepts and slopes of the straight lines shown in Fig. 6. A plot of log k_2 *vs.* $1/T$ gave a good straight line over the temperature range 14.8–29.9°. A similar plot for log k_1 was not as satisfactory, the result for 20.0° lying somewhat below a straight line through the other three points. The corresponding experimental energies of activation were $E_2 = 26.3$ kcal./mole, and $E_1 = 27 \pm 3$ kcal./mole.

TABLE V

VALUES OF THE RATE CONSTANTS k_1 AND k_2 IN MOLE^{-1} L. SEC.$^{-1}$

T, °C.	$k_1 \times 10^5$	$k_2 \times 10^4$
14.82	0.34	0.31
20.00	0.63	0.71
25.00	1.76	1.43
29.89	4.1	3.11

The entropies of activation for the two processes are $\Delta S^\ddagger = +8$ e.u., and $\Delta S_2^\ddagger = +10$ e.u. These entropy values were calculated for a standard state of one mole per liter of each of the reactants from the equation[18]

$$k_{1,2} = e\frac{kT}{h}e - \frac{E \text{ exp}}{RT} \times e^{\Delta S^\ddagger/R}$$

The term k (without subscript) in this equation is the Boltzmann constant; the other terms have their usual meaning.

The closely similar values of the entropy and enthalpy terms for the rate constants k_1 and k_2 suggest that similar processes are concerned in the rate-controlling steps in equations 6 and 7. A tentative suggestion is that the slow step in each case is the transfer of an electron from one of the thiocyanate ions to the central ferric ion, with the formation of $(SCN)_2^-$ and either ferrous ion (equation 6) or $FeSCN^+$ (equation 7).

We consider now the significance of the kinetic results for fixed total concentration of thiocyanate ion, and varying initial concentrations of ferric ion (Fig. 2). Equation 14 may be written

$$\frac{d(Fe^{++})}{dt} = R = (Fe^{III})B \qquad (18)$$

where

$$B = 2\left[\frac{k_1K_1 + k_2K_1K_2(SCN^-)}{1 + K_1(SCN^-) + K_1K_2(SCN^-)^2}\right](SCN^-)^2 \qquad (19)$$

Equation 18 predicts that the rate of reaction should vary directly with (Fe^{III}), provided the term B remains constant. It is evident that the results of Fig. 2 are in agreement with the mechanism proposed. (The data shown in Fig. 2 have been normalized to a constant value of the term B by means of equation 19.) The values for the equilibrium concentration of thiocyanate ion required for this calculation were in turn calculated from the total concentration by equation 17.

Retardation by Ferrous Ion.—Provided the concentration of thiocyanate ion does not vary during a given experiment, equation 13 may be written as

$$R = \frac{d(Fe^{++})}{dt} = \frac{-\,d(Fe^{III})}{dt} = \frac{k^1(Fe^{III})}{1 + k_5\,(Fe^{++})/(Fe^{III})} \qquad (20)$$

where k^1 includes all terms in k_1, k_2, K_1, K_2 and thiocyanate ion in equation 13, and $k_5 = k_3/k_4$. If the concentration of ferrous ion is zero initially, equation 20 may be integrated in terms of (Fe^{III}) to give

$$k_5 = \frac{k^1t + 2.303 \log (Fe^{III})/(Fe^{III})_0}{2.303 \log (Fe^{III})/(Fe^{III})_0 + (Fe^{III})_0/(Fe^{III}) - 1} \qquad (21)$$

in which $(Fe^{III})_0$ is the initial concentration of trivalent iron. The pseudo-first order rate constant k^1 is that derived from measurements of the initial rate in the absence of ferrous ion. Equation 21 may be used to calculate k_5 for experiments of relatively long duration, *e.g.*, for the results of the kind shown in Fig. 4.

An alternative method for the estimation of k_5 is to measure the effect of added ferrous ion on the initial rate. If R_1 is the initial rate in the absence of added ferrous ion, and R_2 is the corresponding rate for a second identical solution to which ferrous ion has been added, then

$$k_5 = \frac{(R_1/R_2) - 1}{(Fe^{++})/(Fe^{III})} \qquad (22)$$

In equation 22, (Fe^{++}) is the concentration of ferrous ion in the second solution.

The values of k_5 calculated in these two ways are shown in Table II. An experimental error of about ±30% is associated with each value of k_5, because either method for its calculation ultimately involved the determination of the ratios of approximately equal quantities. Within experimental error, k_5 is independent of the concentrations of ferrous to ferric ions in solution. This conclusion is in agreement with the requirements of the mechanism proposed.

---

[18] H. Eyring, S. Glasstone and K. J. Laidler, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 417.

The data in Table II indicate that the temperature coefficients of the rate constants k_3 and k_4 are roughly equal.

Stoichiometry of the Reaction.—Thiocyanogen is known to hydrolyze in aqueous solution according to[19,20]

$$4H_2O + 3(SCN)_2 \longrightarrow 7H^+ + 5SCN^- + HCN + SO_4^= \quad (23)$$

Equation 23, together with the net result of equations 2 to 9, suggest that the over-all stoichiometry of the present system is

$$2Fe^{+++} + 2SCN^- = 1.67SCN^- + 0.33CN^- + 0.33SO_4^= + 2Fe^{++} \quad (24)$$

If these be the only processes occurring, then the argentometric titer of a reaction mixture should remain constant, and sulfate ion should appear in solution, as the reaction proceeds. The results of experiments to test these points are given in Table VI.

TABLE VI

TITRATION OF REACTION MIXTURES WITH 0.01 M SILVER NITRATE

A: 0.0790 M SCN^-, 0.00 M Fe^{III} (reference soln.); B: 0.0790 M SCN^-, 0.0115 M Fe^{III}.

Time, hr.	Soln. A, ml.	Soln. B, ml.	Reduction Fe^{III}, %
0	40.46 ± 0.01	40.43 ± 0.01	0
24	40.45 ± .01	40.20 ± .01	28
48	40.41 ± .01	40.12 ± .02	38
213	40.30 ± .01	39.92 ± .01	71

A gradual but slight decrease takes place in the total concentration of thiocyanate + cyanide as the reaction proceeds, *e.g.*, 0.9% in 213 hours when 71% of the total ferric ion is reduced. In addition, sulfate ion as barium sulfate was detected in solution at the end of the experiment. Although these observations cannot be taken as proof of the stoichiometric requirements of equation 24, they are in essential agreement with such a mechanism. The slight changes with time of the thiocyanate + cyanide content of solution B point to alternate and minor modes of disappearance of thiocyanogen. We have noticed a faint smell of hydrogen sulfide given off by solutions which have stood for long periods, but we are not in a position to discuss this aspect any further at the present time.

Reactivities of Other Species in Solution

Adamson[21] has pointed out that the very slow electron transfer between hexacyanoferrate(III) and either iodide or cyanide ions, to form iodide atoms or cyanogen radicals, involved considerable positive increment in free energy. Similar consideration may possibly account for the absence of simple electron transfer processes in the ferric + iodide system.[22] However, these reactions proceed at an appreciable rate when I_2^- or $(CN)_2^-$ are intermediates.[21,22] The following result suggests that the analogous electron transfer between Fe^{+++} and thiocyanate ion to form thiocyanate radicals is also very slow. For a solution containing trivalent iron in the proportions $(Fe^{+++}) = 65\%$, $(FeSCN^{++}) = 32\%$ and $(Fe(SCN)_2^+) = 3\%$ (based on $K_1 = 114$ and $K_2 = 20$), the expected rate of reaction calculated from the rate constants k_1 and k_2 given in Table V was 1.0×10^{-9} mole^{-1} sec.$^{-1}$. The observed rate was 0.9×10^{-9} mole l.$^{-1}$ sec.$^{-1}$. This result implies that the rate constant for electron transfer between thiocyanate ion and uncomplexed ferric ion is very much less than either k_1 or k_2. Insufficient data are available to attempt any analysis of the energetics concerned; however, it is not unlikely that this process is slow because of unfavorable energy requirements.

At 25°, the rate of reduction of ferric ion by thiocyanate ion at $\mu = 1.28$ increases nearly linearly with increasing concentration of thiocyanate ion in the range of 0.1 to 0.3 M. Now at 0.1 M thiocyanate, for low concentrations of ferric ion, virtually no trivalent iron remains uncomplexed, ($(Fe^{+++}) = 3\%$, $(FeSCN^{++}) = 32\%$ and $(Fe(SCN)_2^+) = 65\%$), and formation of higher complexes can occur only at the expense of the two lower complex ions. It thus appears that the similarity already noted in the values of the rate-constants k_1 and k_2 persists for the higher complex species as well. This similarity may arise of course from a fortuitous cancellation of entropy and enthalpy terms, and further measurements at different temperatures are necessary to decide this question. In this connection, it is interesting to note that the entropies and energies of activation for electron transfer between ferrous ion and either $FeCl^{++}$ or $FeCl_2^+$ are not markedly affected by changes in the net charge of the ferric ion.[23]

Acknowledgments.—One of us (R.H.B.) wishes to acknowledge a grant of leave of absence from Atomic Energy of Canada, Ltd., Chalk River, Ontario. We are also indebted to Imperial Chemical Industries, Ltd., for the loan of apparatus.

LEEDS, ENGLAND

---

(19) H. Lecher, M. Wittwer and W. Speer, *Ber.*, **56**, 1104 (1923).

(20) R. Gauguin, *J. chim. phys.*, **42**, 138 (1945).

(21) A. W. Adamson, *J. Phys. Chem.*, **56**, 858 (1952).

(22) A. J. Fudge and K. W. Sykes, *J. Chem. Soc.*, 119 (1952).

(23) J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952).