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Kinetics and Mechanism of Aquation and Formation of Monoazidoiron(III) Ion in Acidic Solution. Equilibrium Properties of Monoazidoiron(III)[1]

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The kinetics of the forward and reverse directions of the iron(III) azide complex formation reaction were studied, using the stopped-flow technique, as a function of hydrogen ion concentration and temperature. Activation parameters were evaluated for the rate constants describing the two aquation pathways for the monoazido complex. Possible mechanisms associated with the transition state of composition $\{(H_2O)_{5+x}FeN_3{}^{2+}\}^*$ are discussed in terms of the magnitude of the activation entropy and the value of formation rate constants for a number of iron(III) complexes. Independent kinetic and equilibrium data indicate that reported values of the formation equilibrium quotient of monoazidoiron(III) ion are high because of neglect of formation of appreciable diazido complex.

Introduction

The net equation for the complex formation equilibrium of hydrazoic acid, hexaaquoiron(III), and azidopentaaquoiron(III) ions in acidic solution is given in eq 1. We have carried out an extensive study of the

$$(H_2O)_6Fe^{3+} + HN_3 = (H_2O)_5FeN_3{}^{2+} + H^+ + H_2O \qquad (1)$$

rate of approach to equilibrium in this rather rapid reaction using the stopped-flow technique with spectrophotometric detection. Seewald and Sutin[2] previously reported a kinetic study of the rate of the reverse (aquation) reaction; these authors used available equilibrium data to compute rate constants for the forward (formation) reaction.

The main points to be settled by our work are these: (1) a direct rather than indirect measure of the formation rate constants, (2) a study of the temperature dependence of the rate constants for aquation to obtain activation parameters, (3) a further inference[3,4] from ΔS^* associated with the aquation rate law term $k[FeN_3{}^{2+}]$ on whether the primary products of this path are the otherwise kinetically indistinguishable $Fe^{3+} + N_3{}^-$ or $FeOH^{2+} + HN_3$, and (4) a kinetic check on the equilibrium quotient[5,6] for reaction 1.

In the course of our examination of points 1 and 4, it became apparent that we were obtaining internally inconsistent results under different reaction conditions especially between studies with high concentrations of hydrazoic acid or of iron(III). Similarly, our results on direct spectral evaluation of the equilibrium quotient differed in the two concentration extremes. The various kinetic and thermodynamic anomalies were removed by considering formation of a diazidoiron(III) complex at the higher hydrazoic acid concentrations; published values[5,6] of the equilibrium quotient Q_1 for reaction 1 appear to be $\sim 20\%$ high by virtue of this unjustified neglect.

Experimental Section

Reagents.—Hydrated iron(III) perchlorate was crystallized from solutions of the chloride in perchloric acid. Chloride ion was volatilized by boiling the solution to fumes of perchloric acid until silver ion failed to produce a visible precipitate. The solid obtained in this procedure was recrystallized at least once. Iron(III) perchlorate solutions were analyzed by standard volumetric procedures with cerium(IV). Some of the solutions were analyzed also spectrophotometrically in 0.3–0.6 *F* perchloric acid using the 2400-A peak of aquoiron(III) with a molar extinction coefficient of 4160 M^{-1} cm^{-1}. The perchloric acid content of the iron(III) perchlorate solutions was analyzed by passing aliquots of the solution through columns of Dowex 50-W cation-exchange resin in the hydrogen ion form and titrating the washings with sodium hydroxide. The hydrogen ion concentration was calculated from the base in excess of that required for the 3 moles of hydrogen ion released per mole of iron(III).

Reagent grade sodium azide was recrystallized twice from water. Hydrazoic acid solutions were used in all experiments at high HN_3 to avoid uncertainty in $[H^+]$. Solutions of HN_3 were prepared from the sodium salt by cation exchange.[6] Azide solutions were analyzed by oxidation with excess cerium(IV) and titration with iron(II). Hydrazoic acid solutions were analyzed also by direct titration with hydroxide ion.

Lithium perchlorate and sodium perchlorate used to maintain ionic strength were twice recrystallized from the reagent grade perchlorate, or were recrystallized from solutions prepared from the reagent grade carbonate and perchloric acid. Reagent grade perchloric acid was used without further purification. Water used in all solutions was redistilled from alkaline permanganate in a tin-lined Barnstead still.

Stopped-Flow Apparatus.—The equipment used in our rapid reaction studies was based on the design of Dulz and Sutin.[7] Mixing was accomplished by causing a motor-driven block (with slip clutch) to push the plungers of two reagent syringes, forcing reagents into an eight-jet Teflon mixing chamber, thence into a 3-mm id quartz observation tube. As a measure of mixing effectiveness, reaction between 0.01 *M* *p*-nitrophenol and 0.01 *F* sodium hydroxide[8] was complete in the time required for the solution to reach the observation tube (3–5 msec). The most efficient mixing was obtained when the two solutions had approximately equal densities, which were satisfactorily obtained by having each solution at roughly the same ionic strength.

The changing transmittance of the solution in the observation tube was observed spectrophotometrically. A Beckman Model

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[1] Work done in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission; Contribution No. 2026.

[2] D. Seewald and N. Sutin, *Inorg. Chem.*, **2**, 643 (1963).

[3] T. W. Swaddle and E. L. King, *ibid.*, **4**, 532 (1965).

[4] T. W. Swaddle and E. L. King, *ibid.*, **3**, 234 (1964).

[5] R. M. Wallace and E. K. Dukes, *J. Phys. Chem.*, **65**, 2094 (1961).

[6] D. Bunn, F. S. Dainton, and S. Duckworth, *Trans. Faraday Soc.*, **57**, 1131 (1961)

[7] G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963). The main components of the stopped-flow system were obtained from Atom-Mech Machine Co., Patchogue, N. Y. The smoothing circuit and balancing potential were taken from the design of Nakamura [S. Nakamura, Ph.D. Thesis, University of Chicago, 1964, p 128].

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

DU monochromator with a tungsten lamp was used. The lamp was operated by three 6-v storage batteries wired in parallel with a conventional battery charger. The light intensity was monitored by an EMI 6256 B photomultiplier tube, biased by a continuously variable 0–1000-v, 0–20-ma, regulated power supply (Kepco No. ABC 1000M). The monochromator slit was opened to 2.0 mm for all experiments described here; the resulting high light level reduced noise from the photomultiplier tube by permitting the bias voltage to be kept low. Photomultiplier bias for these experiments ranged from 440 to 630 v and was typically about 500 v.

The signal from the photomultiplier provided the *A* input of a Tektronix 535A oscilloscope, *via* an amplifying and smoothing circuit.[7] A constant balancing potential was connected to the *B* input of the oscilloscope, and the difference $(A - B)$ was amplified. The balancing potential permitted amplification of changes as small as 6 mv to the full vertical scale of the oscilloscope without amplifying the total signal of up to 6 v. A triggering circuit initiated a single sweep of the oscilloscope at the instant the mixed solution filled a stopping syringe, and a second sweep could be provided manually. The oscilloscope traces were photographed with a Polaroid camera.

The ordinate of the recorded trace represents the transmittance change. Provided the absorbance change is limited to less than *ca.* 0.1, absorbance and transmittance are directly proportional, and the trace may be treated as an ordinary concentration–time curve. The time scale of the oscilloscope was calibrated with a time mark generator, Tektronix Model 181.

Kinetics Experiments.—Four types of rate experiments were carried out and in the interest of distinguishing these they are described and considered separately. First were experiments (type A) similar to those described by Seewald and Sutin,[2] in which iron(III) and hydrazoic acid were in the separate reactant compartments, then mixed rapidly. Concentrations of hydrogen ion and the reactants were chosen such that formation of the small equilibrium concentration of azidoiron(III) ion appreciably changed the concentrations of neither aquoiron(III) nor hydrazoic acid. The intense light absorption of the complex, however, allowed observation of its formation at these low levels. As will be proved later, in this type of experiment one measures only the specific rate for the reverse of eq 1, aquation of the complex, despite the fact that one monitors an increase in absorbance accompanying its net formation.

In the second class of experiment (type B) an equilibrium solution of the azidoiron(III) complex at a lower hydrogen ion concentration was diluted with an equal volume of somewhat more concentrated acid. Dilution and the simultaneous increase in $[H^+]$ caused the reaction to shift toward iron(III) and hydrazoic acid. Again, concentrations in these experiments were chosen so that the equilibrium concentration of the azido complex was very small relative to both iron(III) and hydrazoic acid, as in type A, and as in the type A runs, these reactions measured the aquation rate constant only. The point of runs of type B lay in showing that the reaction equilibrium could be approached from either side with identical kinetic results. In this type of experiment the initial concentration of azidoiron(III) was substantially above its equilibrium value. As a consequence of this, the reaction conditions of type B allowed rate measurements at concentrations of iron(III) and hydrazoic acid considerably below the limit in type A experiments where the concentration of complex under such conditions would never have attained a detectable level.

The third category of kinetic experiments (type C) consisted of runs in which an appreciable fraction of the limiting reagent was converted to the monoazido complex. These runs were carried out at relatively low hydrogen ion concentration (0.05 *M*) with one of the reagents in large excess and the other at a quite low concentration (say 10^{-5}–10^{-4} *F*). These experiments, as shown below, permitted evaluation of the formation (forward) rate constant for eq 1.

A fourth type of rate experiment (type D) bore the same relation to C that B did to A; namely, the concentrations were similar to C, but the reaction was initiated by diluting an equilibrium mixture rather than by mixing the separate reactants.

It will be shown below that under all conditions employed here the rate of approach to equilibrium followed pseudo-first-order kinetics. Values of the ordinate, in arbitrary units proportional to the output voltage *V* of the photomultiplier follower, and transmittance change and absorbance change (see above) were read from the photograph. First-order rate constants were calculated from slopes of conventional plots of log $|V_t - V_\infty|$ *vs.* time, or from plots (based on the method of Guggenheim[9]) of log $|V_t - V_{t+\tau}|$ *vs.* time.

Equilibrium Studies.—Spectrophotometric measurements similar to those of Bunn, Dainton, and Duckworth[6] were made under concentration conditions similar to theirs—high hydrazoic acid (0.01–0.1 *F*), low iron(III) ($\sim 10^{-4}$ *F*), and low acid ($\sim$0.05 *M* H^+) concentrations. The equilibrium measurements were extended to include the opposite concentration ratio: high iron(III) (0.01–0.07 *F*) and low hydrazoic acid ($\sim 10^{-4}$ *F*) concentrations at 0.05 and 0.1 *M* H^+. Absorbance readings were made in a thermostated cell with a Cary Model 14 spectrophotometer.

Absorbance measurements in the equilibrium experiments were made at 4600 A (a peak for azidoiron(III)) as were most kinetic measurements. A number of rate studies were also carried out at 3950 and 6000 A, especially for solutions where the absorbance changes at 4600 A would exceed the limit where transmittance and absorbance could be assumed to be closely proportional. In the kinetics experiments the absorbance changes seen in the 3-mm light path lay in the range 0.003–0.11, and typically were *ca.* 0.05.

Results

Rate Equations and Kinetic Derivations.—The hydrogen ion concentration in every experiment was high relative to the amount of chemical change. As a working hypothesis we assumed the rate equation written

$$d[FeN_3^{2+}]/dt = k_f'[Fe^{3+}][HN_3] - k_{aq}'[FeN_3^{2+}] \qquad (2)$$

in terms of the species predominant at the acidities under consideration. The rate constants in eq 2 represent pseudo-constants that will show a dependence upon $[H^+]$ both because of the form of the net reaction (eq 1) and because the mechanism consists of parallel paths with different numbers of protons.[2] The form of the equilibrium quotient for reaction 1 requires that the pseudo-rate constants be related to the equilibrium quotient by eq 3. When one substitutes into eq 2 the

$$Q_1 = k_f'[H^+]/k_{aq}' \qquad (3)$$

conditions derived from stoichiometry and from the equilibrium condition, the rate law takes the form given in eq 4. Under some conditions, including all

$$d[FeN_3^{2+}]/dt = \{k_f'([Fe^{3+}]_{eq} + [HN_3]_{eq}) + k_{aq}'\} \times \\ ([FeN_3^{2+}]_{eq} - [FeN_3^{2+}]) + k_f'([FeN_3^{2+}]_{eq} - [FeN_3^{2+}])^2 \qquad (4)$$

those employed here, the last term in eq 4 is negligible, and the rate equation simplifies to the form

$$d \ln |[FeN_3]_{eq} - [FeN_3]|/dt = k_f'([Fe^{3+}]_{eq} + [HN_3]_{eq}) + k_{aq}' \qquad (5)$$

On the basis of eq 5 and the assumption made above about the validity of eq 2, the following conclusions are reached: (1) the rate of approach to equilibrium will follow pseudo-first-order kinetics when eq 5 holds; (2) the pseudo-first-order rate constant so evaluated is $k_f'([Fe^{3+}]_{eq} + [NH_3]_{eq}) + k_{aq}'$; (3) in experiments

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[9] E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

(types A and B) where the value of $[FeN_3^{2+}]_{eq}$ is very small relative to $[Fe^{3+}]$ and $[HN_3]$, which are experiments where $[Fe^{3+}]_{eq}$ and $[HN_3]_{eq}$ are small, the first term in the rate constant is very small, and the observed rate constant is k_{aq}'; (4) in experiments at high $[HN_3]$ or high $[Fe^{3+}]$ where an appreciable fraction of the limiting reagent is complexed, both k_f' and k_{aq}' are obtained from a plot of k_{obsd} *vs.* $[HN_3] + [Fe^{3+}]$ in experiments at a particular hydrogen ion concentration.

Kinetic Data at Constant Acidity.—Several series of experiments were done to duplicate the conditions of Seewald and Sutin.[2] In three separate series of experiments, all at 0.44 M H^+, 25.0°, $I = 1.00$ M (sodium perchlorate), the average value of k_{obsd} is 22.8 sec^{-1} (± 0.8 standard deviation, 12 runs). This can be compared with the value observed by Seewalda nd Sutin[2] of 22.1 sec^{-1} at 0.44 M H^+ (read from the straight line in their Figure 1). We carried out a series of measurements, also at 0.44 M H^+ and 25.0°, in which lithium perchlorate was used in place of sodium perchlorate. These experiments covered the concentration ranges of 10^{-4}–0.010 F iron(III) and 10^{-4}–0.015 F hydrazoic acid and consisted of both mixing runs of type A and dilution runs of type B (Table I). The observed rate constants from both types of runs are in excellent agreement. The excellent constancy of k_{obsd} over this entire range of reactant concentrations confirms the earlier report that the rate constant is independent of iron(III) and hydrazoic acid concentrations[2] and that the reaction follows pseudo-first-order kinetics over an extended range of concentrations as predicted by eq 5.

Since the observed first-order rate constant really represents the composite indicated in eq 5, to what extent is it possible to neglect the contribution of the k_f' term under these conditions thereby identifying the measured value exclusively with aquation? Since the equilibrium quotient for formation of azidoiron(III) has been determined,[5,6] it is possible to calculate a value for k_f'. This calculation implies that, although the contribution to k_{obsd} of the k_f' term is very small at the lower concentrations, in some of these type A and B runs at 0.44 M H^+ the contribution is not entirely negligible. At the highest value of $[Fe^{3+}] + [HN_3]$ studied (0.026 M) at 0.44 M H^+, this correction amounts only to 3%, which is about the limit of the experimental error. These corrections also are included in the data of Table I. In some series of experiments at lower $[H^+]$, however, where formation of azidoiron(III) ion is favored, the correction for this effect becomes somewhat more important.

Variation of $[H^+]$.—The acid dependence of the rate constants was ignored in deriving the rate law eq 2–5. Seewald and Sutin's variation of $[H^+]$ led to the dependence shown in eq 6, with the values $k_{2aq} = 19.0 \pm$

$$k_{aq}' = k_{2aq} + k_{1aq}[H^+] \qquad (6)$$

1.4 sec^{-1} and $k_{1aq} = 7.0 \pm 1.4$ M^{-1} sec^{-1} at 25.0° and $I = 1.00$ M ($NaClO_4$). Our experiments at 25.0° covered the range 0.01–0.98 M H^+ and led to the rate constants $k_{2aq} = 20.0 \pm 0.9$ sec^{-1} and $k_{1aq} = 5.1 \pm 1.3$ M^{-1} sec^{-1} at 25.0° and $I = 1.00$ M ($LiClO_4$); see Figure 1. The differences reflect a systematic difference in the results, but the disagreement is not outside the variation one might expect between Na^+ and Li^+. The uncertainties associated with the individual parameters suggest, however, that the results of the two studies are not greatly different.

TABLE I

AQUATION RATE OF AZIDOIRON(III)[a]

$10^3[Fe^{3+}]$, M	$10^3[HN_3]$, M	Type[b]	No. of runs	k_{obsd}, sec^{-1}	Cor k_{aq}, sec^{-1}
0.10	4.00	B	4	22.0	21.9
0.30	0.30	B	2	24.1	23.9
0.90	3.00	A	2	22.5	22.4
2.00	1.50	A	3	23.2	23.1[c]
2.00	8.0	A	5	22.3	22.0
2.00	15.0	A	4	23.8	23.4
3.38	3.00	A	3	23.3	23.1
3.38	3.00	A	6	22.9	22.8[c]
3.38	3.00	B[d]	4	23.7	23.6
4.00	0.10	B	4	24.4	24.3
4.00	1.80	A	4	23.5	23.3
6.00	6.00	A	4	23.3	23.0
8.00	0.75	A	3	22.9	22.7
10.00	3.00	A	4	23.6	23.2
10.00	3.00	A	3	22.9	22.6[c]
10.00	15.00	A[e]	4	24.4	23.8
10.00	15.00	A[f]	4	23.8	23.2

[a] Conditions: $[H^+] = 0.44$ M, temperature 25.0°, $I = 1.00$ M ($LiClO_4$), λ 4600 A. [b] See text. [c] Sodium perchlorate rather than lithium perchlorate used to maintain ionic strength. [d] λ 4200 A. [e] λ 3950 A. [f] λ 6000 A.

Temperature Dependence of Aquation Rate Constants.—Rate measurements were also made at 15.8 and 34.2° and are shown in Figure 1. The observed aquation rate constants were fitted to eq 6, assuming an absolute rate theory expression holds for each rate constant. This fit of $[H^+]$ and temperature dependence was carried out simultaneously using a nonlinear least-squares computer program.[10] In this calculation each rate constant carried a weighting of the reciprocal of its square since the per cent uncertainty in a given measurement was roughly constant. (Of the 252 individual rate constants, 25 with deviations >10% were not included in a second computation.) Values of the activation parameters and the standard deviations calculated by the program are: $\Delta H^*_{2aq} = 14.7 \pm 0.2$ kcal/mole, $\Delta S^*_{2aq} = -3.2 \pm 0.6$ eu and $\Delta H^*_{1aq} = 19.6 \pm 1.4$ kcal/mole, $\Delta S^*_{1aq} = 11 \pm 5$ eu.

Competing Reactions.—Two competing equilibria, eq 7 and 8, cause the molarities of hydrogen and of

$$Fe^{3+} + H_2O = FeOH^{2+} + H^+ \qquad (7)$$

$$2Fe^{3+} + 2H_2O = Fe(OH)_2Fe^{4+} + 2H^+ \qquad (8)$$

aquoiron(III) to change somewhat from their formal values. These reactions must be taken into account in

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(10) This program is based on a report from Los Alamos Scientific Laboratory, LA2367 plus addenda. We are grateful to Drs. T. W. Newton and R. H. Moore for supplying us with the computer programs and to Mr. J. P. Birk for adapting them to the IBM 360 computing facilities.

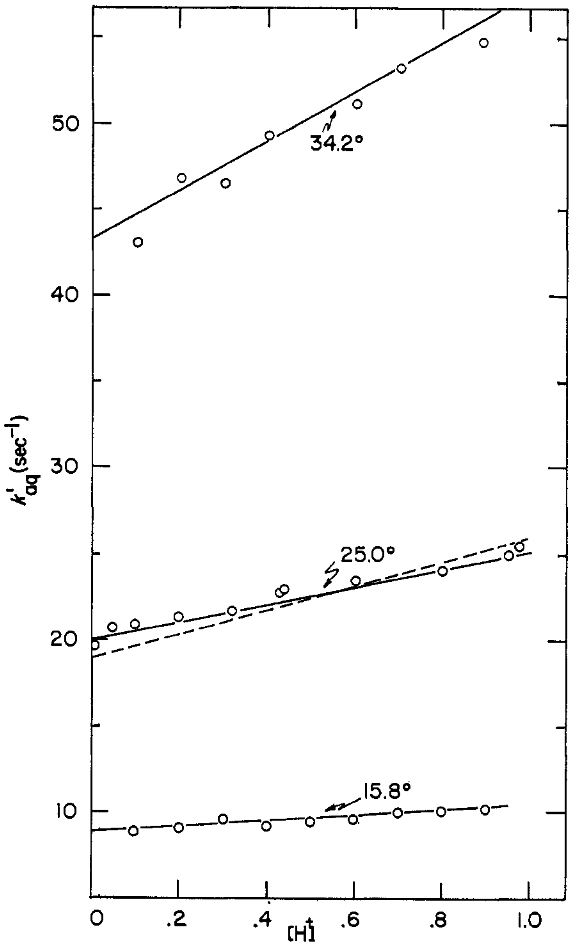

Figure 1.—Linear variation of k_{aq}' with $[H^+]$ at unit ionic strength at each temperature. The points are the average k_{aq}' values in type A or B runs at a particular $[H^+]$, corrected (see text) for small contributions to k_{obsd} from the formation reaction. The lines are the computer-calculated fit based on all data at various $[H^+]$ and temperatures. The dashed line at 25.0° represents data of Seewald and Sutin[2] also at 1.00 *M* ionic strength, but maintained with sodium rather than lithium perchlorate.

computing $[Fe^{3+}]$ and $[H^+]$ in both kinetic and equilibrium studies at high iron(III) concentrations.

The equilibrium quotients for reactions 7 and 8 are known at 25.0° and unit ionic strength; the values are $Q_7 = 1.65 \times 10^{-3}$ *M* and $Q_8 = (1.9 \pm 0.6) \times 10^{-3}$ *M*.[11] These constants were used to compute $[Fe^{3+}]$ and $[H^+]$, although the uncertainty in Q_8 caused some leeway in the values. Subsequent agreement among the several kinetic series and between kinetic and equilibrium values led us to choose the value $Q_8 = 2.4 \times 10^{-3}$ *M* in our computations.[12]

Formation Rate Constants.—Experiments at a higher concentration of iron(III) or of hydrazoic acid and at low $[H^+]$ (types C and D), where the equilibrium in reaction 1 lay much farther toward the complex, permitted calculation of the apparent rate constant k_f' for formation of azidoiron(III). Equation 5 suggests that, at a particular acid concentration, a plot of k_{obsd} *vs.* $([Fe^{3+}]_{eq} + [HN_3]_{eq})$ should be linear; this equation was derived assuming $[H^+]$ remained constant. The experiments at high iron(III) had values of $[H^+]$ that varied somewhat among the different solutions, because of eq 7 and 8. The variation in $[H^+]$ will still allow graphical presentation of the data, as follows. The results given earlier for k_{aq}' showed that at 0.05 *M* H^+ 98.7% of the aquation was carried by the acid-independent k_{aq} term. The principle of microscopic reversibility requires, therefore, that the opposing formation rate term, that showing the concentration dependence $[Fe^{3+}][HN_3]/[H^+]$, likewise carry 98.7% of the opposing reaction at 0.05 *M* H^+. The small variation in $[H^+]$ among these runs can, therefore, be taken into account by plotting k_{obsd} *vs.* $([Fe^{3+}]_{eq} + [HN_3]_{eq})/[H^+]$; the data from series C and D are shown in Figure 2. The slope of this line is identified as $k_f'[H^+]$.

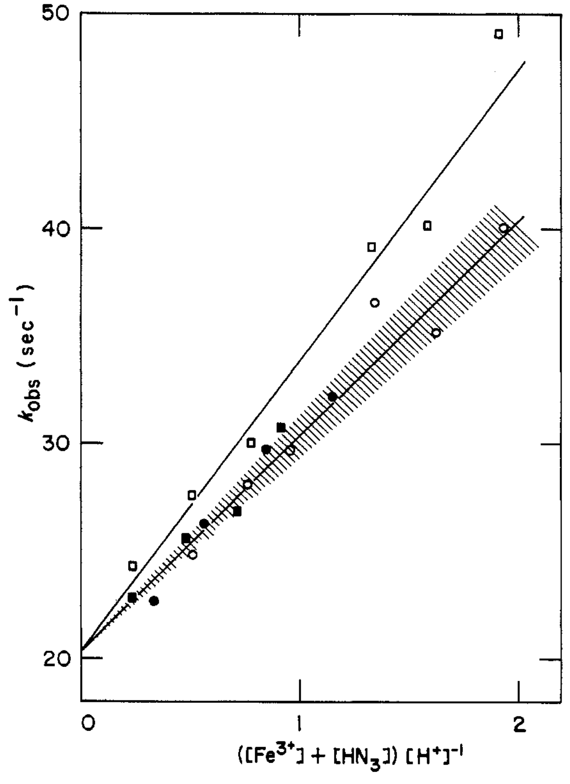

Figure 2.—Evaluation of the formation rate constant k_f' in a plot suggested by eq 5. The points refer to the following series of rate experiments all at 25.0° and 1.00 *M* ionic strength: ○, type C, high HN_3; ●, type C, high Fe; ■, type D, high Fe, and □, type D, high HN_3. The first three series are represented by a single line and the last series lies above the others. The shaded area outlines two standard deviations on either side of the line which is the value found in the least-squares computer fit of the data in the first three series.

The results of some experiments at high $[HN_3]$ disagreed with those at high $[Fe^{3+}]$, however, and the rate constants at high $[HN_3]$ varied, depending on whether one approached equilibrium in a particular

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[11] R. M. Milburn, *J. Am. Chem. Soc.*, **79**, 537 (1957).

[12] The mixing technique in the stopped-flow experiments causes the separate reactant solutions each to be diluted by a factor of exactly 2. The rate of decomposition of the iron(III) dimer has been studied [T. J. Conocchioli, E. J. Hamilton, Jr., and N. Sutin, *J. Am. Chem Soc.*, **87**, 926 (1965)], and it is slow relative to the reaction being studied here. The composition of the solution of interest in treating the kinetic data is that immediately upon dilution, rather than that after eq 8 has reached equilibrium. The latter equilibrium is assumed to pertain to the iron(III) solution *prior* to its dilution and reaction.

solution from the side of aquoiron(III) (mixing runs type C) or the complex (dilution runs type D). The rate constants obtained in these experiments fell into two groups. The dilution experiments of type D at high hydrazoic acid concentrations yielded rate constants that were appreciably higher than those with high iron(III), and higher also than mixing runs at high hydrazoic acid.

With the values of Q_7 and Q_8 given above, the three series type C high iron and high HN_3 and type D high iron were in good agreement. All the experiments gave an intercept (20.3 sec^{-1}) agreeing with the value in type A and B runs at 0.05 M H^+. The value of the slope in the three catagories of experiments cited above is 10.1 ± 0.2 sec^{-1}, whereas in the type D high HN_3 runs it is 13.5 ± 0.5 sec^{-1}. These two values of the quantity $k_f'[H^+]$ lead to calculated equilibrium quotients for eq 1 of $Q_1 = 0.498 \pm 0.035$ and $Q_1 = 0.67 \pm 0.05$, respectively. Although these values lie near the published value[5,6] $Q_1 = 0.591$ under these conditions, both deviations are larger than acceptable for experiments of this precision and especially the systematic direction of the deviations requires further explanation. Repetitive analyses of the various solutions by independent methods, including analyses of the mixed equilibrium solutions, did not result in a changed value or in a closer agreement of the rate parameters of the equilibrium quotient values.

Equilibrium Measurements.—A series of spectrophotometric measurements at 4600 A, where the only absorbing species is the azido complex, was carried out at unit ionic strength, 25.0°, and $[H^+] = 0.0500$ M. These studies were similar to the earlier work[5,6] and covered the concentrations of 10^{-4}–5×10^{-3} F iron(III) and 10^{-3}–0.35 F hydrazoic acid, with 0.950 F lithium perchlorate also present.

In addition to checking earlier equilibrium work, we made two series of measurements in which iron(III) rather than hydrazoic acid was in excess. Iron(III) was extended to 0.07 F in each set at very low $[HN_3]$. One set of experiments was done at 0.051–0.056 M H^+ and the other, at 0.100–0.103 M H^+, with ionic strength 1.00 M at 25.0° maintained with lithium perchlorate.

In all equilibrium studies the quantity $\bar{\epsilon}$ is defined as $\Delta D/C_{\text{lim}}$ where ΔD represents the absorbance enhancement due to complex formation and C_{lim}, the formal concentration of the substance at low concentrations. On this basis eq 9 and 10 are derived in the form sug-

$$\text{high }[HN_3]:\quad \bar{\epsilon} = \epsilon_1 - Q^{-1}(\bar{\epsilon}[H^+][HN_3]^{-1}) \qquad (9)$$

$$\text{high }[Fe^{3+}]:\quad \bar{\epsilon} = \epsilon_1 - Q^{-1}(\bar{\epsilon}[H^+][Fe^{3+}]^{-1}) \qquad (10)$$

gested by Newton and Arcand.[13] These relations allowed evaluation both of ϵ_1, the molar extinction coefficient of azidoiron(III), and its formation quotient Q_1. An iterative process was employed using the previous Q_1 to calculate $[HN_3]$ and $[Fe^{3+}]$ and then using these concentrations to reevaluate ϵ_1 and Q_1. The results are presented graphically in Figure 3 in the plot suggested by these equations.

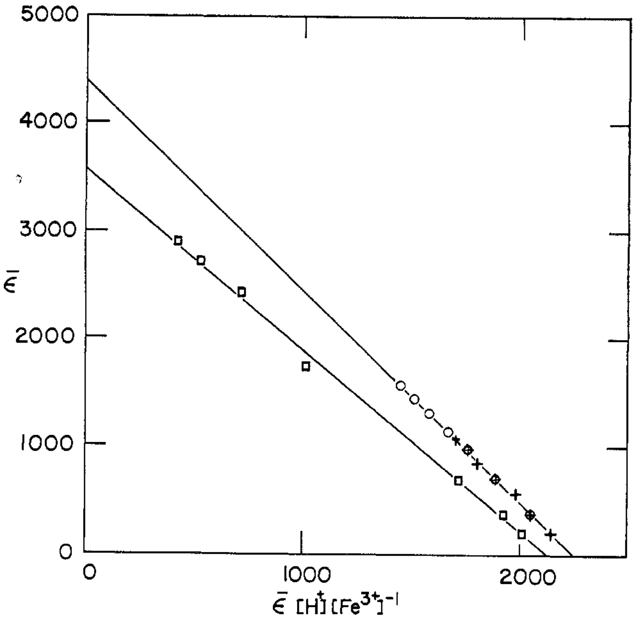

Figure 3.—Evaluation of the equilibrium quotient for reaction 1 and the molar extinction coefficient of monoazidoiron(III) at 4600 A in plots suggested by eq 9 and 10. The lower line refers to data at high hydrazoic acid, and the upper, to data at high iron at 0.0500 F (O) and 0.100 F (+) perchloric acid. The abscissa at high $[HN_3]$ is $\bar{\epsilon}[H^+][HN_3]^{-1}$.

Our results lead to $Q_1 = 0.596 \pm 0.015$ and $\epsilon_1 = 3570 \pm 60$ M^{-1} cm^{-1} at high HN_3, which are in excellent agreement with the published values[5,6] derived from measurements under similar concentration conditions. The values in the high iron series, again using $Q_8 = 2.4 \times 10^{-3}$ M in treating these data, are $Q_1 = 0.512 \pm 0.015$ and $\epsilon_1 = 4400 \pm 160$ M^{-1} cm^{-1} at 0.05 and 0.10 M H^+.

Interpretation and Discussion

Equilibrium and Rate Discrepancies.—An assumption built into the equilibrium computations is the existence of but a single monoazidoiron(III) complex in all of these solutions. Significant amounts of a second complex formed at the higher hydrazoic acid concentrations would not necessarily be revealed by these experiments. Kruh[14] and Baes[15] have considered this problem in some detail and have shown that conditions of stability and absorbancy indices for the second complex exist that allow it to remain undetected in certain spectral experiments. Linearity of the data in the plot suggested by eq 6 is a necessary condition when a single species forms, but *such linearity does not constitute a sufficient condition for concluding that only one complex is formed.*

We have arrived at the following conclusions: (1) only the equilibrium studies at high iron(III) and low hydrazoic acid correctly evaluated the properties of the monoazidoiron(III) complex—$Q_1 = 0.512 \pm 0.015$ and $\epsilon_1 = 4400 \pm 160$ M^{-1} cm^{-1}; (2) the formation rate constant k_f' was correctly evaluated in both types of kinetic runs with excess iron(III); the value at 0.0500 M H^+ is $k_f' = 200 \pm 9$ M^{-1} sec^{-1} and leads to $Q_1 = 0.498 \pm 0.035$, in agreement with the directly deter-

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(13) T. W. Newton and G. M. Arcand, *J. Am. Chem. Soc.*, **75**, 2449 (1953).

(14) R. F. Kruh, *ibid.*, **76**, 4865 (1954).

(15) C. F. Baes, *J. Phys. Chem.*, **60**, 878 (1956).

mined value as well as that in type C mixing runs at high HN_3; (3) the type C mixing experiments at high HN_3 gave the correct values of k_f' and Q_1 because the first reaction is formation of monoazido complex—diazido forms more slowly and in a stepwise manner from monoazido; (4) interference of appreciable diazidoiron(III) ion in the equilibrium studies at high HN_3 and in those kinetic studies at high HN_3 studied in the aquation direction (type D) led to misleading results for Q_1 and k_f'; and (5) the two incorrect values for Q at high HN_3 (equilibrium, 0.60; kinetic type D, 0.67) are not equal; the kinetic value contains a disproportionately larger contribution from the diazido complex since its aquation rate is undoubtedly higher than that of monoazido and since its concentration relative to FeN_3^{2+} is greater at the start of a dilution run than it is at equilibrium.

Formation Kinetics.—The form of the rate expression for aquation (eq 6) and the equilibrium quotient for the net reaction (eq 1) indicate that the formation rate law is given by the expression in eq 11. The experiments

$$d[FeN_3^{2+}]/dt = (k_{1f} + k_{2f}[H^+]^{-1})[Fe^{3+}][HN_3] \qquad (11)$$

described above evaluated the quantity $k_{1f} + k_{2f}[H^+]^{-1}$ at $[H^+] \sim 0.05\ M$ and 25.0°; the value is 10.1 ± 0.2 sec^{-1}. This is largely (>98%) the contribution of the term k_{2f}. The following relation (eq 12) holds for the

$$Q_1 = k_{1f}/k_{1aq} = k_{2f}/k_{2aq} = k_f'[H^+]/k_{aq}' \qquad (12)$$

kinetic and equilibrium parameters, where it is understood that the primed k's represent apparent rate constants at the same particular value of $[H^+]$. Table II presents a summary of the kinetic and equilibrium parameters.

TABLE II

KINETIC AND EQUILIBRIUM PROPERTIES OF MONOAZIDOIRON(III) ION

$$-\frac{d[FeN_3^{2+}]}{dt} = (k_{2aq} + k_{1aq}[H^+])[FeN_3^{2+}] - (k_{2f}[H^+]^{-1} + k_{1f})[Fe^{3+}][HN_3]$$

Parameter	Value at 25.0°
k_{2aq}, sec^{-1}	20.0 ± 0.9
k_{2f}, sec^{-1}	10.0 ± 0.2
k_{1aq}, $M^{-1}\ sec^{-1}$	5.1 ± 1.3
k_{1f}, $M^{-1}\ sec^{-1}$	2.6 ± 0.8
Q_1[a]	0.51 ± 0.01
ϵ_1 (4600 A), $M^{-1}\ cm^{-1}$	4400 ± 160

[a] Based both on direct equilibrium studies at high iron(III) and on kinetic data, type D high iron and type C.

Reaction Mechanism and Rate Comparisons.—The form of the rate equation indicates parallel formation of two activated complexes as shown by the net activation processes, eq 13 and 14. The transition

$$Fe^{3+} + HN_3 = \{FeHN_3^{3+}\}^* = FeN_3^{2+} + H^+ \qquad (13)$$

$$Fe^{3+} + HN_3 = H^+ + \{FeN_3^{2+}\}^* = FeN_3^{2+} \qquad (14)$$

state for the second pathway can be formulated in terms of two reasonable elementary processes, eq 15 and 16.

$$(H_2O)_6Fe^{3+} + N_3^- \rightleftharpoons (H_2O)_5FeN_3^{2+} + H_2O \qquad (15)$$

$$(H_2O)_5FeOH^{2+} + HN_3 \rightleftharpoons (H_2O)_5FeN_3^{2+} + H_2O \qquad (16)$$

The rate constants for each of these reactions in the forward direction can be calculated from the measured value of k_{2f} and the appropriate acid dissociation quotient. For aquoiron(III) ion the value of Q_a is $1.65 \times 10^{-3}\ M$[11] and for hydrazoic acid it is $7 \times 10^{-5}\ M$.[16] The rate constant calculated assuming the k_{2f} term of the reaction of Fe^{3+} and N_3^- (eq 15) is $1.4 \times 10^5\ M^{-1}\ sec^{-1}$, and that obtained assuming it represents $FeOH^{2+} + HN_3$ (eq 16) is $6.1 \times 10^3\ M^{-1}\ sec^{-1}$. The alternative formulations are not kinetically distinguishable, however, since the acid dissociation reactions of iron(III) and hydrazoic acid are quite rapid. A detailed study of ionic strength dependence or of solvent effects can offer no hope of leading to a distinction, since the preequilibria are affected to an exactly compensating extent.

Seewald and Sutin[2] noted the similarity of rate constants for processes analogous to eq 15 for a series of iron(III) complexes where this type of ambiguity does not exist (*i.e.*, for the reactions of Fe^{3+} with Cl^-, Br^-, NCS^-, HF, and HN_3); values of k all lie in the range 2.6 for HN_3 (this work) to 127 $M^{-1}\ sec^{-1}$ for NCS^-. Moreover, this range of rate constants is substantially lower than the range found for processes analogous to reaction 16, again considering cases of unambiguous interpretation (*i.e.*, for reaction of $FeOH^{2+}$ with Br^-, Cl^-, NCS^-, SO_4^{2-}); values of k are 10^4–$3 \times 10^5\ M^{-1}\ sec^{-1}$. These groups of rate constants presumably represent substitution on $(H_2O)_6Fe^{3+}$ and on $(H_2O)_5FeOH^{2+}$, respectively.[2] The calculated value for $Fe^{3+} + N_3^-$ lies outside the range of values for other substitution reactions of Fe^{3+} by a factor of $>10^3$, whereas the alternate formulation in eq 15 gives a value close to the range ascribed to substitution on $(H_2O)_5FeOH^{2+}$. They concluded, therefore, that eq 16 is probably the correct formulation.[2] On the basis of this reasonable postulate, the rate-determining feature of eq 16 can be viewed as elimination of water in an outer-sphere complex $((H_2O)_5FeOH \cdot HN_3)^{2+}$.

An alternative approach to the question of the detailed mechanism of this rate step was suggested by Swaddle and King[4] in their study of the analogous monoazidochromium(III) ion. Swaddle and King[4] based their arguments for azidochromium(III) on a comparison of activation entropies for aquation of complexes of the similar ions azide and thiocyanate. They noted that the value of ΔS^* for aquation of a given azide complex was unusually positive compared to that for the analogous thiocyanate complex. For the aquochromium(III) and amminecobalt(III) complexes considered, this difference amounted to *ca.* 20 eu. The quite reasonable interpretation offered for this result was that it corresponded to the reaction of $(H_2O)_5CrOH^{2+} + HN_3$ rather than $(H_2O)_6Cr^{3+} + N_3^-$. These authors discussed the mechanism of the chromium(III)–fluoride complex formation reaction relative to other halo complexes on this same basis.

A kinetic study has been reported[8] on the aquation

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[16] M. Quintin, *Compt. Rend.*, **210**, 625 (1940).

of monothiocyanatoiron(III) ion,[17] $(H_2O)_5FeNCS^{2+}$. The transition state of composition $\{(H_2O)_{5+x}FeNCS^{2+}\}^*$ (which almost certainly yields the products aquoiron(III) and thiocyanate ion, and not hydroxoiron(III) ion and thiocyanic acid) has an activation entropy for aquation of -9.6 ± 5 eu. Thus in the case of iron(III) the activation entropy difference $\Delta S^*_{FeN_3} - \Delta S^*_{FeNCS}$ is $+6 \pm 5$ eu. This value is positive, but it is substantially smaller than the analogous values for $(H_2O)_5Cr^{III}$ and $(NH_3)_5Co^{III}$.

The entropy of acid dissociation of aquoiron(III)[11] is 8 eu more positive than that of aquochromium(III).[18] It would appear that the expected value of $\Delta S^*_{MN_3} - \Delta S^*_{MNCS}$, assuming parallel mechanisms, should be still more positive for iron than for chromium, in view of the additional entropy developed in forming the hydroxoiron(III) species. The conclusion one would reach on the basis of entropy comparisons alone would probably be different from that presented earlier, namely, that this pathway represented reaction of $(H_2O)_6Fe^{3+} + N_3^-$ rather than $(H_2O)_5FeOH^{2+} + HN_3$.

This particular application of the entropy argument to the case of azidoiron(III) ion seems to contain a major weakness, however, especially in the extrapolation from comparisons of Cr(III) (d^3) and Co(III) (d^6) to Fe(III) (d^5), that renders it a less certain criterion of mechanism. The Cr(III) and Co(III) complexes (configurations t_{2g}^3 and t_{2g}^6, respectively) experience considerable ligand field stabilization, whereas Fe(III) ($t_{2g}^3e_g^2$) does not. The effect on relative ΔS^* values is not easy to predict, however. Changes in bond distances necessarily accompanying the activation process are likely to be somewhat different in the case of the d^5 configuration than for d^3 and d^6—possible intermediates are stabilized not at all or to different extents—so that values of ΔS^*, which depend strongly on ionic radii, cannot be assumed to have the same relative magnitudes even for mechanisms that are quite similar. The present status of theory with regard to the substitution process—indeed whether these substitutions pass through configurations of reduced or expanded coordination number—does not permit us to go farther at this time.

We conclude, therefore, that the evidence advanced by Seewald and Sutin[2] in favor of elementary reaction 16 corresponding to the transition state $\{(H_2O_{5+x}FeN_3^{2+}\}^*$ is valid, that the sign of $\Delta S^*_{FeN_3} - \Delta S^*_{FeNCS}$ is consistent with this assignment, and that the magnitude of the ΔS^* difference does not detract from this formulation in any way.

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(17) A. Haim and N. Sutin, *J. Am. Chem. Soc.*, **88**, 438 (1966). These authors present convincing arguments for nitrogen-bonded thiocyanate ion in $(H_2O)_5FeNCS^{2+}$.

(18) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955).

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Kinetic Study on the Alkaline Hydrolysis of Oxalato, Fumarato, and Maleato Complexes of Pentaamminecobalt(III)

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The rate for the hydrolysis of the fumarato and maleato complexes of pentaamminecobalt(III) was found to be first order in hydroxide ion and in the complex. At 25° (μ = 1.0, NaCl), for the fumarato complex k, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ are 8.00×10^{-5} M^{-1} sec^{-1}, 28.5 kcal mole^{-1}, and 18.3 cal mole^{-1} deg^{-1}. These values for the maleato complex are 2.80×10^{-5} M^{-1} sec^{-1}, 28.0 kcal mole^{-1}, and 14.4 cal mole^{-1} deg^{-1}. The oxalato complex was found to have a term in the rate law first order in hydroxide ion (k_1) and a term second order in hydroxide ion (k_2). The kinetic parameters k_1, $\Delta H_1^{\ddagger}$, and $\Delta S_1^{\ddagger}$ (25°, μ = 1, NaCl) are 2.45×10^{-4} M^{-1} sec^{-1}, 31.7 kcal mole^{-1}, and 32.2 cal mole^{-1} deg^{-1}; k_2, $\Delta H_2^{\ddagger}$, and $\Delta S_2^{\ddagger}$ (25°, μ = 1, NaCl) are 0.61×10^{-4} M^{-2} sec^{-1}, 23.7 kcal mole^{-1}, and 2.5 cal mole^{-1} deg^{-1}.

Introduction

The series of carboxylatopentaamminecobalt(III) complexes presents a favorable system for studies of the effect of ligand properties on hydrolysis rates. The atom bound to cobalt is the same in all cases but the properties of the ligand may be varied in a systematic way as judged from their organic chemistry.

Previous studies have shown that these complexes may undergo both Co–O and O–C bond breaking.[1] Subsequent work on halo-substituted acetato complexes[2] has confirmed the prediction of Basolo, Bergman, and Pearson[3] that Co–O bond breaking should be easier the smaller the pK of the carboxylic acid.

The present results extend this study to a series of dicarboxylic acids and further indicate the factors influencing the ease of cobalt–oxygen and carbon–oxygen bond breaking.

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(1) R. B. Jordan and H. Taube, *J. Am. Chem. Soc.*, **88**, 4406 (1966).

(2) N. S. Angerman and R. B. Jordan, *Inorg. Chem.*, **6**, 379 (1967).

(3) F. Basolo, J. G. Bergman, and R. G. Pearson, *J. Phys. Chem.*, **56**, 22 (1952).