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# Kinetics of the Aquation of Iron(III) Monophenolate Complexes; Absence of the Acid-dependent Path

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The complex formation between Fe(III) and 10 kinds of phenols was investigated using a stopped-flow apparatus. It was confirmed that the reaction rate is acid-independent in the acid region 0.01—1.0 M. A mechanism for the aquation of the iron(III)-phenol complex is proposed in which a proton transfers intramolecularly from a co-ordinated water molecule to a phenolate ion, *viz.*, $Fe(OH_2)_5A^{2+} \rightarrow Fe(OH_2)_4(OH) \cdot AH^{2+}$. From the observed isotope effects it was concluded that the state of a proton of HA in $Fe(OH_2)_4(OH) \cdot AH^{2+}$ differs from that in a free phenol.

Extensive work has been made on the kinetics of the ligand substitutions of tervalent iron in aqueous solution.[1] Recently Cavasino and Di Dio obtained the substitution rate of Fe(III) for various monophenols using the temperature-jump method.[2] They concluded that in the acid region 0.01—0.09 M $HClO_4$, the complexes is formed through the reaction between $Fe(OH)^{2+}$ and a phenol molecule and that the rate of formation, $1.5 \times 10^3\ M^{-1}sec^{-1}$, is almost independent of the kind of entering phenol.

The rate constants they obtained for the reaction of $Fe(OH)^{2+}$ and phenols are of the same order of magnitude as for the other ligands and in line with the proposal that the rate-determining step is the release of a co-ordinated water molecule from $Fe(OH)^{2+}$. However, the absence of the reaction path involving $Fe(OH_2)_6{}^{3+}$ and a phenol molecule means that the rate-determining step is no longer the release of a water molecule from $Fe(OH_2)_6{}^{3+}$. In other words, it is impossible to form the complex from the outer-sphere complex between $[Fe(OH_2)_6]^{3+}$ and a phenol molecule. This is an interesting result. However, the acid concentration chosen by Cavasino and Di Dio is not sufficiently high to conclude that there is no reaction path between $Fe(OH_2)_6{}^{3+}$ and a phenol molecule. We therefore performed the kinetic investigation of the reaction by pH-jump method at a higher acidity region (0.1—1.0 M $HClO_4$). It was confirmed that the reaction between $Fe(OH_2)_6{}^{3+}$ and a phenol does not lead to the complex in the acidity region studied. We conclude that during the course of the aquation reaction, proton transfer occurs intramolecularly from a co-ordinated water molecule to a phenolate ion. The isotope effect was also studied and discussed on the basis of the mechanism.

## Experimental

*Materials.* Iron(III) perchlorate was prepared by heating the chloride with a small excess of perchloric acid and recrystallized *in vacuo*. The concentration of iron(III) was determined titrimetrically with EDTA. The perchloric acid content was determined by passing an aliquot of the solution through a column of cation-exchange resin in the hydrogen-form, and titrating the effluent with sodium hydroxide. The ionic strength was adjusted with the purified reagent grade sodium perchlorate.[3]

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[1] Recent results are summarized in F. P. Cavasino, *J. Phys. Chem.*, **72**, 1378 (1968).

[2] F. P. Cavasino and E. Di Dio, *J. Chem. Soc., A*, **1970**, 1151.

[3] Y. Kawai, T. Takahashi, K. Hayashi, T. Imamura, H. Nakayama, and M. Fujimoto, This Bulletin, **75**, 1417 (1972).

Phenols were purified according to Milburn.[4] The purity was confirmed by melting point and thin-layer chromatography.

*Measurements.* The optical densities were measured with a Hitachi recording spectrophotometer Model EPS-3T. pH was measured with a Radiometer equipped with G 200B glass electrode and K 100 reference calomel electrode. pD of the deuterium oxide solution was evaluated as 0.4 plus the pH-meter reading.[5] Kinetic measurements were performed using a Yanagimoto stopped-flow spectrophotometer Model SPS-1.

In the acid region, the equilibrium of the complex formation is written as

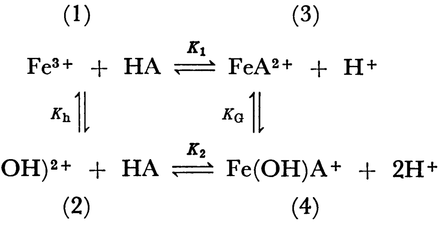
$$\mathrm{Fe^{3+} + HA \rightleftharpoons FeA^{2+} + H^+},$$

where HA denotes a phenol molecule. Since the equilibrium constant is in the order of $10^{-2}$ for monophenols, the concentration of the complex is greatly reduced in such a high acid region as 0.1—1.0 M. It is therefore difficult to obtain the rate constant at a high proton concentration by the ordinary mixing method. To overcome this difficulty, we rapidly mixed a solution of the complex in low acidic media with a solution containing a large amount of proton. The rapid pH-jump shifts the equilibrium towards dissociation. Since the proton transfer of aquo-iron(III) is generally much faster than the complex formation,[6] the observed decrease in the optical density corresponds to the aquation process of the complex in a high acid medium.

For the measurement of kinetic isotope effect a temperature-jump apparatus (Messanlagen Studiengesellschaft, Göttingen) was used.

## Results

*Static Measurements.* Although the stability constants of complexes between iron(III) and various kinds of phenol were obtained by Milburn,[4] no consideration was given on the possibility of protolysis of a coordinated water in the complexes. We therefore tried to estimate the degree of the protolysis of the complex, spectrophotometrically, following scheme I.



$$\begin{array}{ccccc} & (1) & & (3) & \\ \mathrm{Fe^{3+} + HA} & & \overset{K_1}{\rightleftharpoons} & & \mathrm{FeA^{2+} + H^+} \\ K_h \Big\Updownarrow & & & & K_G \Big\Updownarrow \\ \mathrm{H^+ + Fe(OH)^{2+} + HA} & & \overset{K_2}{\rightleftharpoons} & & \mathrm{Fe(OH)A^+ + 2H^+} \\ & (2) & & (4) & \end{array}$$

Scheme I.

Under the conditions of $[\mathrm{Fe(III)}]_t \ll [\mathrm{HA}]_t$ ($[\;]_t$ denotes the total concentration), the following relationship is derived from $A$, the optical density due to the complex, $a$, the total concentration of the phenol, and $b$, the total concentration of Fe(III).

$$\frac{1}{A} = \frac{1}{\varepsilon b}\left(1 + \frac{[\mathrm{H^+}]+K_h}{aK}\right) \tag{1}$$

where $\varepsilon$ and $K$ are defined as

$$\varepsilon = (\varepsilon_1 + \varepsilon_2 K_G/[\mathrm{H^+}])/(1+K_G/[\mathrm{H^+}])$$

and

$$K = K_1(1+K_G/[\mathrm{H^+}])\,.$$

$\varepsilon_1$ and $\varepsilon_2$ denote the extinction coefficients of $\mathrm{FeA^{2+}}$ and $\mathrm{Fe(OH)A^+}$, respectively, and $K_G = K_2K_h/K_1$.

Figure 1 shows the plots of $A^{-1}$ *vs.* $a^{-1}$ for *p*-nitrophenol; the phenol forms a stable complex with Fe(III). The ratio $([\mathrm{H^+}]+K_h)/(\mathrm{slope})$ was found to be almost constant; they are $5.2\times10^{-2}$ ($[\mathrm{H^+}]=1.7\times10^{-2}$ M), $5.8\times10^{-2}$ ($8.8\times10^{-3}$ M), $6.1\times10^{-2}$ ($5.6\times10^{-3}$ M) and $5.7\times10^{-2}$ ($2.4\times10^{-3}$ M). Since the ratio is equal to $\varepsilon_1 bK_1(1+\varepsilon_2/\varepsilon_1\cdot K_G/[\mathrm{H^+}])$, this result indicates that the value of $\varepsilon_2/\varepsilon_1\cdot K_G/[\mathrm{H^+}]$ is so small as to be within experimental error. The upper limit of $K_G$ is estimated to be $10^{-4}$ M, assuming that $\varepsilon_2/\varepsilon_1$ is in the order of unity. The contribution of $\mathrm{Fe(OH)A^+}$ to the optical density can also be neglected under the experimental conditions. In discussing the kinetic data, we used the stability constants obtained by Milburn.[4]

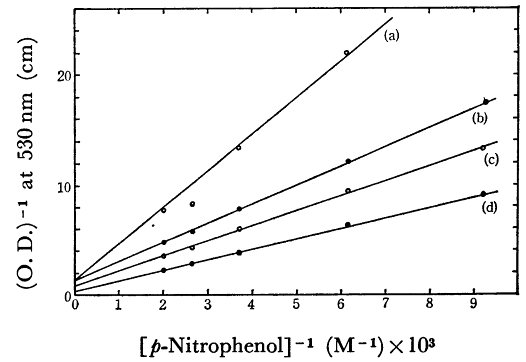


Fig. 1. Plots of equation (1) for *p*-nitrophenol. $[\mathrm{Fe^{3+}}]=1.03\times10^{-3}$ M, $[\mathrm{H^+}]=$(a) 1.70)$\times10^{-2}$ M, (b) $8.77\times10^{-3}$ M, (c) $5.55\times10^{-3}$ M, (d) $2.36\times10^{-3}$ M, at 25.0°C.

*Kinetics.* The decrease in the optical density on the pH-jump measurements corresponds to the aquation of $\mathrm{Fe(OH_2)_5A^{2+}}$ as elucidated above. Following a derivation similar to that of Cavasino and Di Dio,[2] the first-order rate constant is expressed in terms of the rate constants of individual paths in the above scheme as

$$k_{\mathrm{obs}} = \frac{k_{13}[\mathrm{H^+}]}{K_cK_H} + \frac{k_{24}K_h}{K_cK_H}, \tag{2}$$

where $k_{13}$ and $k_{24}$ are the forward rate constants for the reaction between $\mathrm{Fe^{3+}}$ and HA, and between $\mathrm{Fe(OH)^{2+}}$ and HA, respectively. The proton concentration at which the first term becomes predominant is expected to be above 0.3 M, since $K_h=3\times10^{-3}$ M and $k_{13}/k_{24}$ is in the order of $10^{-2}$ for the reaction of Fe(III) with analogous ligands.[1] The proton concentration is higher than that chosen by Cavasino and Di Dio by one order of magnitude. For this very reason we performed the pH-jump experiment in such a high acidity region as 0.1—1 M.

Figure 2 shows the values of the first-order rate constant $k_{\mathrm{obs}}$ obtained for *p*-nitrophenol in the proton concentration range 0.01—0.9 M. The plots were found to be independent of proton concentration at

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[4] R. M. Milburn, *J. Am. Chem. Soc.*, **77**. 2064 (1955).

[5] P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, **64**, 188 (1960).

[6] P. Hemmes, L. D. Rich, D. L. Cole, and E. M. Eyring, *ibid.*, **75**, 929 (1971).

TABLE 1. THE RATE CONSTANTS OF THE COMPLEX FORMATION AND AQUATION AT 25°C AND THE ACTIVATION PARAMETER FOR SUBSTITUTED PHENOLS. IONIC STRENGTH IS 0.1 M

| HA | $10^{10}\times K_H$[a] (M) | $10^{-2}\times k_{obs}$ (sec$^{-1}$) | $10^{-3}\times k_{24}$ (M$^{-1}$ sec$^{-1}$) | $E_a$ (kcal) | $\Delta S^{\ne}$ (e. u.) |
|---|---|---|---|---|---|
| *m*-$CH_3$ | 1.32 | 2.6 | 0.9 | 10.3 | −16.3 |
| *o*-$CH_3$ | 0.63 | 1.7 | | 13.0 | −8.1 |
| H | 1.26 | 3.4 | 1.1 | 13.4 | −5.4 |
| *p*-Cl | 7.94 | 2.2 | 1.2 | 13.1 | −2.5 |
| *o*-Cl | 46.8 | 1.2 | 1.0 | 14.0 | −4.0 |
| *p*-Br | 9.86 | 2.0 | 0.7 | 11.7 | −10.8 |
| *o*-Br | 60.2 | 0.9 | 1.9 | 11.9 | −13.1 |
| *p*-$NO_2$ | 955 | 1.2 | 0.8 | 15.1 | −0.4 |
| *m*-$NO_2$ | 91.2 | 1.4 | 0.7 | 15.2 | 0.3 |

a) From Ref. 4.

TABLE 2. ISOTOPE EFFECTS OF THE EQUILIBRIUM CONSTANTS AND AQUATION RATES AT 25.0°C

| Equilibrium | $K_H$ | $K_D$ | $K_H/K_D$ |
|---|---|---|---|
| $Fe^{3+} \rightleftharpoons Fe(OH)^{2+} + H^+$ | $3.45\times10^{-3}$ M | $2.40\times10^{-3}$ M | 1.44 |
| $AH \rightleftharpoons A^- + H^+$ | $9.67\times10^{-8}$ M | $2.22\times10^{-8}$ M | 4.36 |
| $Fe^{3+} + A^- \rightleftharpoons Fe(OH)^{2+} + AH$ | $3.57\times10^4$ | $10.8\times10^4$ | 0.331 |
| Reaction | $k_H$ sec$^{-1}$ | $k_D$ sec$^{-1}$ | $k_D/k_H$ |
| $FeA^{2+} \rightleftharpoons Fe(OH)^{2+} + AH$ | 173 | 73 | 2.37 |

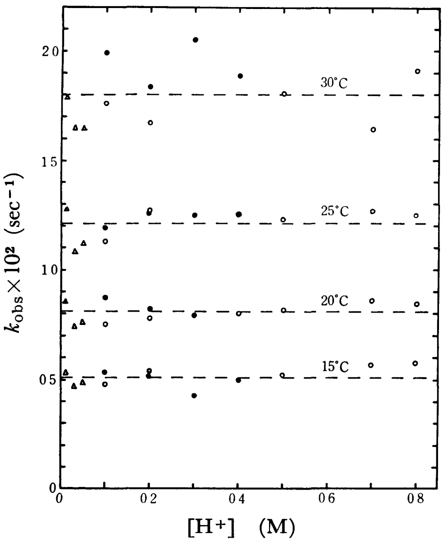

Fig. 2. Dependence of the first-order rate constant on the proton concentration for *p*-nitrophenol.
Ionic strength is (△) 0.10 M, (●) 0.65 M, (○) 1.00 M.

each temperature. The upper limit of $k_{13}$ is estimated to be 1 M$^{-1}$ sec$^{-1}$. The value is smaller than the rate constants obtained in the analogous reactions of $Fe(OH_2)_6^{3+}$ (10—10$^2$ M$^{-1}$ sec$^{-1}$) by one or two order of magnitude. Figure 2 also shows that the rate of aquation is independent of the ionic strength.

Similar results were obtained for other phenols. In Table 1 are summarized the rate constants of the complex formation and aquation at an ionic strength 0.1 (M) and at 25.0°C together with the activation parameters from the data between 15 and 30°C.

Isotope effect on the rate constants was measured by the temperature-jump method. The rate, pH and optical densities were all measured at 95, 53 and 0% $D_2O$. The values were extrapolated to 100% $D_2O$ by parabola. The results are given in Table 2 together with the isotope effects of the equilibrium constants of the protolysis of $Fe(OH_2)_6^{3+}$ and of the acid dissociation of *p*-nitrophenol.

## Discussion

The results demonstrate that the rate constant is independent of the acid concentration. According to Eq. (2), this means that even in the acid concentrations 0.1—1.0 M, no reaction path is involved between $Fe^{3+}$ and a phenol molecule in contrast to other ligands.[1] We attribute this anomalous fact to the proton transfer from an entering phenol molecule to $OH^-$ in $Fe(OH)^{2+}$ in the course of the complex formation between $Fe(OH)^{2+}$ and AH, *viz.*,

$$Fe(OH_2)_4(OH)AH^{2+} \underset{K_I}{\rightleftharpoons} Fe(OH_2)_5A^{2+}, \qquad (3)$$

where $K_I$ is the equilibrium constant of the reaction. In the case of the reaction between $Fe(OH_2)_6^{3+}$ and a phenol molecule, the complex is not formed *via* a transient complex $Fe(OH_2)_5AH^{3+}$ as in (3), because $Fe(OH_2)_5AH^{3+}$ has no proton acceptor like $OH^-$ in its ligands. Even 2,4-dinitrophenol, with an acid dissociation constant higher than that of acetic acid, follows this mechanism. The neutral species of acetic acid, $CH_3COOH$, reacts with $Fe(OH_2)_6^{3+}$ with the rate constant of 4.8 M$^{-1}$ sec$^{-1}$.[7] Thus, the absence of the reaction path between $Fe(OH_2)_6^{3+}$ and a phenol molecule cannot be attributed only to the strong bonding of a proton to a phenolate ion. At the present stage it is not clear what factor in phenols brings about such an anomaly.

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[7] F. Accascina, F. P. Cavasino, and E. Di Dio, *Trans. Faraday Soc.* **65**, 489 (1969).

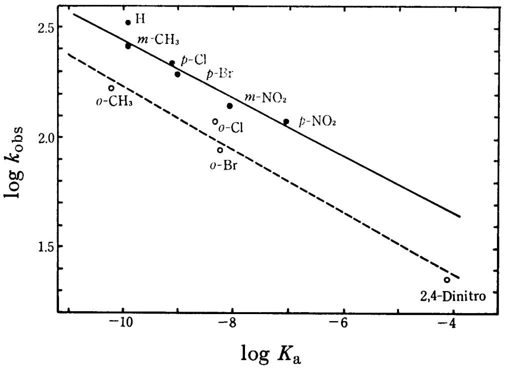

Fig. 3. Dependence of the first-order rate constants on the acid dissociation constants for substituted phenols.

In Fig. 3 is shown the dependence of the aquation rate on $K_a$ of each phenol. Meta- and para-substituted phenols are on a straight line with a slope of 0.11. Ortho-substituted phenols are roughly on a line with a slope of the same magnitude but about 0.2 below the above groups. The linear dependence means that the stronger the bonding of a proton to a pnenolate ion, the lower the aquation rate. It is interpreted that $K_1$ increases with decrease in $K_a$. The small slope, however, indicates that the change in $K_a$ has a relatively small influence on $K_1$. This suggests that the proton of AH in $Fe(OH_2)_4(OH)AH^{2+}$ is in a different state from that in a free phenol molecule.

The isotope effects of kinetics and equilibrium lead us to a similar conclusion concerning the state of the proton in AH of $Fe(OH_2)_4(OH)AH^{2+}$. As shown in Table 2, the equilibrium constant of the following intermolecular proton transfer in $D_2O$, $K_D$ is greater than that in $H_2O$, $K_H$,

$$Fe(OH_2)_5(OH)^{2+} + AH \xrightleftharpoons[K_H]{} Fe(OH_2)_6{}^{3+} + A^- \qquad (4)$$

Since a proton transfers from AH to OH coordinated to $Fe^{3+}$ in both equilibria (3) and (4), we can expect the same isotope effect in equilibrium (3). Supposing that the isotope effect in the aquation reaction lies mainly in (3), we expect that the aquation rate is higher in $D_2O$ than in $H_2O$. However, the observed aquation rate in $H_2O$ is 2.37 times greater than in $D_2O$. The isotope effect was interpreted in terms of zero-point energy of the vibration of a proton.[8] Comparing the zero-point energy of the vibration of a proton of AH on the left-hand with that of $OH_2$ on the right-hand side of Eqs. (3) and (4), the observed isotope effects are expressed as

$$\frac{1}{2}h\nu_{OH} - \frac{1}{2}h\nu_{OD} > \frac{1}{2}h\nu_{AH} - \frac{1}{2}h\nu_{AD} \text{ in (3)}$$

$$\text{and} \quad \frac{1}{2}h\nu'_{OH} - \frac{1}{2}h\nu'_{OD} < \frac{1}{2}h\nu'_{AH} - \frac{1}{2}h\nu'_{AD} \text{ in (4)}$$

where $\nu_{OH}$ and $\nu_{AH}$ are the frequencies of vibration of proton of $OH_2$ in $Fe(OH_2)_5A^{2+}$ and of AH in $Fe(OH_2)_4(OH)AH$, respectively, and $\nu'_{OH}$ and $\nu'_{AH}$ in $Fe(OH_2)_6{}^{3+}$ and in a free HA, respectively. If the proton in $H_2O$ is not much affected in complexation,[9] or $\nu_{OH} = \nu'_{OH}$, we get

$$\frac{1}{2}h\nu_{AH} - \frac{1}{2}h\nu_{AD} < \frac{1}{2}h\nu'_{AH} - \frac{1}{2}h\nu'_{AD} \text{ or}$$

$$\nu_{AH} < \nu'_{AH}\,.$$

It then follows that a proton of AH in $Fe(OH_2)_4(OH)$-AH is more loosely bound to a phenolate than a proton of a free AH, and that this causes the depedence of an aquation rate on $K_a$ to be small.

Another interesting feature is the composition of iron(III)-phenol complex. It is known that iron(III) forms only a 1 : 1 complex with phenols even in 500 time excess of phenol.[10] The above scheme predicts that 1 : 2 complexes would be formed *via* the reaction between $Fe(OH_2)_4(OH)A^+$ and HA. However, the hydrolysis is greatly depressed by the complexation. Thus, from the kinetic point of view, 1 : 2 complexes between iron(III) and a phenol molecule is very unlikely because of the above mechanism and the low hydrolysis of 1 : 1 complexes.

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[8] K. J. Laidler, "Chemical Kinetics," 2nd ed., McGraw-Hill, New York (1965), p. 90.

[9] For example, the frequency of NH stretching vibration (3240 cm$^{-1}$) in $[Co(NH_3)_6]^{3+}$ differs only by 0.4% from that of NH stretching vibration (3252 cm$^{-1}$) in $[CoCl_2(NH_3)_4]^+$; see I. Nakagawa, T. Shimanouchi, and J. Hiraishi, Proceedings of the 8th International Conference on Coordination Chemistry, Vienna, Sept. 1964.

[10] G. Ackermann and D. Hesse, *Z. Anorg. Allgem. Chem.* **367**, 243 (1969).