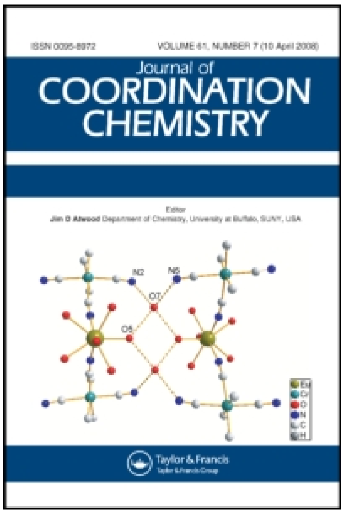

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THE KINETICS OF THE COMPLEX FORMATION BETWEEN Fe(III) AND CHLOROACETIC, DICHLOROACETIC AND TRICHLOROACETIC ACIDS. LIGAND DEPENDENCE OF THE RATE CONSTANTS

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The kinetics of the reactions between Fe(III) and mono-, di-, and trichloroacetic acids have been investigated at 25°C and an ionic strength of 1 *M*, using the *T*-jump method. The rate constants for the reaction between $Fe(OH)^{2+}$ and the anions of the acids exhibited values which are "normal" for this cation. Assuming those between $Fe(OH)^{2+}$ and the undissociated acids to be also normal, the rate constants for the reaction of Fe^{3+} with the anions were evaluated, and found to depend on the basic strength of the ligand. For the rate constants of the reaction between Fe^{3+} and the undissociated acids, only very approximate values could be estimated. The results are compared with the rate of water exchange. The formation constants of the complexes were measured using a spectrophotometric method.

INTRODUCTION

The rate constants for the formation of labile complexes are in general independent of the nature of the ligand, and characteristic for the metal ion. This is satisfactorily explained by the Eigen mechanism[1] according to which the observed rate constant equals $K_0 k^*$, where K_0 is an outer sphere association constant, and k^* the first order constant for the rate at which the ligand changes places with a water molecule in the inner coordination sphere of the metal ion. The Fe^{3+}-ion seemed to be an exception to this rule – the rate of substitution was found to be higher the more basic the ligand. It was suggested by Eigen[1] that the phenomenon was due to internal hydrolysis. The discrepancy seemed quantitatively resolved after Seewald and Sutin[2] drew attention to the "proton ambiguity",[3] namely the fact that the reaction between the Fe^{3+} and the ligand has exactly the same pH-dependence as that between the hydrolysis product $Fe(OH)^{2+}$ and the undissociated acid. When the ligand is Cl^- or Br^-, the existence of the undissociated acid can be neglected, and a rate constant characteristic for Fe^{3+} can be obtained. On the other hand, when the acid is extremely weak, the concentration of the anion is so low that its contribution to the observed rate can be neglected. On this assumption, rate constants for the reaction between $Fe(OH)^{2+}$ and the conjugate acids of the ligands were obtained which vary over a fairly narrow range and may be taken as characteristic for this cation. They are considerably higher than those for the unhydrolyzed Fe^{3+}.

When the ligands are anions of the acids of intermediate strength, both paths make comparable contributions to the observed rate. Since the activated complexes of the two reactions are identical (or differ by one molecule of water), there is no hope of differentiating between them by kinetic means;[4] not only the dependence on pH must be the same, but also, for example, that on ionic strength. But if we *assume* $Fe(OH)^{2+}$ to have a characteristic rate, then we can isolate the rate constant for Fe^{3+} and ascertain whether it is still ligand dependent *even after the reaction involving the fully hydrolyzed form,* $Fe(OH)^{2+}$, *has been taken into account.*

The information about complex formation with such anions is comparatively scarce. Only $H_2PO_2^-$, CNS^-, HSO_4^-, SO_4^{2-} and $HC_2O_4^-$ are reported.[3,5–11] It seemed worth while to obtain additional information on this point. Tri- and dichloroacetic acids seemed suitable for the purpose. In order to complete this series, the reaction with monochloroacetic acid was reinvestigated,[12] at the same temperature and ionic strength as those which served for the stronger acids.

The formation constants of the complexes are not available in the literature and had to be determined. Furthermore, the hydrolysis constant of Fe^{3+} to form $Fe(OH)^{2+}$ was redetermined at our ionic strength.

EXPERIMENTAL

Materials

Iron(III) was used in the form of $Fe(ClO_4)_3 \cdot 9H_2O$ (Fluka, Reagent Grade). A 10^{-2} *M* stock solution was prepared, containing 10^{-2} *M* perchloric acid to prevent hydrolysis. The Fe(III)-concentration was determined by complexometric titration with di-sodium EDTA. The perchloric acid concentration was determined as described by Milburn and Vosburgh.[13]

The monochloroacetic acid was B.D.H., Analytical Reagent, the dichloroacetic acid Riedel de Haën, and the trichloroacetic and perchloric acids were Merck.

Stock solutions of the acids were titrated with CO_2-free sodium hydroxide solution.

The ionic strength was regulated by the addition of sodium perchlorate (Fluka) and the hydrogen ion concentration by the addition of perchloric acid, taking the dissociation of the organic acid into account.

Triple distilled water was used throughout.

Kinetic Experiments

All the experiments were carried out by the *T*-jump method, using an apparatus constructed by Messanlagenstudiengesellschaft m.b.H., Göttingen, equipped with a reference photomultiplier. The ionic strength was 1*M*, regulated by the addition of sodium perchlorate. The temperature after the jump was 25°C. The wave-length was at or near 290 nm.

Relaxation times ranged between (3 to 18) x 10^{-3} sec. Every solution was "jumped" 4 times; the results differed by ±10% at most , but usually much less.

Static Measurements

Spectrophotometric measurements were carried out with a Hilger-Gilford spectrophotometer.

Calculations were carried out with a programmable desk calculator (Compucorp., Model 344).

Relaxation times were evaluated manually, using a device developed in our Department.[14]

RESULTS

Equilibrium Constants

The hydrolysis constant of Fe^{3+}. The hydrolysis constant of Fe^{3+} is defined as

$$K_{OH} = \frac{[Fe(OH)^{2+}][H^+]}{[Fe^{3+}]} \tag{1}$$

From the expression for the absorption, *A*, of a solution containing both Fe^{3+} and $Fe(OH)^{2+}$ we obtain by a suitable transformation

$$\frac{1}{A/[Fe(III)] - \epsilon_{Fe}} = \frac{1}{\epsilon_{FeOH} - \epsilon_{Fe}} + \frac{[H^+]}{(\epsilon_{FeOH} - \epsilon_{Fe})K_{OH}} \tag{2}$$

The value of ϵ_{Fe} was determined in 1 *M* acid solution, where the hydrolysis can be neglected. The left-hand side of equation (2) can therefore be evaluated and plotted against $[H^+]$. Working under conditions where dimerisation can be neglected[13] ($[Fe(III)] = (1-3) \times 10^{-4}$ *M* and $[H^+] = 10^{-3}$ to 10^{-2} *M*) we got from the slope and intercept of the straight line obtained at 290 nm

$$\epsilon_{FeOH} = (2.22 \pm 0.16) \times 10^3$$

(using $\epsilon_{Fe} = (4.29 \pm 0.01) \times 10^2$) and

$$K_{OH} = (1.63 \pm 0.01) \times 10^{-3}$$

in excellent agreement with previous measurements.[13]

Formation constants. We define the formation constants of our complexes as

$$K_1 = \frac{[FeA^{2+}]}{[Fe^{3+}][A^-]} \tag{3}$$

but the quantity amenable to measurement by spectrophotometric methods is an "apparent" equilibrium constant

$$K_{app} = \frac{[FeA^{2+}]}{[Fe^{3+}]([A^-] + [HA])} \tag{4}$$

which gives the ratio between the concentration of total complexed and total uncomplexed participants, and depends on $[H^+]$. In this equation, $[FeOH^{2+}]$ has been omitted, since at the hydrogen ion concentrations employed, it is very much smaller than $[Fe^{3+}]$. But $\epsilon_{FeOH} \gg \epsilon_{Fe}$, and the contribution of $FeOH^{2+}$ to the observed absorption cannot be

TABLE I

Dissociation constants, K_{HA}, and formation constants of complexes with Fe^{3+}, K_1, for mono-, di- and trichloroacetic acids

(λ = 290 nm)

Acid	K_{HA} M^{-1}	a M	b M	$[H^+]$ M	K_1 M^{-1}
$CH_2ClCOOH$	[a]2.5×10^{-3}				[a]126
$CHCl_2COOH$	[b]$(8.0 \pm 1.0) \times 10^{-2}$	10^{-3}	$(2.5 \text{ to } 8.8) \times 10^{-2}$	0.1	6.8 ± 0.5
CCl_3COOH	[b]~ 1	2×10^{-3}	$(4.5 \text{ to } 8.3) \times 10^{-2}$ $(5.0 \text{ to } 25.0) \times 10^{-2}$ $(1.0 \text{ to } 4.0) \times 10^{-1}$	0.1 0.25 0.36	0.91 ± 0.10

[a] D.D. Perrin, *J. Chem. Soc.*, 1959, 1710.

[b] B. Perlmutter-Hayman and E. Tapuhi, *J. Chem. Eng. Data*, accepted for publication.

neglected. Defining a weighted absorption coefficient

$$\epsilon_{Fe(III)} = \epsilon_{Fe} \frac{[H^+]}{K_{OH} + [H^+]} + \epsilon_{FeOH} \frac{K_{OH}}{K_{OH} + [H^+]} \tag{5}$$

we can write, provided the ligand is in large excess over the metal,

$$\frac{a}{A - \epsilon_{Fe(III)}a} = \frac{1}{\epsilon_{FeA} - \epsilon_{Fe(III)}} + \frac{1}{(\epsilon_{FeA} - \epsilon_{Fe(III)})K_{app}b} \tag{6}$$

where a is the stoichiometric concentration of Fe(III) and b that of the ligand. At constant $[H^+]$, a plot of the left-hand side of equation (6) against $1/b$ is a straight line from whose slope and intercept we get K_{app}. The association constant K_1 follows from a knowledge of the dissociation constant of the acid, K_{HA}. For trichloroacetic acid [Ha] is always considerably smaller than $[A^-]$, so that K_{app} differs by at most 12% from K_1. For this reason, the large uncertainty in K_{HA} is therefore of comparatively little importance. The results are summarized in Table I. For the sake of comparison, values for monochloroacetic acid are included.

Kinetic results

Our reaction scheme comprises four possible reactions, namely,

$$Fe^{3+} + A^- \rightleftharpoons FeA^{2+} \tag{I}$$

$$Fe^{3+} + HA \rightleftharpoons FeA^{2+} + H^+ \tag{II}$$

$$Fe(OH)^{2+} + A^- \rightleftharpoons FeA^{2+} + OH^- \tag{III}$$

$$Fe(OH)^{2+} + HA \rightleftharpoons FeA^{2+} + H_2O \tag{IV}$$

where we have omitted water molecules which do not take part in the reaction. Assuming the protolytic equilibria between Fe^{3+} and $Fe(OH)^{2+}$ and between HA and A^- to be maintained while the formation of FeA^{2+} proceeds, we see only one relaxation time which can be written

$$\frac{1}{\tau} = \left(k_1 + k_4 \frac{K_{OH}}{K_{HA}} + k_2 \frac{[H^+]}{K_{HA}} + k_3 \frac{K_{OH}}{[H^+]} \right) \times B \tag{7}$$

where B is defined† by[8]

$$B = \frac{1}{K_1} + [Fe^{3+}] \frac{K_{HA}}{[H^+] + K_{HA}} + [A^-] \frac{[H^+]}{[H^+] + K_{OH}} \tag{8}$$

all concentrations referring to their equilibrium values. A plot of $1/\tau B$ as a function of $\log[H^+]$ should be symmetric around a minimum

$$[H^+]_{min} = (k_3 K_{OH} K_{HA}/k_2)^{1/2} \tag{9}$$

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† The derivation of this expression is based on the fact that the concentration of H^+ is much higher than that of the reactants, and can be assumed to remain constant during the reaction. In a few experiments, this is not true with respect to $[A^-]$; instead of $[Fe^{3+}]K_{HA}/([H^+ + K_{HA})$ we then ought to write (B. Perlmutter-Hayman, submitted for publication, see also reference 8) $[Fe^{3+}]\delta_A/(\delta_A + \delta_{HA})$, where δ_i is the difference between the actual and the equilibrium concentrations of substance i. This correction affects a term which constitutes only about 2% of B and has therefore not been applied.

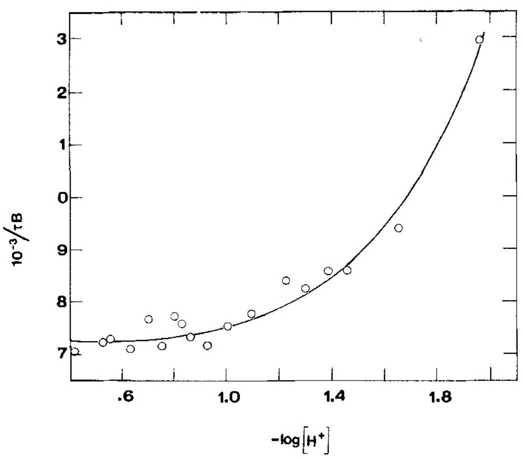

FIGURE 1 A plot of $1/\tau B$ as a function of log $[H^+]$ (where B is defined by equation 8), for monochloroacetic acid.

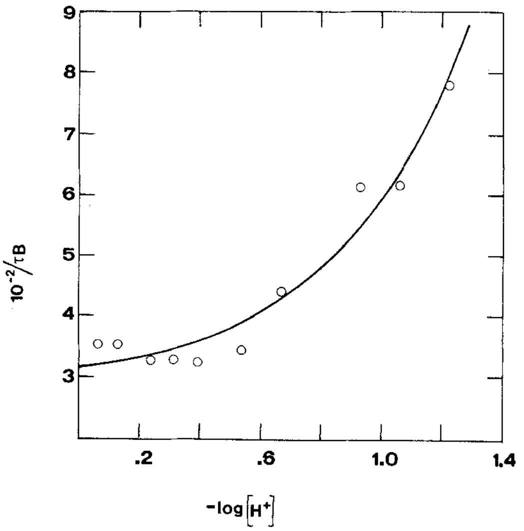

FIGURE 2 As in figure 1, for dichloroacetic acid.

TABLE II
Rate constants for the reaction between Fe(III) and mono-, di- and trichloroacetic acids

Acid	$a \times 10^3$ M	$b \times 10^2$ M	$k_1 + k_4 \frac{K_{OH}}{K_H}$ M^{-1} sec^{-1}	k_2 M^{-1} sec^{-1}	$k_3 \times 10^{-4}$ M^{-1} sec^{-1}
$CH_2ClCOOH$	3.2	2.0	(6.8 ± 0.1) x 10^3	2.1 ± 1.7	4.1 ± 0.2
$CHCl_2COOH$	1.1 to 3.2	0.5 to 2.1	284 ± 18	–[a]	1.9 ± 0.2
CCl_3COOH	2.1 to 3.2	1.0 to 5.0	76 ± 3	–[a]	0.78 ± 0.03

[a]Contribution of path II assumed negligible.

Such plots are shown in Figures 1 to 3. For monochloroacetic acid, we treated $1/\tau B$ as a linear regression[15] in the two variables $[H^+]/K_{HA}$ and $K_{OH}/[H^+]$, and obtained the three parameters k_2, k_3, and $(k_1 + k_4K_{OH}/K_{HA})$, and their standard deviations†. The results are shown in Table II. The difference between our results and those obtained by previous authors[12] at 20°C is satisfactorily explained by the difference in temperature. For dichloroacetic acid inspection of the graph does not reveal whether the use of a three-parameter equation for $1/\tau B$ is warranted; but when we subjected the results to the

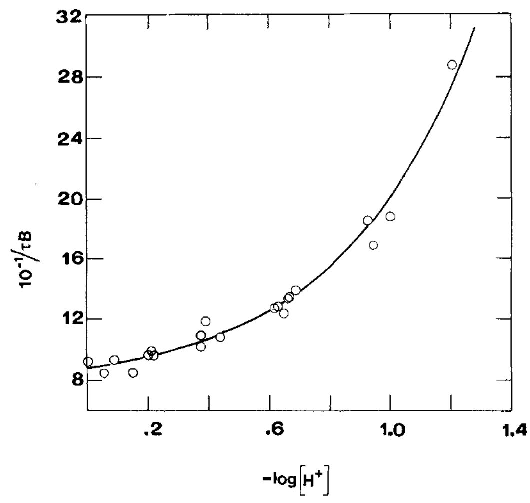

FIGURE 3 As in figure 1, for trichloroacetic acid.

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† The expression for the standard deviation of $(k_1 + k_4K_{OH}/K_{HA})$ was obtained as a special case of the standard deviation of the dependent variable when the two independent variables are equal to zero. See, for example, equation 3.48 of reference 15, where Σ' is defined in equation 3.14.

mathematical treatment applied to monochloroacetic acid, we obtained $k_2 = 6.7 \pm 6.4\ M^{-1}\ \text{sec}^{-1}$ which is devoid of statistical significance. For trichloroacetic acid there seems no doubt that a two-parameter equation is adequate. This is confirmed by the fact that, for the two stronger acids, plots of $1/\tau B$ against $1/[H^+]$ were straight lines which did not exhibit any significant upward curvature at low values of $1/[H^+]$. From their slopes and intercepts we calculated k_3 and $k_1 + k_4K_{OH}/K_{HA}$, respectively. These results are also given in Table II.

DISCUSSION

Our acids are too strong for pathway II to make an appreciable contribution in the $[H^+]$-range limited by the requirement of keeping the ionic strength constant at 1 *M*. This is why k_2 for monochloroacetic acid has such an exceedingly high standard deviation, whereas for the two stronger acids it cannot be calculated as a regression coefficient at all. We can make a rough estimate of k_2 from equation 9, making use of the fact that for trichloroacetic acid, $[H^+]_{\min}$ has not been reached, and assuming that for dichloroacetic acid it has approximately been reached. We get for the latter substance $k_2 \sim 3$ to $6\ M^{-1}\ \text{sec}^{-1}$, and for the former, k_2 lower than 12, probably considerably lower. Such values are reasonable for the reaction between Fe^{3+} and an uncharged acid. In this work, we are interested in reactions in which the ligand is a base; therefore, we did not attempt to get further information on k_2.

In order to calculate k_1, we must make some assumptions about k_4. If, together with Accascina *et al.*,[12] we neglect k_1 in comparison with k_4K_{OH}/K_{HA} when the acid is sufficiently weak, we see from the work of these authors[12] that for acetic and propionic acids the values of k_4 are identical within the limit of experimental error. On the reasonable assumption that k_4 has the same value also for our substituted acetic acids, and making allowance for the influence of temperature on k_4, we calculated the values of k_1 shown in Table III. In this table we have collected data for strong and moderately strong acids, together with acetic acid for the sake of comparison.

The values of k_2, where they are accessable to measurement, vary over a small range, and closely resemble those obtained with weak acids (see, e.g., Table IV of reference 16) where k_2 can be measured more reliably. Similarly, comparison between the three entries for k_3 of thiocyanate, and the rest of the data in the same column, shows that k_3 is constant within the combined uncertainty of results obtained by different authors for the *same* substance. This constancy of k_3 encourages us to estimate k_1 on the basis of the assumption that k_4, too, is not only constant for carboxylic acids, but has a typical value *throughout*, being influenced only by the charge type. Although this assumption introduces considerable uncertainty into the values of k_1 (especially for the weaker acids where a small change in the value assumed for k_4 causes a considerable change in k_1), there can be no doubt that the values of k_1 vary over a wide range and increase with increasing basicity of the ligand.†

Let us now analyze these results in the light of the Eigen mechanism which allows us to calculate the penetration constant[16] k^*, assuming K_0 to be accessable to calculation. We used the Fuoss equation,[17] taking the distance between the centers of the reactants as 5A, and calculating the influence of ionic strength on the electrostatic interaction energy with the aid of the Davies equation[18] (although this is strictly justified only at much lower values of *I*). The resulting values for k^* are also shown in Table III, for all four rate constants.

These values should be compared with $k^*_{H_2O}$, the rate of water exchange between inner-shell and bulk water, as determined directly from O^{17} exchange with the aid of NMR line broadening. This method yields the exchange rate for any particular water-molecule. The rate of exchange of one of the six water molecules in $Fe(H_2O)_6^{3+}$ is six times that value.[19] However, the ligand has to compete for the vacant site with water molecules in the outer sphere. If we assume that this reduces its chance by a factor of eight in accordance with the eight faces of the octahedron, we conclude – together with Neely and Connick[19] – that $k^*_{H_2O}$ must be multiplied by 3/4 before it can be compared with k^*, a statistical correction which is often disregarded. The value of $k^*_{H_2O}$ for Fe^{3+} seems to become lower each time it is reinvestigated. The most recent value[20] we found is $\sim 150\ \text{sec}^{-1}$, *lower* than that reported[21] in 1963 by a

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† A further source of uncertainty which affects all rate constants reported in Table III is the fact that, especially for the anions of strong and moderately strong acids, the complex is weak, and the contribution of the *reverse* reaction predominates in the observed relaxation time. (In our method of calculation, this causes $1/K_1$ to be the leading term in the expression for *B* as defined in equation 8.) As a consequence, all *forward* rate constants are in error almost to the same extent as the corresponding *equilibrium* constants might be in error.

TABLE III

Rate constants for the reaction between Fe(III) and anions of strong and moderately strong acids (I = 1 M unless otherwise stated)

Ligand	pK_{HA}	$k_1 + k_4 K_{OH}/K_H$	k_1	k_2	$k_3 \times 10^{-4}$	$k_4 \times 10^{-4}$	k_1^*	k_2^*	$k_3^* \times 10^{-4}$	$k_4^* \times 10^{-4}$
		M^{-1} sec^{-1}					sec^{-1}			
Cl^-	–	9.4[a] 19[b]	9.4[a] 19[b]	–[c]	1.1[a] 1.2[b]	–[c]	3 6	–	1 1	– –
Br^-	–	50[b]	50[b]	–[c]	4.1[b]	–[c]	17	–	3	–
HSO_4^-	–	~38[d]	~38[d]	–[c]	1–2.6[e]	–[c]	13	–	1–3	–
CNS^-	(–1.8)[f]	127[g] 132[h] 90[i]	127[g] 132[h] 90[i]	–[c]	1.0[g] 4.2[h] 0.5[i]	–[c]	51 26 36	–	2 2.1 1	–
CCl_3COO^-	0[k]	76[l]	63[l]	–[c]	0.78	0.83[m]	21	–	0.6	–
$H_2PO_2^-$	0.8[n]	270[n]	170	13[n]	–	0.83[m]	57	43	–	–
$HC_2O_4^-$	1.07[o]	860[o]	702	–[c]	2.0[o]	0.83[m]	234	–	1.5	–
$CHCl_2COO^-$	1.1[k]	284[l]	118	–[c]	1.9[l]	0.83[m]	40	–	1.5	–
SO_4^{2-}	1.17[d]	3.0×10^3 [d] 4.35×10^3 [p]	2.3×10^3 –	~38 –	11.4[d] 18.7[p]	2.6[e] –	100 –	~13 –	2 –	2.0 –
CH_2ClCOO^-	2.6[q]	6.8×10^3 [l]	1.5×10^3	2.1[l]	4.1[l]	0.83[m]	500	7	3	–
CH_3COO^-	4.5	~4.7×10^5 [r]	–[c]	4.8[r]	–[c]	0.83[r]	–	16	–	2.7

[a] R. E. Connick and C. P. Coppel, *J. Amer. Chem. Soc.*, 81, 6389 (1959).

[b] Reference 22.

[c] Pathway makes negligibly small contribution.

[d] Reference 8, I = 1.2 M.

[e] Assumed by Cavasino (reference 8) from analogy.

[f] T. D. B. Morgan, G. Stedman, and P. A. E. Whincup, *J. Chem. Soc.*, **1965**, 4813, value extrapolated from measurements at very high I.

[g] Reference 5, I = 0.4 M.

[h] Reference 6, I = 0.1 M.

[i] Reference 7, I = 0.5 M.

[k] B. Perlmutter-Hayman and E. Tapuhi, *J. Chem. Eng. Data*, accepted for publication.

[l] This work.

[m] Assumed on the basis of reference 12.

[n] Reference 3.

[o] Reference 10.

[p] Reference 9, I = 0.5 M.

[q] Reference 12.

[r] Reference 12, corrected to 25°.

factor of over one hundred. Thus k^*_{Fe} should be equal to ~110 sec^{-1}. The exchange rate on $Fe(OH)^{2+}$ was found to be higher than that on Fe^{3+} by a factor of about one thousand[20]. This yields $k^*_{FeOH} \sim 10^5$ sec^{-1}.

Comparison with Table III shows that all values of k^*_{FeOH} and most values of k^*_{Fe} are lower than predicted even from the recent, low, values of $k^*_{H_2O}$, and even after the statistical correction has been applied. Although this phenomenon seems to be quite frequent, and has been attributed[19] to water being favored over other ligands in the competition for the vacant site, it is rarely as pronounced. Attention to this fact has been drawn by Yasunaga and Harada[22] for the reaction between Fe^{3+} and Cl^- and Br^-, where the discrepancy is particularly pronounced. They suggest a pentacoordinated intermediate to be formed in a fast preequilibrium; such an intermediate may well react selectively with various ligands. This picture breaks down, however, for the weaker acids. When k_1 not only reaches, but actually exceeds, the value predicted from the rate of water exchange, then internal hydrolysis – which imparts on Fe^{3+} some of the properties of $FeOH^{2+}$ – can serve as an explanation. This does not mean that we can consider internal hydrolysis to be proved beyond doubt, since it is just the high values of k_1 which are most sensitive to the simplifying assumptions which we have made. On the other hand, if k_1 *does* continue to increase as the ligand becomes the anion of a weaker and weaker acid, then it is no longer justified to calculate k_4 for these ligands on the assumption that pathway I can be neglected. This might make k_4 lower than previously reported.

An alternative explanation for the experimental results would be an S_N2 mechanism via an expanded coordination shell in which the ligand enhances the rate of water loss – the more so the more basic the ligand.

Summarizing, we may say that the kinetics of complex formation by Fe(III), though one of the most widely investigated, is still one of the least well understood.

The authors are indebted to Prof. H. J. G. Hayman for programming the desk calculator to give the regression coefficients and their standard deviations for a linear regression in two variables and for his help with the equation for the standard deviation of our independent term.

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