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The Reaction Kinetics of Iron(III) and Thiocyanate at Low Temperatures

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The kinetics of the reaction for the complexing of iron(III) with thiocyanate ion have been studied in the temperature range of −38 to −54°. The solvent was 80% methanol–20% water solution at an ionic strength of approximately 0.1 calculated as for aqueous solutions. The reaction followed the forward rate law of $dC_{FeNCS^{++}}/dt = k_1C_{Fe^{+3}}C_{NCS^-} + k_2C_{Fe^{+3}}C_{NCS^-}/C_{H^+}$. At −45.2° the values of k_1 and k_2 were 0.28 ± 0.03 M^{-1} sec.$^{-1}$ and 0.016 ± 0.002, respectively. Study of the variation of these rates with temperature gave the following values: $\Delta H_1^{\ddagger} = 25.9 \pm 4.5$ kcal./mole, $\Delta H_2^{\ddagger} = 20.1 \pm 2.3$ kcal./mole, $\Delta S_1^{\ddagger} = 53 \pm 20$ e.u. and $\Delta S_2^{\ddagger} = 23 \pm 10$ e.u. at −47.5°. Estimates of the rate of addition of the second thiocyanate ion gave a first order rate constant of 0.4 ± 0.1 M^{-1} sec.$^{-1}$ at −45.2°. Decreasing the water content of the solvent increased the rate constant.

Introduction

The rate of formation of the complex between iron(III) and thiocyanate has been studied at room temperature in aqueous solution by Chance[1] and by Below, Connick and Coppel.[2] Bjerrum and Poulson[3] have suggested that systems such as this might also be studied by using low temperatures and a non-aqueous solvent. Chance[1] reports a second-order rate constant of 1.7×10^4 M^{-1} sec.$^{-1}$ at room temperature assuming the reaction to be first order in ferric ion. Below, Connick and Coppel[2] showed the rate law to be $dC_{FeNCS^{++}}/dt = k_1C_{Fe^{+3}}\,C_{NCS^-} + k_2C_{Fe^{+3}}\,C_{NCS^-}/C_{H^+}$. At 25° and an ionic strength of 0.40 they found $k_1 = 127 \pm 10$ M^{-1} sec.$^{-1}$, and $k_2 = 20.2 \pm 2$ sec.$^{-1}$. From temperature variation studies over the range of 15 to 31°, they determined $\Delta H_1^{\ddagger} = 13.0 \pm 14$ kcal./mole, $\Delta H_2^{\ddagger} = 20.2 \pm 1.4$ kcal./mole, $\Delta S_1^{\ddagger} = -5 \pm 5$ e.u. and $\Delta S_2^{\ddagger} = 15 \pm 5$ e.u.

This work was done in the temperature range of −38° to −54° using 80% methanol–20% water, by volume as the solvent. The effect of variation of the solvent from anhydrous methanol to 20% water was observed. Using an excess of iron, the rate and the enthalpy and entropy of activation were determined for the formation of the first complex. By using an excess of thiocyanate an estimate of the rate of formation of the second complex was obtained.

It has been shown by Bent and French,[4] Lister and Rivington[5] and a large number of other investigators that the first colored compound resulting from a reaction of iron(III) and thiocyanate is $Fe(NCS)^{++}$ and that at least several other higher complexes exist. This work has been thoroughly reviewed by Lewin and Wagner.[6]

Experimental

Reagents.—Analyzed reagent grade chemicals were used throughout without further purification. Iron solutions were prepared from $Fe(NO_3)_3 \cdot 9H_2O$ and analyzed spectrophotometrically against standards prepared from pure iron. Thiocyanate solutions were prepared from dried KNCS and were analyzed by silver nitrate titration. The *p*H adjustments were made by addition of nitric acid or sodium hydroxide. Commercially available anhydrous methanol was used. During withdrawal of methanol, the tanks were vented through calcium chloride tubes. Analysis by the Karl Fischer method indicated water content of less than 0.05%.

Equipment.—Measurements were made using a stopped flow technique with a four channel Teflon mixing chamber of the Hartridge and Roughton[7] type. Solutions were delivered to the mixing chamber from two 50 ml. syringes driven by a motor. The syringes were contained in an insulated constant temperature methanol bath cooled by Dry Ice. The outlet tube from the mixing chamber passed through the bottom of the bath by means of an insulated tube to a jacketed, evacuated tube in a Bausch and Lomb Spectronic 20 Spectrophotometer. The effective light path of the tube was determined to be 0.276 cm. by comparison with the absorption of cobalt chloride solutions in cells of known light path in a Beckman DB spectrophotometer at 505 mμ. All measurements were made at 525 mμ, since maximum absorption of the complex at −50° in anhydrous methanol occurred at that wave length. The variation of absorbance with time was followed on an Esterline Angus 0–1 ma recorder attached through an appropriate amplifier. Temperature measurement was by means of a low temperature thermometer calibrated at solid–liquid equilibrium temperatures of *n*-heptyl alcohol, chlorobenzene and chloroform. Temperature variation with time was measured with a Sargent Thermistor bridge with a low temperature probe and recorded on a Sargent SR recorder. Hydrogen ion concentrations were measured on a Beckman Zeromatic and Beckman Model H *p*H meter using a glass electrode and calomel reference electrode. According to Bacarella, *et al.*,[8] these results should be reliable in methanol solutions, but further standardization was made for most measurements by adjusting a sample of solvent with acid or base until it gave the same *p*H meter reading and then titrating the sample with standard sodium hydroxide.

An attempt was made to maintain a constant ionic strength calculated as for an aqueous solution. However, since KNO_3 precipitated out upon cooling the methanol containing solutions to the desired temperatures, it was not possible to prevent some variation in ionic strength. The ionic strength varied from 0.10 to 0.15.

Results

The molar absorbancy was determined at 525 mμ by measuring the absorbance of solutions containing a large excess of iron and varying amounts of thiocyanate with the ionic strength adjusted to approximately 0.1. It was assumed that under these conditions the absorption was due entirely to the $Fe(NCS)^{++}$ ion, the spectrophotometer having been adjusted to 100% transmittance with the excess iron solution. The value of the molar absorbancy index, *a*, was found to be 2930 ± 182, assuming Beer's law.

Numerous studies have been made on the hydrolysis constants for iron(III) in aqueous solu-

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[1] B. Chance, *J. Franklin Inst.*, **229**, 737 (1940).

[2] J. F. Below, Jr., R. E. Connick and C. P. Coppel, *J. Am. Chem. Soc.*, **80**, 2961 (1958).

[3] J. Bjerrum and K. G. Poulson, *Nature*, **169**, 463 (1952).

[4] H. E. Bent and C. L. French, *J. Am. Chem. Soc.*, **63**, 568 (1941).

[5] M. W. Lister and D. E. Rivington, *Can. J. Chem.*, **33**, 1572 (1955).

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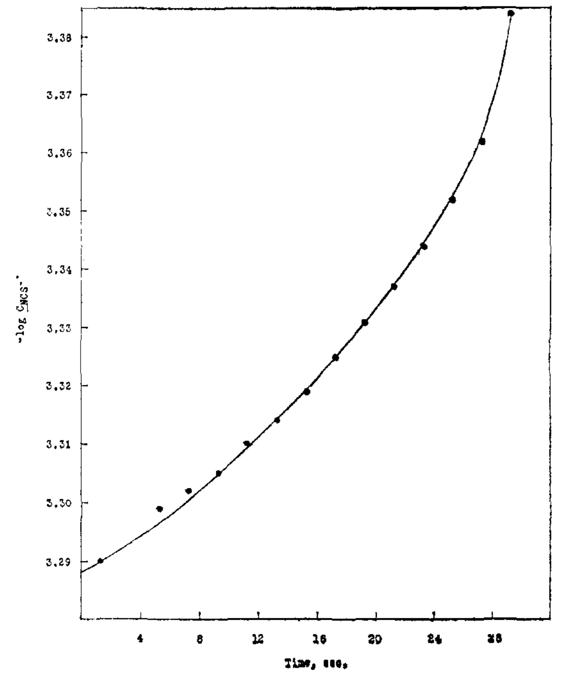

Fig. 1.—Variation of log C_{NCS^-} with time: concn. of NCS^- was 0.000539 *M*, conc. of iron (III) was 0.0091 *M*, *p*H was 1.26, and the temperature of the bath was −52.2°.

tion,[9–12] but data are lacking for the system in methanol. Therefore, solvolysis constants were determined over the temperature range −60 to 25° in 80% methanol–20% water using the method of Siddall and Vosburgh.[11] The values used for the expression $K_S = C_{FeOH^{++}}C_{H^+}/C_{Fe^{+3}}$ at various temperatures are given in Table I. Figure 1 shows a typical plot of log C_{NCS^-} against time. It will be noted that instead of being a straight line as found by Below, Connick and Coppel,[2] this plot has a definite curvature. This can be shown to be due to the temperature variation with time. A typical graph of temperature against time is shown in Fig. 2. Slopes for determination of first order rate constants (with one concentration in excess and therefore considered constant) were taken from the tangent to the plot of log *C* against time, and the temperature at the point of tangency taken from the temperature against time plot. This gave temperatures to ± 0.5°. Corrected for solvolysis, the values of the concentration of iron(III) used in calculating the rate constants were 96% of the total iron(III) concentration at a *p*H of 0.848, 91% at a *p*H of 1.24 and 77% at a *p*H of 1.724.

TABLE I

SOLVOLYSIS CONSTANTS FOR IRON (III) IN 80% METHANOL SOLUTIONS

Temp., °C.	$K_S \times 10^3$
20.0	3.65 ± 0.35
0.0	3.22 ± 1.22
−25.0	0.92 ± 0.51
−41.8	.82 ± .29
−49.7	.35 ± .25
−59.2	.33 ± .08

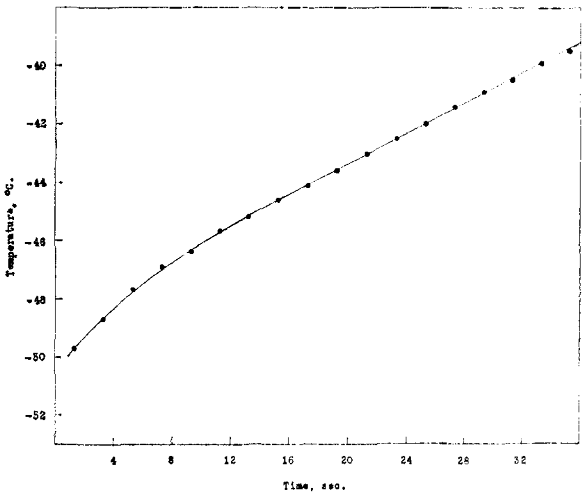

Fig. 2.—Variation of temperature with time; temperature of bath was −52.2°.

Although it is probable that iron(III) that has undergone solvolysis reacts further to form polynuclear species under the conditions used, no correction was made for them. In the plots of rate constants against $1/C_{H^+}$ straight lines were obtained. This is taken as an indication that the correction in concentration of iron(III) for the presence of the polynuclear species is within experimental error.

Table II gives the data for rate constants under various conditions of *p*H and temperature for runs with excess iron. The initial concentration of iron was 0.01 *M* and the initial concentration of the thiocyanate, 0.0005 *M*.

The values of *k* reported are averages of two to four independent determinations, except as indicated by footnotes to the table. The same determinations were used to find *k* at two or three temperatures. The mean deviation of a single measurement found in averaging the values under each set of conditions was 126 parts per thousand.

The variation of rate constant with hydrogen ion concentration was studied. No definite conclusions were possible in experiments with an excess of thiocyanate ion since considerable deviation was observed in the values of *k* found. In the excess iron trials the expression suggested by Below, Connick and Coppel[2] of $-\,dC_{NCS^-}/dt = k_1C_{NCS^-}\cdot C_{Fe^{+3}} + k_2C_{NCS^-}C_{Fe^{+3}}/C_{H^+}$ agreed well with the data.

Plots of log (*k*/*T*) *versus* 1/*T* were straight lines for both k_1 and k_2. $\Delta H^\ddagger$ and $\Delta S^\ddagger$ determined by the Eyring equation are $\Delta H_1^\ddagger = 25.9 \pm 4.5$ kcal., $\Delta H_2^\ddagger = 20.1 \pm 2.3$ kcal., $\Delta S_1^\ddagger = 53 \pm 20$, $\Delta S_2^\ddagger = 23 \pm 10$ e.u. at − 47.5°.

The variation of rate constant *k* with water concentration of solvent at −47.5° was studied, using an excess of thiocyanate, at a *p*H of 1.4. The dependence of rate on water concentration is shown in Fig. 3.

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(10) R. M. Milburn and W. C. Vosburgh, *J. Am. Chem. Soc.*, **77**, 1352 (1955).

(11) T. H. Siddall and W. C. Vosburgh, *ibid.*, **73**, 4270 (1951).

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TABLE II

AVERAGE RATE CONSTANTS FOR EXPERIMENTS USING EXCESS IRON, k_1 M^{-1} SEC.$^{-1}$

C_{H^+}	−38.7°	−39.1°	−39.6°	−41.6°	−43.5°	−44.3°	−45.2°	−47.7°	−48.7°	−50.9°	−53.4°
0.142	1.87	1.83	1.83	1.28	0.725^a	0.76	0.33	0.26^b	0.27	0.19	
.141							.60	.11			
.133	1.89	1.87	1.68	0.93	0.58	.62	.35	.23^b	.17	.11	
.127							.39	.15			
.0575	4.09^b	3.31	3.08	2.18	1.23	.86^b	.79	.46^b	.37	.29	0.18
.0550				1.53^a	1.06^a	.74	.60	.41^b	.37^b	.18	.21^a
.0530	2.99	2.53	2.38				.66	.47	.33	.29	
.0512	3.03	3.09	2.80	1.35	0.88	.72	.76	.49^b	.46	.29	.24
.0398							.59^b	.58^b			
.0288							.35	.17			
.0202	6.75	5.83	5.31	3.06	2.24	2.05		1.04^b	.74	.62	
.0189	4.69	4.65	4.13	2.70	2.07	1.57	1.19	0.94^b	.74	.57	.84^a
.0178							1.09	1.01			

[a] Based on a single determination. [b] Based on 5 to 9 determinations.

With the thiocyanate ion in excess, a definite break was observed in a temperature corrected plot of the absorbancy, A, *versus* time. The plot was linear on both sides of the break. Interpreting this second slope as being due to formation of $Fe(NCS)_2^+$, it was possible to estimate the value of the rate constant, k', for the formation of the second complex assuming the rate law $dC_{Fe(NCS)_2^+}/dt = k'C_{FeNCS^{++}}C_{NCS^-}$. In making the estimate, it was assumed that the reverse rate for formation of the first complex was insignificant, which seems reasonable in light of equilibrium constant values of over 200, as extrapolated from Lister and Rivington's[5] data. The reverse reaction of the formation of the second complex was also assumed to be negligible. This assumption should be reasonable at the start of formation of this complex. Finally, it was assumed that the molar absorbancy index of the second complex is twice the value for the first complex. Lister and Rivington[5] found this to be a good approximation in aqueous solution. With the above assumptions and at high acid concentrations, dA/dt before the break is $m_1 = ad\cdot C_{FeNCS^{++}}/dt = akC_{Fe^{+3}}\ C_{NCS^-}$, where a is the molar absorbancy of $Fe(NCS)^{++}$ for a cell with a light path of unit length. After the break, $m_2 = dA/dt = adC_{Fe(NCS)^{++}}/dt + 2adC_{Fe(NCS)_2^+}/dt$. Considering the reactions of successive complex formation for the first two complex ions, but ignoring further steps, $m_2 = m_1 + ak'C_{Fe(NCS)^{++}}\ C_{NCS^-}$ or $k' = (m_2 - m_1)/AC_{NCS^-}$, if A is the absorbance of the first complex and is relatively constant in the vicinity of the break. The linearity of the curve appears to indicate that these approximations are satisfactory. The value of A and the temperature were taken at the point of the break. These values showed no acid dependence. The value of k' at −45.2° was estimated to be 0.4 ± 0.1 M^{-1} sec.$^{-1}$.

Discussion

The values of k_1 and k_2 reported here may be compared with the determinations of Below, Connick and Coppel,[2] which were in agreement with those of Chance,[1] when the latter were calculated at the same pH. Using the temperature dependence data reported by them for aqueous solvent, their values were extrapolated to −47.5° and then corrected for solvent effect to conditions of 80% methanol in accordance with the results reported here. This gave values of 0.4 and 0.001 for k_1 and k_2, respectively, compared with 0.11 and 0.017 reported here. This disagreement is probably best explained by the long extrapolation over a wide range of temperature and water content. The correction for water content was based only on measurements with excess thiocyanate at a pH of 1.4, and the difference in effect of water on k_1 and k_2 was not studied. In the calculation of the results of this work, it was assumed that the condensed forms of iron(III) may be ignored. Although it is necessary to make this assumption, since no studies under similar conditions have been published, it may not be justified.

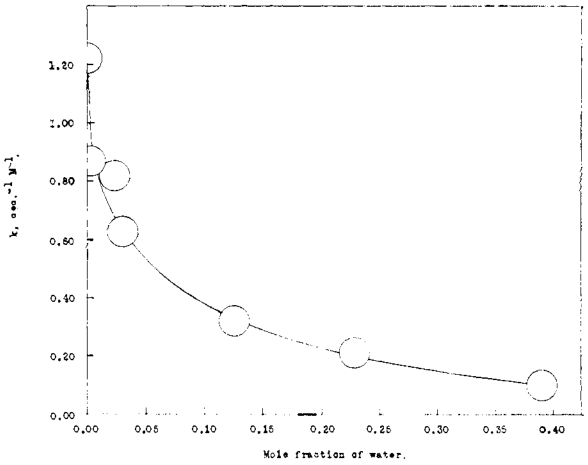

Fig. 3.—Effect of water on rate constants for experiments with excess thiocyanate.

Bjerrum and Poulson's[3] value of k in anhydrous methanol at −47.5° would be about 50 compared to a measured value under the same conditions in this study of 1.2, for an excess thiocyanate determination. While this difference is appreciable, it is probably within the range of accuracy of their determinations.

The determination of the rate constant for the addition of the second thiocyanate ion showed much better precision than for the determination of the first constant using an excess of thiocyanate. Within the limits of accuracy, no acid dependence was observed for these values of k'. This would indicate that formation of the second complex through a base catalyzed path does not occur to a large extent. This would agree with Lister and Rivington's[5] estimate that the hydrolysis constant for hydrolysis of $FeNCS^{++}$ to $Fe(NCS)(OH)^+$ is about one hundred fold smaller than for hydrolysis of iron(III) ion.[13]

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A Manometric Determination of the Solvolysis Rate of Gaseous *t*-Butyl Chloride in Aqueous Solution[1]

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The rate of solvolysis of gaseous *t*-butyl chloride at unit pressure has been determined in a closed vessel from the rate of pressure drop of the vapor over the aqueous solution in which reaction occurs. Extrapolation of the vapor pressure measurements to zero time gives an approximate determination of the solubility of gaseous *t*-butyl chloride. From these measured quantities, the conventional rate of solvolysis at unit concentration is calculated and the values compared with those obtained by independent methods in the literature. Fair agreement is found. The activation energy for the solvolysis of dissolved *t*-butyl chloride agrees with literature values within the experimental error. The rate of solvolysis of gaseous *t*-butyl chloride at unit pressure is reduced in D_2O compared to H_2O by essentially the same factor (~0.72 at 15°) as is the conventional rate constant.

The rate of solvolysis of *t*-butyl chloride at unit concentration k_c in aqueous solution is so rapid that conventional techniques for rate measurement are applied with difficulty.[4] On the other hand, the vapor pressure and solubility of *t*-butyl chloride lend themselves to the precise determination of the rate of solvolysis at unit pressure k_p of the volatile reactant.

In the present paper we report the determination of the rate constant k_p using an experimental technique which has been previously employed to determine the rate of hydration of volatile olefins.[5] The rate of pressure drop of gaseous *t*-butyl chloride in a closed system is measured over the aqueous solution in which the solvolysis reaction occurs. Extrapolation of the vapor pressure measurements to zero time provides an approximate determination of the solubility, h, of gaseous *t*-butyl chloride. From values of h and k_p, the conventional rate constant k_c is obtained. The method has been successfully applied to measurements in ordinary water at 0.99°, 5.00° and 14.85°, to dioxane–water mixtures at 14.85° and to heavy water at 14.85°. Generally, satisfactory accord is obtained between the rate thermodynamic properties from the present and other investigations. In subsequent work,[6] the method is applied to an extensive study of the effects of aqueous electrolytes on the activity coefficient of *t*-butyl chloride and of its solvolysis transition state.

Experimental

Materials.—The *t*-butyl chloride was prepared by reaction of concentrated hydrochloric acid with *t*-butyl alcohol.[7a] The fraction used for the solvolysis experiments boiled at 48.9–49.0° (uncorr.) at 732 mm. A sample of the *t*-butyl chloride was passed through a gas chromatographic column containing 20% (wt.) paraffin oil on C-22 firebrick at 56°. Only a single fraction was obtained. The collected sample gave the same rate and distribution constants within experimental error as the original sample. Similar results were obtained with the sample of *t*-butyl chloride remaining in the filling vial (*cf.* section on rate measurement) after a series of solvolysis reactions.

Distilled water was used in all experiments. Triply distilled water gave equivalent results. Deuterium oxide was obtained from Liquid Carbonic in greater than 99.5% purity. Dioxane was purified by the method of Vogel.[7b]

Measurements of Rate Constants.—The apparatus and methods used are basically those previously described.[5] The following modifications in the basic system (see Fig. 1-ref. 5a) have been made: (1) In place of the 50 ml. reaction flask (F) a 100 ml. or a 250 ml. flask was used; (2) Tube (G), the *t*-butyl chloride filling vial was sealed directly to the system with a precision stopcock (J′) placed at (J) and thereby eliminating the ground glass joint (J); (3) The two-way precision stopcock (S) was replaced by a one-way stopcock (S′).

This new arrangement of stopcocks was found to be quite satisfactory even though gaseous *t*-butyl chloride can attack the stopcock grease. The vapor which is contained in the section between (S′) and (J′) and that in the reaction system, however, was not observed to attack the stopcock (S′).

Solvent was introduced into the reaction flask (F) and the system degassed by evacuating *via* (O″) and (S′) and (J′) closed in a manner described in procedure B. The *t*-butyl chloride in (G) was degassed in a similar manner with (S′) closed and (J′) opened. The system was then completely immersed in a thermostat with regulation to within ± 0.02° as determined by a N.B.S. calibrated thermometer. The system was secured, the flask was shaken to attain tempera-

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[1] The work was supported in part by the Office of Naval Research.

[2] Taken in part from the Ph.D. thesis of G. A. Clarke, The Pennsylvania State University, June, 1960.

[3] Taken in part from the M.S. thesis of T. R. Williams, The Pennsylvania State University, June, 1954.

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