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A Temperature-jump Study of the Kinetics of the Complex Formation of Iron(III) with *m*-Nitrophenol

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By a new method here proposed, an expression of the relaxation time has been obtained for the formation of the monocomplex of iron(III) with a univalent anionic ligand. The method enables us to express the rate equation in a manner analogous to the second-order reaction, and to calculate the relaxation time with less mathematical labor. The validity of the treatment has been confirmed by applying it to the analysis of the complex formation reaction of iron(III) with *m*-nitrophenol. The kinetic measurement was performed with the temperature-jump method in an acidic aqueous solution at 25 °C and at an ionic strength of 0.10. Over the acidity range studied ($0.005 \leq [H^+] \leq 0.026$ M), the complex formation occurs significantly *via* one path: $FeOH^{2+} + m\text{-}NO_2C_6H_4OH \rightleftharpoons m\text{-}NO_2C_6H_4OFe^{2+} + H_2O$. The forward and backward rate constants obtained are $5.9 \times 10^2\ M^{-1}\,s^{-1}$ and $1.8 \times 10^2\ s^{-1}$ respectively. These results have been confirmed by examining the earlier kinetic data on similar reactions.

The reactions of iron(III) complexes in aqueous solutions have been the object of much recent interest[1-3] because of the apparent dependence of the formation rates of the complexes on the basicity of the entering ligand; no such dependence is shown by the bivalent transition or by most alkaline earth metal ions, where the rate-determining step is considered to be the removal of a water molecule from the inner coordination sphere of the cation. The apparent ligand specificity has been almost entirely removed by the general reaction mechanism proposed by Seewald and Sutin[4] and later developed by Cavasino and his co-workers.[5] Also, kinetic studies[4-10] have shown that the reaction mechanism interprets well the rates of the formation of iron(III) complexes with anionic ligands of a wide range of basicity.

Recently, Osugi, *et al.*[11] studied the complex formation of iron(III) with *p*-nitrophenol, which is an anionic ligand of a very high basicity. Soon after, Cavasino and Dio[12] also investigated similar reactions with some monosubstituted phenols. However, there was some inconformity concerning the reaction paths reported by these authors, and little kinetic information has been given elsewhere on complex formation with such ligands of a very high basicity.

The reactions of iron(III) with high-basicity ligands may be important as an extreme example of the reaction mechanism, and so more detailed investigations are required. In the present investigation, the complex formation of iron(III) was studied, with *m*-nitrophenol as the ligand. The kinetic measurement was carried out by the temperature-jump relaxation method. The present author has also proposed a new method of analysis for calculating the relaxation time with less mathematical labor; this method was elucidated in the course of this investigation.

Experimental

Materials. All of the chemicals used were of a reagent grade. Each sample solution was prepared by mixing appropriate ammounts of solutions of 0.05 M $Fe(NO_3)_3$, 0.1 M $m\text{-}NO_2C_6H_4OH$, and 0.1 M $HClO_4$, by then adjusting the ionic strength to 0.10 by the addition of KNO_3, and finally by diluting to a definite volume. The content of iron(III) in the ferric nitrate solution was determined by complexometric titration with disodium EDTA,[13] and the concentration of the acid solution was standardized with sodium hydroxide.

Temperature-jump Apparatus. The temperature-jump apparatus was a modification of those described by Hammes and Fasella[14] and by Kresheck *et al.*[15] It was operated by a single-beam optical system. A schematic diagram and the construction of the observation cell are shown in Figs. 1 and 2 respectively. The cell is constructed from an acryl-resin disk 2 cm thick, through the center of which a hole 1 cm square has been bored. The solution chamber consists of the hole and the gold-coated walls of the brass electrodes, and accommodates 2 cm³ of the solution. Two quartz windows enable optical observation through the solution, with a path of 1 cm. The temperature of the solution is controlled within ±0.2 °C by circulating thermostated ethanol through the hollow electrodes.

A 0.4 μF condenser bank charged to 16 kV was discharged through the cell by means of an air gap. The temperature jump of the solution was 5±0.5 °C, as determined by the change in the absorbance (at 550 mμ) of a phenolphthalein

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[2] H. Wendt and H. Strehlow, *Z. Elektrochem.*, **66**, 228 (1962).

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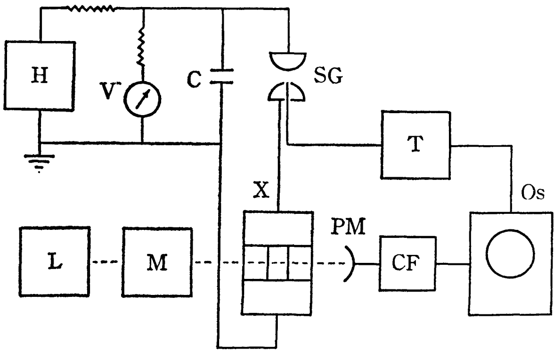

Fig. 1. Schematic diagram of the temperature-jump apparatus.
(L) light source; (M) monochromator; (X) observation cell; (PM) photomultiplier; (CF) cathode follower; (Os) oscilloscope; (H) high voltage generator; (V) vacuum-tube voltmeter; (C) condenser; (SG) spark gap; (T) trigger-pulse generator.

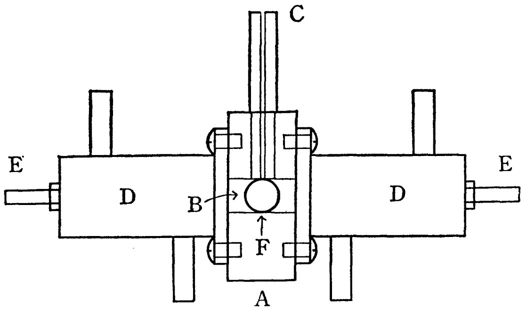

Fig. 2. Construction of the observation cell.
(A) acryl-resin cell; (B) solution space; (C) acryl-resin stopper with an orrifice to exhaust thermal pressure; (D) hollow brass electrodes (gold-coated at the solution sides) with outlets for circulating thermostated liquid; (E) leads to the discharging circuit; (F) quartz windows.
The direction of the observation light beam is perpendicular to the plane of the diagram.

solution. The indicator solution used contained 6×10^{-8} M phenolphthalein and 0.02 M glycine; the pH and the ionic strength were 9.5 and 0.10 (with KNO_3) respectively. The relaxation time of the heating period was 40 μs at this ionic strength.

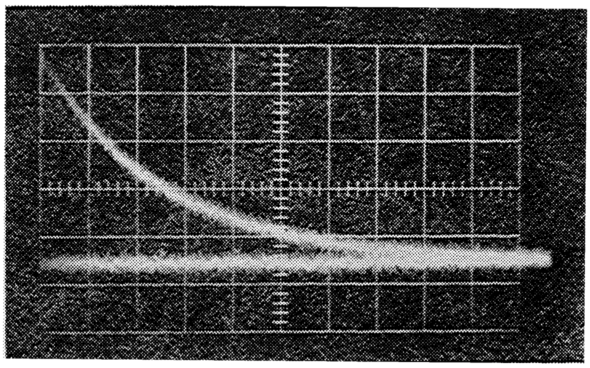

Fig. 3. An oscillograph of the temperature-jump relaxation experiment for iron(III) with *m*-nitrophenol. The data for this system are given in the last raw of Table 1. The sweep rate is 2 ms per division. The upper curve shows the relaxation effect corresponding to an increase in absorbance. The lower straight-line is the following trace of this curve after the intermittent time of 20 ms, showing an attainment of the transient equilibrium.

Results

The temperature-jump measurement was carried out at the wavelength of 508 mμ, where the *m*-NO_2-$C_6H_4OFe^{2+}$ ion exhibits the maximum absorbance.[16] All the solutions cited in Table 1 showed a single relaxation effect in the time range of 2×10^{-4}—0.05 s; this effect may be associated with the complex formation reaction. A second, smaller effect was also observed in the time range longer than this; the relaxation time was very roughly estimated not to be smaller than 0.4 s. The second relaxation effect did not interfere with the evaluation of the relaxation time related to the complexation. Blank solutions containing only ferric nitrate or *m*-nitrophenol at the same conditions of concentration, ionic strength, and pH had not shown any evidence of relaxation effect in the same time ranges. Moreover, there was no discernible kinetic difference between the sample solutions after several hours had elapsed and a few months had, after preparation. A representative relaxation effect of the complex formation is shown in Fig. 3.

TABLE 1. KINETIC DATA FOR THE REACTION OF IRON(III) WITH *m*-NITROPHENOL AT μ=0.10 AND 25 °C

$[Fe(III)]_0$ (10^{-3} M)	$[HA]_0$ (10^{-2} M)	$[HClO_4]_0$ (10^{-3} M)	$[H^+]$ (10^{-3} M)	τ^{-1} (s^{-1})	k_f ($M^{-1}s^{-1}$)	$k_f/(1-\alpha)$ ($M^{-1}s^{-1}$)
1.98	4.81	4.16	5.02	205	229	626
0.992	4.81	5.94	6.30	188	183	582
2.98	3.20	7.13	8.18	179	147	562
9.98	5.00	5.94	9.43	213	153	652
4.96	1.20	8.32	9.76	163	120	523
4.99	5.00	11.9	12.9	197	113	617
9.92	3.20	11.9	14.5	188	98.6	593
9.98	5.00	17.8	19.9	193	77.1	608
9.92	1.20	17.8	19.9	168	68.5	540
4.96	3.20	23.8	24.7	174	58.4	558
9.98	5.00	23.8	26.1	189	59.9	601
						Av. 587±64

The subscript (0) for bracket indicates total stoichiometric concentration.

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[16] Z. L. Ernst and F. G. Herring, *Trans. Faraday Soc.*, **61**, 454 (1965).

The reciprocal relaxation time (τ^{-1}) was evaluated by the plot of the logarithm of the oscilloscope amplitude *vs.* the time. Here, the least-squares method was employed to obtain the most probable value. All the relaxation times quoted in Table 1 are means of at least five runs; the maximum error is about ±10%.

The pH of each solution was measured at 25±0.5 °C with a Hitachi-Horiba pH meter, Model F-7SS, calibrated with standard buffer solutions. The equilibrium hydrogen-ion concentrations were calculated from the measured pH values by using the activity coefficient (0.825)[17]; they are also shown in Table 1. The hydrogen-ion concentration thus obtained agreed within ±3% with that which was evaluated from the stoichiometric concentration of perchloric acid by taking into account the reaction equilibria, (3), (4), and (5).

Discussion

Potentiometric[18] and spectrophotometric[19–23] studies have shown that the following equilibria exist in an aqueous acid solution containing ferric ions with m-nitrophenol:

$$HA \rightleftharpoons A^- + H^+ \qquad K_H \tag{1}$$

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

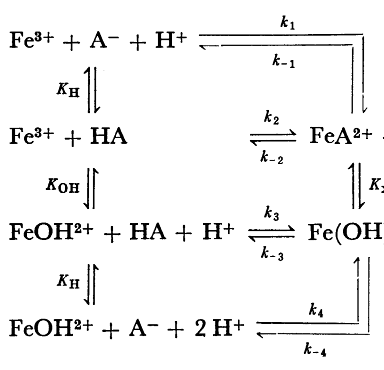
$$Fe^{3+} + HA \rightleftharpoons FeA^{2+} + H^+ \qquad K_b \tag{3}$$

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+ \qquad K_{OH} \tag{4}$$

$$2\,FeOH^{2+} \rightleftharpoons Fe_2(OH)_2{}^{4+} \qquad K_d \tag{5}$$

where HA indicates m-$NO_2C_6H_4OH$ and where K_H, K_c, K_b ($=K_HK_c$), K_{OH}, and K_d are the equilibrium constants for the corresponding reactions. Here, the presence of $Fe(OH)_2{}^+$ may be ignored.[24,25] Reaction (5) occurs so slowly that it may contribute little to the complex formation kinetics; for the present conditions, the reported rate constants[26,27] give $\tau \geqq 0.4$ s, which corresponds with the second relaxation time observed.

With these hypotheses, the overall mechanism for the formation of the FeA^{2+} complex may be expressed in a general form:[5,6,9)]



(6)

where the water molecule was omitted from the reactions for the sake of simplicity. The protolytic reactions (vertical steps) occur rapidly relative to the complex formation reactions, and are considered to be in equilibria throughout the course of the complex formation. Hence, only one relaxation time, associated with slower metal-complex formation reactions, can be obtained from the reaction scheme; the solution has already been given by Cavasino and his co-workers.[5,6,9] However, the present author will present here a different method of analysis, one which simplifies the rate equation and which makes it possible to calculate the relaxation time with less mathematical labor.

We notice the rapid protolytic reactions and express the overall free metal ions, free ligands, and metal-complexes by M, L, and ML, respectively, defining their concentrations as follows:

$$[M] \equiv [Fe^{3+}] + [FeOH^{2+}] \tag{7}$$

$$[L] \equiv [A^-] + [HA] \tag{8}$$

$$[ML] \equiv [FeA^{2+}] + [Fe(OH)A^+] \tag{9}$$

with these conditions and definitions:

$$\alpha \equiv \frac{[Fe^{3+}]}{[M]} = \frac{[H^+]}{K_{OH}+[H^+]} \tag{10}$$

$$\beta \equiv \frac{[A^-]}{[L]} = \frac{K_H}{K_H+[H^+]} \tag{11}$$

$$\gamma \equiv \frac{[FeA^{2+}]}{[ML]} = \frac{[H^+]}{K_x+[H^+]} \tag{12}$$

where K_x is the equilibrium constant of the hydrolysis of FeA^{2+}. Then, the rate equation is given by:

$$\frac{d[ML]}{dt} = k_f[M][L] - k_b[ML] = k_f\left([M][L] - \frac{[ML]}{K}\right) \tag{13}$$

where:

$$k_f = k_1\alpha\beta + k_2\alpha(1-\beta) + k_3(1-\alpha)(1-\beta) + k_4(1-\alpha)\beta \tag{14}$$

$$k_b = k_{-1}\gamma + k_{-2}\gamma[H^+] + k_{-3}(1-\gamma)[H^+] + k_{-4}(1-\gamma) \tag{15}$$

$$K = \frac{k_f}{k_b} = K_c\left(\frac{\alpha\beta}{\gamma}\right) \tag{16}$$

Here, k_f and k_b may be called the (apparent) overall forward and backward rate constants respectively.

By expanding Eq. (13) in the vicinity of the equilibrium concentrations and by using conservation relations:

$$\Delta[M] = \Delta[L] = -\Delta[ML] \tag{17}$$

we obtain:

$$\frac{d\Delta[ML]}{dt} = -k_f\left([M]+[L]+\frac{1}{K}-\frac{[ML]}{K^2}\frac{\Delta K}{\Delta[ML]}\right)\Delta[ML] \tag{18}$$

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[17] R. P. Frankenthal, "Handbook of Analytical Chemistry," 1st Ed., ed. by L. Meites, McGraw-Hill Book Co., Inc., London (1963), p. 1-6.

[18] K. E. Jabalpurwala and R. M. Milburn, *J. Amer. Chem. Soc.*, **88**, 3224 (1966).

[19] R. M. Milburn, *ibid.*, **77**, 2064 (1955).

[20] R. M. Milburn, *ibid.*, **89**, 54 (1967).

[21] A. G. Desai and R. M. Milburn, *ibid.*, **91**, 1958 (1969).

[22] R. M. Milburn and W. C. Vosburgh, *ibid.*, **77**, 1352 (1955).

[23] R. M. Milburn, *ibid.*, **79**, 537 (1957).

[24] A. B. Lamb and A. G. Jacques, *ibid.*, **60**, 1215 (1938).

[25] P. Hemmes, L. D. Rich, D. L. Cole, and E. M. Eyring, *J. Phys. Chem.*, **75**, 929 (1971).

[26] H. Wendt, *Z. Elektrochem.*, **66**, 235 (1962).

[27] H. Wendt, *Inorg. Chem.*, **8**, 1527 (1969).

where the symbol Δ indicates the deviation from the equilibrium value. From Eq. (18), the relaxation time, τ, is given by:

$$\frac{1}{\tau} = k_f B \tag{19}$$

where:

$$B = [\mathrm{M}] + [\mathrm{L}] + \frac{1}{K} + \phi \tag{20}$$

and:

$$\phi \equiv -\frac{[\mathrm{ML}]}{K^2}\frac{\Delta K}{\Delta[\mathrm{ML}]} = \frac{(\alpha-\beta-\gamma+1)^2[\mathrm{M}][\mathrm{L}]}{[\mathrm{H}^+]+\alpha(1-\alpha)[\mathrm{M}]+\beta(1-\beta)[\mathrm{L}]+\gamma(1-\gamma)[\mathrm{ML}]} \tag{21}$$

The term ϕ results from the fact that K is a function of $[\mathrm{H}^+]$, which varies rapidly following the slower complex formation reactions. The last form of Eq. (21) can readily be obtained from Eqs. (16), (10), (11), and (12) by using the condition of electroneutrality together with Eq. (17); here, the contribution of $[\mathrm{OH}^-]$ has been ignored in the calculations. All the quantities in Eqs. (19), (20), and (21) are expressed by the equilibrium values, and the K defined in Eq. (16) reduces to the apparent equilibrium constant, or to what is called the "apparent stability constant": $K = [\mathrm{ML}]/[\mathrm{M}][\mathrm{L}]$.

The evaluation of B from Eqs. (20) and (21) requires the values of [M], [L], [ML], α, β, and γ. In the present case, the hydrolysis constant, K_x, could, unfortunately, not be found in the literature. However, that of FeSCN^{2+} has been reported to be $K_x = 6.5\times10^{-5}$ at $\mu = 1.2$ and 25 °C.[28] Moreover, the second hydrolysis constant of the ferric ion[24,25] may be regarded as the hydrolysis constant of the FeOH^{2+} complex: $K_x = (0.8\text{—}2)\times10^{-5}$ at $\mu\approx0$ and 25 °C. As these complexes give similar K_x values in spite of the large difference between the basicities of the thiocyanate and hydroxide ions (*i.e.*, $\mathrm{p}K_\mathrm{H} = 1$ and 16), the same order of magnitude may be assigned to the K_x value for the monocomplex of iron(III) with the univalent anionic ligand. Therefore, in the acidity range ($[\mathrm{H}^+] = 0.005\text{—}0.026$ M) of the present work, the condition of $K_x \ll [\mathrm{H}^+]$, which is equivalent to that of $[\mathrm{Fe(OH)A}^+] \ll [\mathrm{FeA}^{2+}]$, may be satisfied, and we obtain $\gamma = 1$ and $[\mathrm{ML}] = [\mathrm{FeA}^{2+}]$ by means of Eq. (12). This corresponds to the steady-state assumption for the concentration of $\mathrm{Fe(OH)A}^+$ usually adopted.[5-12] Under the present acidity conditions, the concentration of the free phenolate ion, A^-, is much lower than that of the acid ligand, HA, as $\mathrm{p}K_\mathrm{H} = 8$ for *m*-nitrophenol; $\beta\approx[\mathrm{A}^-]/[\mathrm{HA}]$ is in the range $10^{-6}\text{—}10^{-7}$. Therefore, we need only the $[\mathrm{Fe}^{3+}]$, $[\mathrm{FeOH}^{2+}]$, [HA], and $[\mathrm{FeA}^{2+}]$ concentrations to evaluate B. These equilibrium concentrations were obtained from the total stoichiometric concentrations of iron(III) and *m*-nitrophenol, from the equilibrium hydrogen-ion concentration, in Table 1, and from the equilibrium constant, K_b, K_OH, and K_d.

Milburn and his co-workers[18-21] reported several values of K_b in the course of their potentiometric[18] and spectrophotometric[19-21] studies. Desai and Milburn[21] obtained, most recently, by their careful spectrophotometric measurements: $K_\mathrm{b} = 0.94\times10^{-2}$ at $\mu = 0.10$ and 25 °C. As the somewhat larger values reported earlier[18-20] left moderately large uncertainties in the absolute values,[21] this value was adopted as the most reliable value available at present. The values of K_OH and K_d at $\mu = 0.10$ and 25 °C were obtained from Milburn and Vosburgh's measurements[22]: $K_\mathrm{OH} = 2.89\times10^{-3}$ and $K_\mathrm{d} = 1.7\times10^2$.

The overall forward rate constant, k_f, was calculated by means of Eq. (19), using the $1/\tau$ value in Table 1 and the value of B. The results are also shown in Table 1. As could be expected from Eq. (14), the k_f value depends only on the hydrogen-ion concentration; it decreases with an increase in the hydrogen-ion concentration. From the present condition, $\beta\approx 10^{-6}\text{—}10^{-7}$, together with the k_f value in Table 1, it seems that we may safely ignore the first and fourth terms in Eq. (14); if these terms contribute significantly to k_f, the k_1 and k_4 values should be greater than $10^6\ \mathrm{M^{-1}\,s^{-1}}$, values such as have not been observed for other univalent anionic ligands.[4,5,8,9] Ignoring β with respect to 1 in the second and third terms in Eq. (14) and dividing by $(1-\alpha)$, we obtain:

$$\frac{k_f}{1-\alpha} = \frac{k_2[\mathrm{H}^+]}{K_\mathrm{OH}} + k_3 \tag{22}$$

As is shown in the last column of Table 1, the value of $k_f/(1-\alpha)$ is practically independent of the hydrogen-ion concentration; the deviations from the mean value are almost within the limits of the experimental errors in τ (*ca.* ±10%). Therefore, the first term of Eq. (22) may be ignored, and the k_3 value is determined to be $(5.9\pm0.6)\times10^2\ \mathrm{M^{-1}\,s^{-1}}$.

By inserting the approximate relations $k_f = k_3(1-\alpha)$, $\gamma = 1$, and $\beta = K_\mathrm{H}/[\mathrm{H}^+]$ into Eq. (16), and by using the equilibrium relations of $K_\mathrm{H}K_\mathrm{c} = K_\mathrm{b}$ and $k_3/k_{-3} = K_x K_\mathrm{b}/K_\mathrm{OH}$, we obtain:

$$k_\mathrm{b} = \frac{k_3 K_\mathrm{OH}}{K_\mathrm{b}} = k_{-3} K_x \tag{23}$$

The last form of Eq. (23) corresponds to the third term of Eq. (15). From the second form of Eq. (23), the k_b value was obtained as $(1.8\pm0.2)\times10^2\ \mathrm{s^{-1}}$.

From the above results, the following reaction path may be said to contribute mainly to the rate of the complex formation:

$$\mathrm{FeOH}^{2+} + \mathrm{HA} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{Fe(OH)A}^+ + \mathrm{H}^+ \underset{K_x}{\rightleftharpoons} \mathrm{FeA}^{2+} + \mathrm{H_2O} \tag{24}$$

where the forward and backward rate constants correspond to k_3 and k_b respectively.

For the monocomplex formation of iron(III) with substituted phenols, earlier kinetic studies have been made by Osugi *et al.*[11] and by Cavasino and Dio[12] with temperature-jump measurements at $\mu = 0.10$ and at 25 °C. With *p*-nitrophenol as the ligand, the former

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

authors[11] obtained the same reaction path as (24), showing a considerable contribution of the reaction path involving the rate constant, k_2. On the other hand, the latter authors[12] found the sole effective reaction path to be (24), with some monosubstituted phenols. The above authors[11,12] reported k_3 values over the range of $(1.1\text{—}3.2)\times10^3\ \mathrm{M^{-1}\,s^{-1}}$; these values are two times or more larger than the present value. However, the k_3 values of the above authors[11,12] may require some corrections, for they used in their calculations Milburn[20] or Ernst and Herring[12] K_b values, which are, except for the case of (unsubstituted) phenol, somewhat larger than those of Desai and Milburn,[21] whose value was adopted in this study as the most recent and reliable value. According to Cavasino and Dio's approximation,[12] the k_3 value is almost proportionally affected by the K_b value used: $k_3 \approx K_b/(K_{OH}\tau)$.

The kinetic data of the above authors[11,12] were then re-examined by using Desai and Milburn's K_b values and by using the present method of calculation. All the data examined, including that of Osugi *et al.*, did not show any significant contribution of the rate constant, k_2, to the complex formation rates. The value, $k_2=32\ \mathrm{M^{-1}\,s^{-1}}$, reported by Osugi *et al.*[11] may result mainly from their method of estimation, which overweighes the data in the low-acidity region. The above results confirm again the present conclusion of the sole reaction path (24). The k_3 values in Table 2 are those estimated by the present author, except that for m-cresol, which is the original value.[12] The K_b values used for the calculation and the pK_H values for the ligand are also shown in the same table. As has been expected, the k_3 values re-estimated are all smaller than the original ones, except for the case of phenol, which gives the same value as the original one.[12]

Table 2. Kinetic data for the formation of iron(III) monocomplexes with substituted phenols at $\mu=0.10$ and 25 °C

Sub-stituent group	$10^{-2}\,k_3$ [a] ($\mathrm{M^{-1}\,s^{-1}}$)	$10^2\,K_b$ [c]	pK_H [c]	Ref. [f]
m-CH_3	16 [b]	1.00 [d]	9.88 [e]	C-D
H	15	0.92	9.80	C-D
p-Cl	6.6	0.60	9.16	C-D
m-Cl	13	1.26	8.80	C-D
o-Cl	3.5	0.69	8.25	C-D
m-NO_2	8.0	0.94	8.12	C-D
m-NO_2	5.9	0.94	8.12	T
p-NO_2	8.2	1.39	6.89	C-D
p-NO_2	9.1	1.39	6.89	O-N-F

a) Value estimated by the present author, unless otherwise noted.
b) Original value.[12]
c) Desai and Milburn's value,[21] unless otherwise noted.
d) Ernst and Herring's value.[12]
e) Biggs and Robioson's value.[12]
f) C-D: Cavasino and Dio[12] T: Present author O-N-F: Osugi, Nakatani, and Fujii.[11]

These values conform well with the present author's value.

We notice further that the k_3 values in Table 2 lie in a comparatively narrow range, $(3.5\text{—}16)\times10^2\ \mathrm{M^{-1}\,s^{-1}}$, in spite of the different nature and position of the substituent groups in the aromatic ring and the different basicity of the entering ligand ($pK_H=7\text{—}10$). As has been pointed out by Cavasino and Dio,[12] this suggests that the first step of reaction path (24) may proceed through the S_N1 mechanism, which involves the loss of a water molecule in the rate-determining step. However, the k_3 values in Table 2 are somewhat smaller than those reported in the earlier kinetic studies[4,5,9,10] for the corresponding reactions with HN_3,[4,5] HF,[4,5] CH_3CO_2H,[9] $ClCH_2CO_2H$,[9] $C_2H_5CO_2H$,[9] and $C_6H_5CH(OH)CO_2H$[10]: $k_3=(2.56\text{—}7.4)\times10^3\ \mathrm{M^{-1}\,s^{-1}}$ at 20—25 °C and at $\mu=0.1\text{—}1.0$. A full explanation must await further investigations.

As is shown in Eqs. (7)—(21), the present method of analysis is mathematically simpler and more suggestive than the treatments of the previous investigators.[3,5,6,8,9,11,12] However, except for the different definitions of k_f and B, the present expression of the relaxation time, Eq. (19), is essentially equivalent to that of Cavasino and his co-workers[5,6,9] (with $\gamma=1$), and also to that of Osugi *et al.*[11] (with $\gamma=1$ and $\beta=0$). The apparent forward rate constant (usually designated as k_f or k_{obs}) differs from author to author, simply because they select different reactions as representative in the reaction scheme. Cavasino and his co-workers[5,9] took the reaction involving Fe^{3+} with A^- as representative; the k_{obs} used by them corresponds to the $k_f/\alpha\beta$ in the present expression, which exhibits a much higher order of magnitude with such ligands of a very high basicity as phenols.[12] Osugi *et al.*[11] selected the reaction of Fe^{3+} with HA as representative; the k_f used by them is equivalent to the k_f/α (with $\beta=0$) in the present study.

The k_f defined by Eq. (14) has a more general form, without taking any definite reaction as representative, and may give the value of the moderate magnitude with a ligand of a wide range of basicity. From the reasons above, the present author considered it appropriate as an (apparent) overall forward rate constant of complexation. A similar treatment has been given by Hammes and Schimmel,[29,30] but they ignored the term corresponding to ϕ in Eq. (20) and so their expression may be applicable only to strongly buffered reaction systems.[30] The present treatment may be easily extended to the analysis of more complicated reactions, such as protonated complex formation reactions.

Through this investigation, the present author considered that the validity of the present method of analysis may be well confirmed, and also that the functioning of the newly built temperature-jump apparatus was satisfactory.

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29) G. G. Hammes and P. R. Schimmel, *J. Phys. Chem.*, **70**, 2319 (1966).

30) G. G. Hammes and P. R. Schimmel, *ibid.*, **71**, 917 (1967).