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Temperature-jump Studies of the Kinetics of the Formation of the Monochloro and Monobromo Complexes of Iron(III)

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The temperature-jump method was used to study the kinetics of $FeCl^{2+}$ and $FeBr^{2+}$ complex formations in aqueous solutions. Complex formation is composed of two paths. In the acid-independent path, the rate-determining step of complex formation may be the reaction between $Fe(H_2O)_5{}^{3+}$ and X^- ($X^- = Cl^-$, Br^-). The other path is that *via* the hydrolysis of ferric ions, and the rate-determining step is the loss of a water molecule from the inner coordination sphere of the metal ion. The kinetic values obtained are in good agreement with the results obtained by the flow method.

Many of the fast metal complex formation reactions in solution have been studied with the help of the relaxation methods developed mainly by Eigen and Mayer,[1] and a step-by-step association picture has been presented to explain their relaxation phenomena.

Some of the complex formation reactions of Fe(III) have also been studied by the flow method,[2-6] the pressure-jump method,[7] and, most recently, the temperature-jump method.[8,9] By the temperature-jump method Cavasino[8,9] has reexamined a few of the Fe(III) complex formation reactions previously studied by the flow method and has given the kinetic values and interpreted the reactions.

The present study was undertaken in order to obtain kinetic information on the $FeCl^{2+}$ complex formation reaction over a wide range of acidity and temperature by the temperature-jump method. Moreover, since there has been very little information on the kinetics of the $FeBr^{2+}$ complex formation reaction,[3] we aimed to establish the mechanisms in more detail and to obtain the kinetic values of the reaction. Another purpose was to test the operation of a newly-built device at the beginning of the temperature-jump study.

Experimental

All the inorganic chemicals were of a reagent grade. Stock solutions of $Fe(NO_3)_3$ and NaCl were prepared. The concentration of ferric ion was determined photometrically. The chloride concentration was checked by titration with a standard silver nitrate solution. The hydrogen ion concentration was changed by the addition of $HClO_4$. The ionic strength was adjusted to $\mu = 1.0$ by the addition of $NaClO_4$. The temperature-jump apparatus used was a modification of that described by Hammes and Fasella.[10] A schematic diagram of our apparatus is shown in Fig. 1. The 0.1 μF condenser was charged to 18000 V and discharged

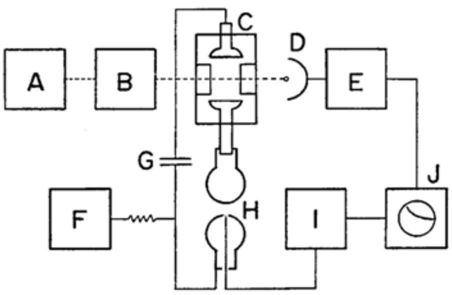

Fig. 1. Schematic diagram of temperature-jump apparatus.
(A) light source; (B) monochromator; (C) observation cell; (D) photomultiplier; (E) amplifier; (F) high voltage; (G) condenser; (H) spark gap; (I) trigger; (J) oscilloscope

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[1] M. Eigen and L. De Mayer, "Technique of Organic Chemistry," Vol. VIII, 2nd Ed., S. L. Friess, E. S. Lewis and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y. (1963), Part 2, p. 895.

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[8] F. Accascina, F. P. Cavasino and S. D'Alessandro, *J. Phys. Chem.*, **71**, 2474 (1967).

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[10] G. G. Hammes and P. Fasella, *J. Am. Chem. Soc.*, **84**, 4644 (1962).

through the air gap. The observation cell was connected in parallel with the condenser *via* two gold-plated electrodes. The concentration changes were observed by single-beam-designed optical techniques. The temperature jump of the solution between the two electrodes was 5±1°C. The magnitude of the temperature jump was calibrated by comparing the change in the absorbance value of a test sample induced by discharge with the values previously measured at various temperatures. The test sample was a 0.02 M glycine solution ($\mu=1.0$) at pH 9 containing phenolphthalein; it was followed at 550 mμ.

In all the ferric chloride solutions, the relaxation spectrum was characterised by a single relaxation time. A representative relaxation effect is shown in Fig. 2. Blank solutions containing only $Fe(NO_3)_3$ or NaCl with $NaClO_4$ gave no relaxation phenomena in the same range of time. The reciprocal relaxation time was calculated from a plot of $-\log \Delta C$ *vs.* the time, where ΔC is the deviation of the concentration from its equilibrium value. The wavelength of observation was 390 mμ. The quoted relaxation times and rate constants are the mean values of several runs.

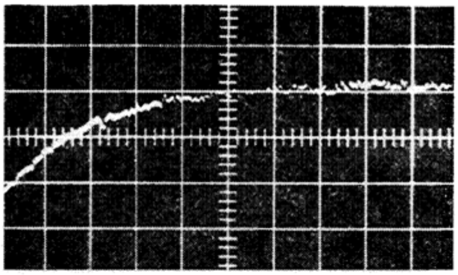

Fig. 2. Experimental relaxation curve at 27°C and $\mu=1.0$.
$\sum[\mathrm{Fe}]=5\times10^{-2}$ M; $\sum[\mathrm{Cl}]=5\times10^{-}$ M; $[\mathrm{H^+}]=$ 0.10 M. The sweep rate is 5 msec per devision.

In the case of $FeBr^{2+}$ complex formation studies, $Fe(NO_3)_3$ and NaBr were used. Experiments were performed over the range of acidity of 0.1 M$\leq[\mathrm{H^+}]\leq$ 0.8 M and at temperatures between 20°C and 40°C at $\mu=1.2$.

Results

In the present studies, the following equilibria are assumed to be present and are attributed to the relaxation:

$$\mathrm{Fe^{3+} + X^- \rightleftarrows FeX^{2+}} \qquad K_\mathrm{X}=\frac{(\mathrm{FeX^{2+}})}{(\mathrm{Fe^{3+}})(\mathrm{X^-})} \tag{1}$$

$$\mathrm{Fe^{3+} + H_2O \rightleftarrows FeOH^{2+} + H^+}$$

$$K_\mathrm{OH}=\frac{(\mathrm{FeOH^{2+}})(\mathrm{H^+})}{(\mathrm{Fe^{3+}})} \tag{2}$$

Taking into account the low concentrations of Fe^{3+} and X^- and the high acidities, the following equilibria may be neglected:

$$\mathrm{FeX^{2+} + X^- \rightleftarrows FeX_2^+} \tag{3}$$

$$\mathrm{FeOH^{2+} + H_2O \rightleftarrows Fe(OH)_2^+ + H^+} \tag{4}$$

$$\mathrm{2FeOH^{2+} \rightleftarrows Fe_2(OH)_2^{4+}} \tag{5}$$

With these hypotheses, the overall mechanism for the complex formation of FeX^{2+} may be expressed as follows:

$$\begin{tikzcd}
\mathrm{H_2O + Fe^{3+} + X^-} \arrow[r, shift left, "k_{12}"] \arrow[d, shift right, "k_{13}"'] & \mathrm{FeX^{2+} + H_2O} \arrow[l, shift left, "k_{21}"] \arrow[d, shift right, "k_{24}"'] & (6) \\
\mathrm{Fe(OH)^{2+} + X^- + H^+} \arrow[r, shift left, "k_{34}"] \arrow[u, shift right, "k_{31}"'] & \mathrm{Fe(OH)X^+ + H^+} \arrow[l, shift left, "k_{43}"] \arrow[u, shift right, "k_{42}"'] & (7)
\end{tikzcd}$$

The protolytic reactions (vertical steps) will be very fast, and the other two processes may correspond to the rate-determining steps of complex formation.

Assuming that $Fe(OH)X^+$ is in a steady state, the rate of FeX^{2+} formation is given by:

$$\frac{\mathrm{d(FeX^{2+})}}{\mathrm{d}t}=k_{12}(\mathrm{Fe^{3+}})(\mathrm{X^-})+k_{34}(\mathrm{FeOH^{2+}})(\mathrm{X^-}) - k_{21}(\mathrm{FeX^{2+}})-k_{43}(\mathrm{Fe(OH)X^+}) \tag{8}$$

and

$$\frac{\mathrm{d}\Delta[\mathrm{FeX^{2+}}]}{\mathrm{d}t}=-\Delta[\mathrm{FeX^{2+}}]([\mathrm{Fe^{3+}}]+[\mathrm{X^-}] + 1/K_\mathrm{X})(k_{12}+k_{34}\cdot K_\mathrm{OH}/[\mathrm{H^+}]) \tag{9}$$

The reciprocal relaxation time is, then, related to the rate constants and the concentrations as follows:

$$\begin{aligned}1/\tau &= (k_{12}+k_{34}\cdot K_\mathrm{OH}/[\mathrm{H^+}])([\mathrm{Fe^{3+}}]+[\mathrm{X^-}]+1/K_\mathrm{X})\\ &=(k_f{}^\circ+k_f{}'/[\mathrm{H^+}])([\mathrm{Fe^{3+}}]+[\mathrm{X^-}]+1/K_\mathrm{X})\\ &=k_f([\mathrm{Fe^{3+}}]+[\mathrm{X^-}]+1/K_\mathrm{X})\end{aligned} \tag{10}$$

with $k_f{}^\circ=k_{12}$; $k_f{}'=k_{34}\cdot K_\mathrm{OH}$; $k_f=k_f{}^\circ+k_f{}'/[\mathrm{H^+}]$. The concentrations of Fe^{3+} and X^- are obtained from the total iron and halide concentrations and the corrected equilibrium constants, K_X and K_OH.

TABLE 1. AVERAGED $1/\tau$[a] VALUES IN FERRIC CHLORIDE SOLUTIONS AT $\mu=1.0$ AND 27°C

$[\mathrm{H^+}]$, M	$\sum$Fe, 10^{-2} M $\sum$Cl, 10^{-2} M	5 5	5 3	5 1	3 2
0.050		202	153	148	140
0.075		100	106	109	120
0.100		94	84	76	84
0.150		67	53	59	58
0.200		50	45	52	47
0.400		26	28	22	27

a) Unit, sec^{-1}

TABLE 2. AVERAGED $1/\tau$[a] VALUES IN FERRIC BROMIDE SOLUTIONS AT $\mu=1.2$ AND 27°C

$[\mathrm{H^+}]$, M	$\sum$Fe, 10^{-2} M $\sum$Br, 10^{-2} M	5 5	5 5	5 1	2 2
0.10		1600	1670	1590	1380
0.20		940	1000	960	1040
0.40		525	550	540	530
0.60		370	375	430	415
0.80		295	290	310	280

a) Unit, sec^{-1}

The relaxation times were affected only very slightly by the ferric and halide concentrations, as is shown in Tables 1 and 2. This can easily be foreseen from the fact that the quantity of the concentration part, $([Fe^{3+}]+[X^-])$, is smaller than $1/K_X$ (maxima: 30% in the case of $FeCl^{2+}$ but only 3% in the case of $FeBr^{2+}$); therefore, it is not necessary to know the concentrations with any great accuracy.

A) $FeCl^{2+}$ Complex Formation Reaction. The formation rate constants were calculated by Eq. (10) with $1/\tau$ values in Table 1, the equilibrium concentrations of the ions, and the dissociation constant. As may be seen in Fig. 3, the observed rate constant depends greatly on the hydrogen ion concentration. The points are linear, with a finite intercept at $1/[H^+]=0$. The intercept and slope of Fig. 3 give values of $k_f{}^\circ=20\pm10$ $M^{-1}sec^{-1}$ and $k_f{}'=26\pm3$ sec^{-1} at 27°C.

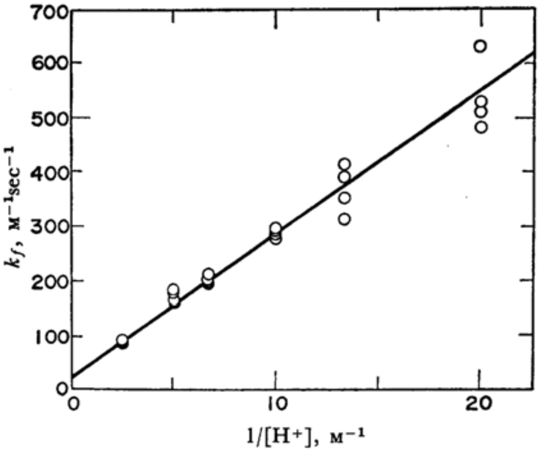

Fig. 3. The acid dependence of the formation rate constant of $FeCl^{2+}$ at 27°C and $\mu=1.0$.

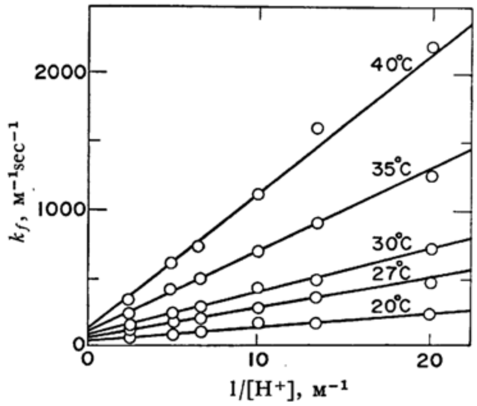

Fig. 4. k_f of $FeCl^{2+}$ vs. $1/[H^+]$ plot at various temperatures and $\mu=1.0$.

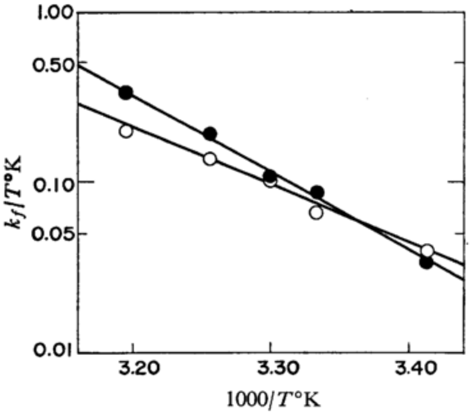

Fig. 5. Temperature dependence of $k_f{}^\circ$ (○) and k'_f (●) of $FeCl^{2+}$ at $\mu=1.0$.

In order to determine the enthalpies and entropies of activation, a series of experiments was run covering the temperature range from 20°C to 40°C. The equilibrium constants for ferric chloride at various temperatures have been estimated by the van't Hoff equation using the value at 25°C of 4.03 M^{-1} and $\Delta H=6.0$ kcal mol^{-1}.[2] K_{OH} has been estimated in the same way with the values of $\Delta H=10.2$ kcal mol^{-1} and $K_{OH}=1.60\times10^{-3}$ M^{-1} at 25°C.[11] The rate constants were calculated by means of Eq. (10), with the concentrations corrected for the temperatures; the results are shown in Fig. 4.

TABLE 3. KINETIC DATA FOR $FeCl^{2+}$ FORMATION AND DISSOCIATION AT $\mu=1.0$ AND 25°C

Formation reaction		Dissociation reaction	
k_{12}, M^{-1} sec^{-1}	19 ± 10	k_{21}, M^{-1} sec^{-1}	4.7 ± 2
$k_f{}'$, sec^{-1}	18.5 ± 3	$k_b{}'$, sec^{-1}	4.6 ± 0.7
k_{34}, M^{-1} sec^{-1}	$1.15(\pm0.2)\times10^4$	k_{43}, M^{-1} sec^{-1}	$2.85(\pm0.5)\times10^3$
k^*_{FeOH}, sec^{-1}	1×10^4		
$\Delta H^{\ne}_{12}$, kcal. mol^{-1}	16 ± 5	$\Delta H^{\ne}_{21}$, kcal. mol^{-1}	10 ± 5
$\Delta H^{\ne}_{34}$, kcal. mol^{-1} a)	11 ± 2	$\Delta H^{\ne}_{43}$, kcal. mol^{-1}	15 ± 2
$\Delta S^{\ne}_{12}$, e. u.	1 ± 17	$\Delta S^{\ne}_{21}$, e. u.	-21 ± 17
$\Delta S^{\ne}_{34}$, e. u.	-3 ± 7	$\Delta S^{\ne}_{43}$, e. u.	8 ± 7

a) Calculated from $\Delta H^{\ne}_{f'}$ and the enthalpy change of reaction (12).

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

Figure 5 shows a plot of log $k_f{}^\circ/T$ °K *vs.* $1000/T$ °K, and similarly for $k_f{}'$. From the slopes of these lines, $\Delta H^{\neq}{}_{f^\circ}=16\pm5$ kcal mol and $\Delta H^{\neq}{}_{f'}=21\pm2$ kcal mol^{-1} were calculated using the Eyring equation. $k_f{}^\circ$ and $k_f{}'$ at 25°C were taken to be $k_f{}^\circ=19\pm10$ M^{-1} sec^{-1} and $k_f{}'=18.5\pm3$ sec^{-1} (*cf.* Fig. 5). These values are in good agreement with Connick's values,[2] $\Delta H^{\neq}{}_{f^\circ}=16.6$ kcal mol^{-1}, $\Delta H^{\neq}{}_{f'}=23.3$ kcal mol^{-1}, $k_f{}^\circ=9.5$ M^{-1} sec^{-1}, and $k_f{}'=18.0$ sec^{-1} at 25°C. The other kinetic values for $\mathrm{FeCl^{2+}}$ formation and dissociation reactions are also listed in Table 3.

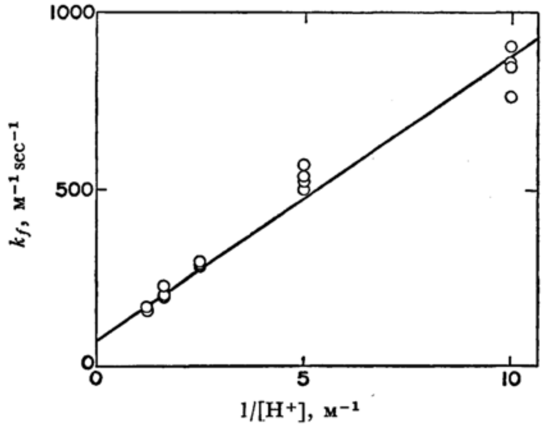

Fig. 6. The acid dependence of the formation rate constant of $\mathrm{FeBr^{2+}}$ at 27°C and $\mu=1.2$.

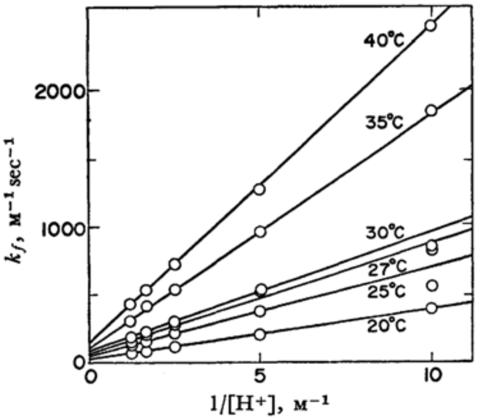

Fig. 7. k_f of $\mathrm{FeBr^{2+}}$ *vs.* 1/[H$^+$] plot at various temperatures and $\mu=1.2$.

B) $\mathrm{FeBr^{2+}}$ Complex Formation Reaction. The formation rate constants were calculated from the data in Table 2 and the equilibrium constants, $K_{\mathrm{Br}}=0.56$ M^{-1} and $K_{\mathrm{OH}}=1.78$ M^{-1} at $\mu=1.2$ and 27°C. Plots of the rate constants against 1/[H$^+$] in Fig. 6 gave values of $k_f{}^\circ=73\pm20$ M^{-1} sec^{-1} and $k_f{}'=80\pm5$ sec^{-1} at 27°C. The enthalpies and entropies of activation were calculated from the data in Fig. 7. The kinetic values for the $\mathrm{FeBr^{2+}}$ formation and for the dissociation reactions are listed in Table 4.

Discussion

Taking into account the fact that the rate constant of the complex formation is composed of two terms, one independent of hydrogen ion concentration and the other dependent on it, the complex formation reaction *via* rapid ion-pair formation, followed by the rate-determining loss of a water molecule in the inner coordination sphere of the metal ion, may be proposed as this reaction mechanism:

$$\mathrm{Fe(H_2O)_6{}^{3+} + X^-} \underset{}{\xrightleftharpoons{K^\circ{}_{\mathrm{Fe}}}} \mathrm{(H_2O)_5Fe^{3+}(H_2O)X^-} \xrightleftharpoons{k^*{}_{\mathrm{Fe}}} \mathrm{(H_2O)_5FeX^{2+} + H_2O} \tag{11}$$

$$\mathrm{Fe(H_2O)_6{}^{3+}} \xrightleftharpoons{K_{\mathrm{OH}}} \mathrm{(H_2O)_5Fe(OH)^{2+} + H^+} \tag{12}$$

$$\mathrm{(H_2O)_5Fe(OH)^{2+} + X^-} \xrightleftharpoons{K^\circ{}_{\mathrm{FeOH}}} \mathrm{(H_2O)_4Fe(OH)^{2+}(H_2O)X^-} \xrightleftharpoons{k^*{}_{\mathrm{FeOH}}} \mathrm{(H_2O)_4Fe(OH)X^+ + H_2O} \tag{13}$$

$$\mathrm{(H_2O)_4Fe(OH)X^+ + H^+} \xrightleftharpoons{\text{fast}} \mathrm{(H_2O)_5FeX^{2+} + H_2O} \tag{14}$$

where K° is the ion-pair equilibrium constant and k^* is the rate constant for the rate-determining step of the inner coordinated water substitution. The two rate constants obtained above, k_{12} and k_{34}, have the following relationships:

$$k_{12} = K^\circ{}_{\mathrm{Fe}} \cdot k^*{}_{\mathrm{Fe}} \tag{15}$$

TABLE 4. KINETIC DATA FOR $\mathrm{FeBr^{2+}}$ FORMATION AND DISSOCIATION AT $\mu=1.2$ AND 25°C

Formation reaction		Dissociation reaction	
k_{12}, M^{-1} sec^{-1}	50 ± 20	k_{21}, sec^{-1}	94 ± 20
k_f, sec^{-1}	65 ± 5	k_b, sec^{-1}	125 ± 5
k_{34}, M^{-1} sec^{-1}	$(4.1\pm0.3)\times10^4$	k_{43}, M^{-1} sec^{-1}	$(7.9\pm0.3)\times10^4$
$k^*{}_{\mathrm{FeOH}}$, sec^{-1}	4×10^4		
$\Delta H^{\neq}{}_{12}$, kcal. mol^{-1}	12 ± 2	$\Delta H^{\neq}{}_{21}$, kcal mol^{-1}	6 ± 2
$\Delta H^{\neq}{}_{34}$, kcal. mol^{-1} [a]	6 ± 2	$\Delta H^{\neq}{}_{43}$, kcal mol^{-1}	10 ± 2
$\Delta S^{\neq}{}_{12}$, e. u.	-10 ± 7	$\Delta S^{\neq}{}_{21}$, e. u.	-29 ± 7
$\Delta S^{\neq}{}_{34}$, e. u.	-18 ± 7	$\Delta S^{\neq}{}_{43}$, e. u.	-2 ± 7

[a] Calculated from $\Delta H^{\neq}{}_{f'}$ and the enthalpy change of reaction (12).

TABLE 5. RATE CONSTANTS[a] FOR Fe(III) COMPLEX FORMATION REACTIONS AT 25°C

Complex	μ	k_{12}	k'_{12}[b]	$k_{34}\times10^{-4}$	k'_{34}[c] $\times10^{-4}$	Ref.
$FeCl^{2+}$	1.0	19	—	1.2	—	This work
$FeCl^{2+}$	1.0	9.4	—	1.1	—	2
$FeBr^{2+}$	1.2	50	—	4.1	—	This work
$FeBr^{2+}$[d]	1.7	20	—	2.6	—	3
$FeCNS^{2+}$	0.4	127	—	1.0	—	4
$FeSO_4^+$	0.6	—	—	24	2.4	7
$FeSO_4^+$	0.5	—	—	—	14.5	5
FeF^{2+}	0.5	—	11	—	0.32	14
FeN_3^{2+}	1.0	—	4	—	0.68	6
FeN_3^{2+}	0.1	—	—	—	0.74	8

a) Unit, $\text{M}^{-1}\,\text{sec}^{-1}$

b) k'_{12} corresponds to $Fe^{3+}+HX \xrightarrow{k'_{12}} FeX^{2+}+H^+$

c) k'_{34} corresponds to $FeOH^{2+}+HX \xrightarrow{k'_{34}} Fe(OH)X^{+}+H^+$

d) $t=22$°C

$$k_{34} = K^\circ_{\text{FeOH}}\cdot k^*_{\text{FeOH}} \tag{16}$$

Unfortunately, K° cannot be determined experimentally; therefore, it has become customary to estimate K° from the Fuoss equation.[12,13] Assuming that the distance of the closest approach of the ion-pair partners is about 5 Å, K°_{Fe} and K°_{FeOH} can be calculated to be about 5 and 1 respectively at $\mu=0.5$—1.0, for the corresponding type of ion pairs. The value of K° in this calculation is uncertain because of the large ionic strength correction made in the calculation. The value of k^* for some of the Fe(III) complex formation reactions can be estimated from K° and the rate constants in Table 5.

The rate constants for the rate-determining process of reaction (13), k^*_{FeOH}, lie approximately in the same order, $(1-4)\times10^4$, irrespective of the nature of the entering ligand. According to Connick and Genser,[15] the rate constant for the water exchange on $(H_2O)_5FeOH^{2+}$ is estimated to be of the same order as these values ($\sim10^4\,\text{sec}^{-1}$). These facts indicate that the substitution of a water molecule in the inner coordination sphere of the metal ion is the rate-determining process of the complex formation reaction.

On the other hand, we must admit that the k_{12} and k_{12}' values also fall in nearly the same order. With $K^\circ_{\text{Fe}}=5$, k^*_{Fe} can be calculated to be 1—25 sec^{-1} by Eq. (15). Comparing k^*_{Fe} with the rate constant for water exchange on $Fe(H_2O)_6^{3+}$, $2.8\times10^2\,\text{M}^{-1}\,\text{sec}^{-1}$,[15] these values are a little too small. This shows that Eq. (11) is not the best possibility for the mechanism of reaction (6). An alternate mechanism consistent with the data may be proposed:

$$Fe(H_2O)_6^{3+} \overset{\text{fast}}{\rightleftharpoons} Fe(H_2O)_5^{3+} + H_2O \tag{17}$$

$$Fe(H_2O)_5^{3+} + X^- \rightleftharpoons Fe(H_2O)_5X^{2+} \tag{18}$$

where the reaction (17) is fast and where the rate-determining step is the reaction (18). This mechanism seems reasonable in view of two facts: the water exchange reaction rate is faster than the complex formation rate, and the complex formation rate of Fe(III) depends on the nature of the entering ligand.

Among the activation parameters for the complex formations of Fe(III), Cavasino[9] indicated some discrepancy in the reaction with Cl^- and attributed it to the high ionic strength at which the kinetic studies were carried out. In this work, however, we could not observe any such discrepancy in either $FeCl^{2+}$ or $FeBr^{2+}$ formation reactions; this fact also suggests that the rates of Fe(III) complex formation reactions are controlled by the rate of loss of a coordinated water molecule from the cation.

Further studies with other complexes of Fe(III) are in progress and will be reported on in due course.

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13) G. G. Hammes and J. I. Steinfeld, *ibid.*, **84**, 4639 (1962).

14) D. Pouli and W. MacF. Smith, *Can. J. Chem.*, **38**, 567 (1960).

15) R. E. Connick and E. E. Genser, quoted in Ref. 6.