Kinetics and Equilibria of the Interaction of Titanium(III) with Oxalic Acid

By **Phalguni Chaudhuri** and **Hartmut Diebler,*** Max Planck Institute for Biophysical Chemistry, Göttingen-Nikolausberg, Germany

Rate and equilibrium data have been determined for the complex-formation reactions of Ti^{III} with oxalate in aqueous solution. In order to suppress the hydrolysis of Ti^{III}, fairly high concentrations of hydrogen ion have been used. At 10.0 °C and ionic strength $I = 1.0$ mol dm^{-3} (NaCl) the following stability constants have been obtained by spectrophotometry: $Ti^{3+} + [C_2O_4]^{2-} \rightleftharpoons [Ti(C_2O_4)]^+$, $K_1 = 2.8 \times 10^6$ dm^3 mol^{-1}; $[Ti(C_2O_4)]^+ + [C_2O_4]^{2-} \rightleftharpoons [Ti(C_2O_4)_2]^-$, $K_2 = 1.2 \times 10^6$ dm^3 mol^{-1}. The kinetics of the complex-formation reactions have been studied by the temperature-jump relaxation technique. At $[H^+] = 0.2$—0.8 mol dm^{-3} complex formation occurs predominantly *via* reaction with the monoprotonated ligand. For the first step, $Ti^{3+} + [HC_2O_4]^- \xrightleftharpoons{k_{1b}} [Ti(C_2O_4)]^+ + H^+$, a rate constant of $k_{1b} = 3.9 \times 10^5$ dm^3 mol^{-1} s^{-1} is evaluated and for $[Ti(C_2O_4)]^+ + [HC_2O_4]^- \xrightleftharpoons{k_{2b}} [Ti(C_2O_4)_2]^- + H^+$, $k_{2b} = 8.0 \times 10^6$ dm^3 mol^{-1} s^{-1} (10.0 °C, $I = 1.0$ mol dm^{-3}). The kinetic data available indicate that substitution at the $[Ti(OH_2)_6]^{3+}$ ion proceeds by an associative mechanism.

KINETICS and mechanism of metal complex-formation reactions have been studied very extensively during recent years, in particular of those involving bivalent metal ions.[1] Information about the complex-formation mechanism of trivalent metal ions is often more difficult to obtain, mainly because of the strong hydrolysis which most of these metal ions undergo. The problems arising in such a case may be of the following kind: (*i*) low-pH conditions limit the range of suitable ligands; (*ii*) polynuclear hydrolysis products lead to additional reaction effects; (*iii*) indistinguishable reaction paths can be formulated in cases involving protonable ligands, *e.g.* $M^{3+} + L \longrightarrow [ML]^{3+}$ and $[M(OH)]^{2+} + HL^+ \longrightarrow [ML]^{3+}$ (proton ambiguity). Plausibility arguments sometimes allow conclusions as to which of two such paths is the more likely.[2,3]

One metal ion about which very little is known with respect to the complex-formation kinetics is Ti^{3+}(aq). Except for the rate of water exchange,[4] only the kinetics of its complex formation with thiocyanate have been reported.[5] In the present paper studies are described which refer to the equilibria and the kinetics of complex formation of Ti^{III} with oxalate.

EXPERIMENTAL

Materials.—Titanium(III) is gradually oxidized by perchlorate;[6] therefore all the studies were carried out in chloride solution. Acidic solutions of titanium(III) chloride were either obtained commercially (Riedel–de Haen, free from iron) or prepared by dissolving titanium hydride (Fluka, $\geqslant 99.5\%$) in HCl.[7] In order to ensure absence of Ti^{IV}, these solutions were reduced electrolytically at a mercury-pool cathode for 2—3 h before use (current *ca.* 200 mA, nitrogen atmosphere).[5] The exact concentration of Ti^{III} was determined by titration with dichromate, $[Cr_2O_7]^{2-}$, using diphenylbenzidine sulphonate as indicator.[8] The concentration of free HCl was evaluated from a titration with standard alkali after an aliquot portion of the solution had been passed down a column of Amberlite IR-120(H) cation-exchange resin (in the H^+ form). The spectrum of the titanium(III) solution showed an absorption maximum at 503 nm with ε 3.90 dm^3 mol^{-1} cm^{-1} in 0.2—1.0 mol dm^{-3} HCl solution, in good agreement with literature data.[9-11] Under these conditions $[Ti(OH_2)_6]^{3+}$ is the predominant metal species (see Discussion section). At *ca.* 300 nm the absorption was negligible, indicating the absence of Ti^{IV}.[10]

Sodium chloride, sodium oxalate, and other substances used were of the best grade available (E. Merck, *pro analysi*).

Methods.—Titanium(III) solutions were always kept and handled under an atmosphere of nitrogen. Other solutions used in preparing the reactant solutions were deoxygenated by purging with purified nitrogen for at least 15 min. All the measurements were made at 10.0 °C and at an ionic strength $I = 1.0$ mol dm^{-3}, adjusted with NaCl. The low temperature was chosen since the system Ti^{III}–$[NCS]^-$ had been studied under similar conditions for technical reasons.[5]

The pK values of oxalic acid under the conditions of this study were determined from pH measurements of 0.02 mol dm^{-3} solutions of sodium oxalate to which 0.005—0.1 mol dm^{-3} HCl had been added. The measurements were made with a Metrohm type E 388 instrument and a combined electrode type EA 125. A calibration curve which had been constructed from pH measurements of solutions of known amounts of HCl in 1.0 mol dm^{-3} NaCl was used for the conversion of pH values into H^+ concentrations.

Data on the extent of complex formation between Ti^{III} and oxalate were evaluated from spectrophotometric measurements of solutions of varying metal : ligand ratios, using a recording Cary 118 spectrophotometer with thermostatted cells. The kinetics of complexation of Ti^{III} with oxalate were studied by the temperature-jump relaxation technique.[12] A high-voltage condenser of 0.05 μF was charged to 30 kV and then discharged through the solution which had been thermostatted at 7.0 °C, raising its temperature by 3.0° within 1 μs. The chemical-relaxation process was followed spectrophotometrically. The photographed oscilloscope curves were evaluated using an electronic device which produced exponential curves of variable time constant and amplitude. The relaxation time

---

[1] See, for instance, M. Eigen and R. G. Wilkins, *Adv. Chem. Ser.*, 1965, **49**, 55; K. Kustin and J. Swinehart, *Progr. Inorg. Chem.*, 1970, **13**, 107.

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

[3] R. C. Patel and H. Diebler, *Ber. Bunsengesellschaft Phys. Chem.*, 1972, **76**, 1035.

[4] A. M. Chmelnick and D. Fiat, *J. Chem. Phys.*, 1969, **51**, 4238.

[5] H. Diebler, *Z. phys. Chem.* (*Frankfurt*), 1969, **68**, 64.

[6] F. R. Duke and P. R. Quinney, *J. Amer. Chem. Soc.*, 1954, **76**, 3800.

[7] W. E. Shaefer and W. W. Becher, *Analyt. Chem.*, 1953, **25**, 1226.

[8] R. H. Pierson and E. St. Clair Gantz, *Analyt. Chem.*, 1954, **26**, 1809.

[9] H. Hartmann and H. L. Schläfer, *Z. phys. Chem.*, 1951, **197**, 116.

[10] J. P. Birk and T. P. Logan, *Inorg. Chem.*, 1973, **12**, 580.

[11] J. D. Ellis and A. G. Sykes, *J.C.S. Dalton*, 1973, 2553.

[12] M. Eigen and L. De Maeyer, in 'Technique of Organic Chemistry,' 2nd edn., ed. A. Weissberger, Interscience, 1963, vol. VIII/2, p. 895.

constants given in this paper are the mean values of five or six individual measurements.

RESULTS

Protolytic Equilibria.—Values of the dissociation constants of oxalic acid, $K_{H1} = [H^+][C_2O_4^{2-}]/[HC_2O_4^-]$ and $K_{H2} = [H^+][HC_2O_4^-]/[H_2C_2O_4]$ were calculated from equations (1) and (2) as described by Moorhead and Sutin.[13]

$$K_{H1} = \frac{[H^+]([C_2O_4]_T - [H]_T + [H^+])}{[H]_T - [H^+]} \qquad (1)$$

$$K_{H2} = \frac{[H^+]^2(2[C_2O_4]_T - [H]_T + [H^+])}{K_{H1}([H]_T - [H^+]) + [H^+]([H]_T - [H^+] - [C_2O_4]_T)} \qquad (2)$$

In these equations $[C_2O_4]_T$ and $[H]_T$ denote the total concentrations of oxalate and of added HCl, whereas $[H^+]$ is the concentration of free hydrogen ions. Equation (1) is a simplified expression, valid only for conditions in which $[H_2C_2O_4]$ is negligible; therefore only data obtained with low values of $[H]_T$ were used in evaluating K_{H1}. At 10.0 °C and $I = 1.0$ mol dm^{-3}, the following values have been obtained: $K_{H1} = (3.0 \pm 0.05) \times 10^{-4}$ and $K_{H2} = (6.5 \pm 0.3) \times 10^{-2}$ mol dm^{-3}. The value of K_{H1} is slightly larger and that of K_{H2} is somewhat smaller than the ones reported [13] at 25 °C. Qualitatively, these variations with temperature agree with those found at $I = 0.5$ mol dm^{-3}.[14]

Complexation Equilibria.—Complex formation between Ti^{III} and oxalate leads to a change in colour from red to yellow. The spectrum of a species which is supposed to be a bis(oxalato)titanium(III) complex has been published.[15] It shows a strong absorption at *ca.* 400 nm, an area in which the absorption of uncomplexed Ti^{III} is very weak.

In the present study spectrophotometric measurements were made at high metal : ligand ratios. Under these conditions, predominantly 1 : 1 complexes should be formed. The hydrogen-ion concentration was varied from 0.3 to 0.8 mol dm^{-3}, in which range most of the free ligand is in the diprotonated form. Even then, however, the extent of complex formation is large and low concentrations of total ligand had to be used to make possible the evaluation of the binding constant. The measurements therefore had to be made with a spectrophotometer cell of 10-cm path length and in the absorbance range 0—0.5. Total ligand $[C_2O_4]_T$ was always 5×10^{-4} mol dm^{-3} and total metal $[Ti]_T$ was varied between 0.005 and 0.025 mol dm^{-3} in each series. The observed spectra were corrected for the relatively small absorption due to uncomplexed Ti^{III}. The corrected spectra showed an absorption maximum at 380 nm.

The spectrophotometric data can be accounted for by assuming that only 1 : 1 complexes are being formed under the given conditions. With $K_1 = [Ti(C_2O_4)^+]/[Ti^{3+}][C_2O_4^{2-}]$ and $K_1' = [Ti(HC_2O_4)^{2+}]/[Ti^{3+}][HC_2O_4^-]$ and with the absorbance per cm path length given by $A = \varepsilon_1[Ti(C_2O_4)^+] + \varepsilon_1'[Ti(HC_2O_4)^{2+}]$, the following expressions may be derived,[13]

$$\frac{A}{[Ti^{3+}]} = \frac{[C_2O_4]_T\{\varepsilon_1 K_1 + (\varepsilon_1' K_1'[H^+]/K_{H1})\}}{\alpha} - \frac{A\{K_1 + (K_1'[H^+]/K_{H1})\}}{\alpha} \qquad (3)$$

$$\alpha = 1 + \frac{[H^+]}{K_{H1}} + \frac{[H^+]^2}{K_{H1}K_{H2}} \qquad (4)$$

and where ε_1 and ε_1' are the absorption coefficients of $[Ti(C_2O_4)]^+$ and $[Ti(HC_2O_4)]^{2+}$, respectively. Thus at constant $[C_2O_4]_T$ and $[H^+]$, plots of $A/[Ti^{3+}]$ against A should yield straight lines. Experimental data for several $[H^+]$ were obtained at 360 nm (at this wavelength the correction due to uncomplexed Ti^{III} is smaller than at 380 nm) and are shown in Figure 1. Since $[Ti]_T \gg [C_2O_4]_T$, $[Ti^{3+}]$ may be approximated by $[Ti]_T$. More accurate values of $[Ti^{3+}]$ were calculated using a preliminary binding constant which was evaluated from plots of $A/[Ti]_T$ against A.

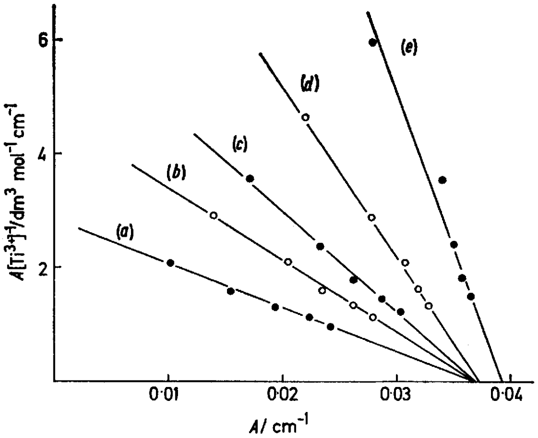

FIGURE 1 Spectrophotometric data for complex formation between Ti^{III} and oxalate at large metal : ligand ratios: plots of $A/[Ti^{3+}]$ against A [equation (3)] at 10 °C, $I = 1.0$ mol dm^{-3}, and 360 nm. $[H^+] = 0.8$ (*a*), 0.6 (*b*), 0.5 (*c*), 0.4 (*d*), and 0.3 mol dm^{-3} (*e*)

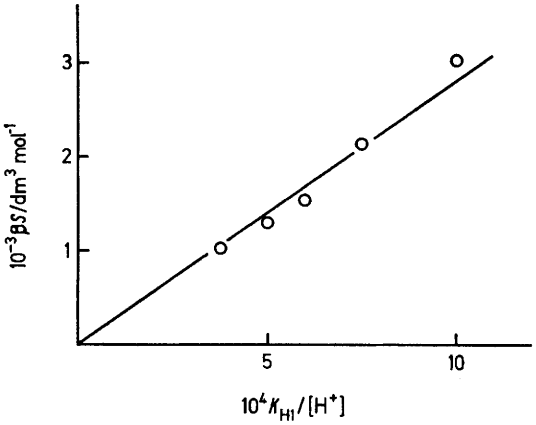

FIGURE 2 Evaluation of the binding constant K_1 from a plot of βS against $K_{H1}/[H^+]$ [equation (5)]

If the negative gradients of the straight lines of Figure 1 are denoted by S, then we obtain (5) where $\beta = \alpha K_{H1}/[H^+]$.

$$\beta S = K_1' + (K_1 K_{H1}/[H^+]) \qquad (5)$$

A plot of βS against $K_{H1}/[H^+]$ is shown in Figure 2. Within experimental error, the intercept is zero, indicating that the formation of protonated complex, $[Ti(HC_2O_4)]^{2+}$, is unimportant under our conditions ($K_1' < 200$ dm^3 mol^{-1}), as was also found for the corresponding iron(III) complex.[13] The gradient of the line of Figure 2 gives (10 °C, $I = 1.0$ mol dm^{-3}): $K_1 = (2.8 \pm 0.3) \times 10^6$ dm^3 mol^{-1}.

---

[13] E. G. Moorhead and N. Sutin, *Inorg. Chem.*, 1966, **5**, 1866.

[14] R. F. Bauer and W. M. Smith, *Canad. J. Chem.*, 1965, **43**, 2755.

[15] R. L. Pecsok, *J. Amer. Chem. Soc.*, 1951, **73**, 1304.

The fact that the straight lines of Figure 1 meet approximately at the same point on the abscissa also indicates that essentially one only complex species is being formed. From this intercept an absorption coefficient of $\varepsilon_1 = 76 \pm 2$ dm^3 mol^{-1} cm^{-1} at 360 nm is evaluated for the species $[\mathrm{Ti(C_2O_4)}]^+$. The absorption coefficient at the maximum is then $\varepsilon_{1(\mathrm{max.})} = 86 \pm 2$ dm^3 mol^{-1} cm^{-1} (380 nm), as follows from the spectra. A Job's plot with low reactant concentrations ($[\mathrm{Ti}]_\mathrm{T} + [\mathrm{C_2O_4}]_\mathrm{T} = 0.001$ mol dm^{-3}, $[\mathrm{H^+}] = 0.4$ mol dm^{-3}) also provided evidence that a mono-oxalato-complex is the principal species being formed under these conditions.

At higher concentrations of free ligand, however, the absorption maximum shifted to 400 nm and a Job's plot with $[\mathrm{Ti}]_\mathrm{T} + [\mathrm{C_2O_4}]_\mathrm{T} = 0.01$ mol dm^{-3} and $[\mathrm{H^+}] = 0.4$ mol dm^{-3} indicates formation of a bis(oxalato) complex of Ti$^{\mathrm{III}}$. Additional spectrophotometric studies were made with $[\mathrm{Ti}]_\mathrm{T} = 0.001$, $[\mathrm{C_2O_4}]_\mathrm{T} = 0.01$—$0.03$, and $[\mathrm{H^+}] = 0.4$—0.6 mol dm^{-3}, using a cell of path length 1 cm. Assuming that under these conditions only the unprotonated forms of the mono-oxalato- and of the bis(oxalato) complexes of Ti$^{\mathrm{III}}$ are important, then $A = \varepsilon_1[\mathrm{Ti(C_2O_4)^+}] + \varepsilon_2[\mathrm{Ti(C_2O_4)_2^-}]$ where ε_2 is the absorption coefficient of $[\mathrm{Ti(C_2O_4)_2}]^-$. With $K_2 = [\mathrm{Ti(C_2O_4)_2^-}]/[\mathrm{Ti(C_2O_4)^+}][\mathrm{C_2O_4^{2-}}]$ and $[\mathrm{Ti}]_\mathrm{T} = [\mathrm{Ti^{3+}}] + [\mathrm{Ti(C_2O_4)^+}] + [\mathrm{Ti(C_2O_4)_2^-}]$, expression (6) is obtained. Rearranging gives[16] (7) and (8). A plot of $[\mathrm{Ti}]_\mathrm{T}/A$ against

$$A = \frac{[\mathrm{Ti}]_\mathrm{T}(\varepsilon_1 K_1[\mathrm{C_2O_4^{2-}}] + \varepsilon_2 K_1 K_2[\mathrm{C_2O_4^{2-}}]^2)}{1 + K_1[\mathrm{C_2O_4^{2-}}] + K_1K_2[\mathrm{C_2O_4^{2-}}]^2} \qquad (6)$$

$$\frac{[\mathrm{Ti}]_\mathrm{T}}{A} = \frac{1}{\varepsilon_2} + \frac{N}{\varepsilon_2 K_1 K_2} \qquad (7)$$

$$N = \frac{1}{[\mathrm{C_2O_4^{2-}}]^2} + \frac{K_1}{[\mathrm{C_2O_4^{2-}}]} - \frac{[\mathrm{Ti}]_\mathrm{T}\varepsilon_1 K_1}{A[\mathrm{C_2O_4^{2-}}]} \qquad (8)$$

N using absorbances measured at 400 nm (ε_1 79 dm^3 mol^{-1} cm^{-1}) is shown in Figure 3. The intercept and gradient of the straight line in Figure 3 yield ε_2 490 ± 50 dm^3 mol^{-1} cm^{-1} at 400 nm and $K_2 = (1.2 \pm 0.1) \times 10^6$ dm^3 mol^{-1} (10 °C, $I = 1.0$ mol dm^{-3}). During this evaluation a preliminary value of K_2 was determined (1.1×10^6 dm^3 mol^{-1}) using the approximation (since $[\mathrm{C_2O_4}]_\mathrm{T} \gg [\mathrm{Ti}]_\mathrm{T}$) $[\mathrm{C_2O_4}]_\mathrm{T} \simeq [\mathrm{C_2O_4^{2-}}] + [\mathrm{HC_2O_4}] + [\mathrm{H_2C_2O_4}] = \alpha[\mathrm{C_2O_4^{2-}}]$. Better values of $[\mathrm{C_2O_4^{2-}}]$ were then calculated with this value of K_2 and those of K_{H1}, K_{H2}, and K_1, and these were introduced into equation (7). The independence of gradient and intercept of the line in Figure 3 of $[\mathrm{H^+}]$ indicate that the protonated form of the bis(oxalato) complex is indeed unimportant.

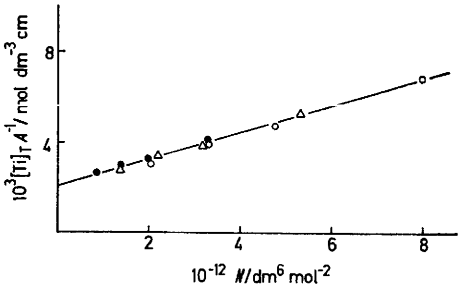

FIGURE 3 Evaluation of the binding constant K_2 from a plot of $[\mathrm{Ti}]_\mathrm{T}/A$ against N [equation (7)] at 10 °C, $I = 1.0$ mol dm^{-3} and 400 nm. $[\mathrm{H^+}] = 0.4$ (●), 0.5 (△), and 0.6 mol dm^{-3} (○)

Complex-formation Kinetics.—Kinetic studies were made at $[\mathrm{H^+}] = 0.2$—0.8 mol dm^{-3}. The reactant concentrations were $[\mathrm{Ti}]_\mathrm{T} = 0.001$—$0.037$ and $[\mathrm{C_2O_4}]_\mathrm{T} = 0.0011$—$0.043$ mol dm^{-3}, with $[\mathrm{Ti}]_\mathrm{T}/[\mathrm{C_2O_4}]_\mathrm{T}$ varying over the range 0.028—33.6. These concentration conditions were determined mainly by the complex stabilities, the optical absorption of the complex species, and by the sensitivity of the temperature-jump apparatus. Both the mono-oxalato- and the bis(oxalato) complex of Ti$^{\mathrm{III}}$ have to be taken into account under the given conditions; in particular, it was not possible to study solutions in which the extent of formation of the bis complex could be neglected.

Experimentally, two relaxation effects were observed in all the solutions (λ 400 nm), one with a time constant τ_1 which varied between 20 and 230 μs, the other one with $\tau_2 = 0.44$—3.2 ms. Both time constants were always well separated; $\tau_2/\tau_1 = 11$—45. Protolytic equilibrations are extremely rapid at the hydrogen-ion concentrations used in this study. Therefore the two observed reaction effects are attributed to the formation of the mono- and bis-oxalato-complexes of Ti$^{\mathrm{III}}$, while protonation steps may be assumed to be rapid pre-equilibria compared with the complex-formation reactions. The paths (9)—(11) are considered for the formation of the 1 : 1 complex, leading to the rate

$$\mathrm{Ti^{3+}} + [\mathrm{C_2O_4}]^{2-} \xrightleftharpoons[k_{-1a}]{k_{1a}} [\mathrm{Ti(C_2O_4)}]^+ \qquad (9)$$

$$\mathrm{Ti^{3+}} + [\mathrm{HC_2O_4}]^{-} \xrightleftharpoons[k_{-1b}]{k_{1b}} [\mathrm{Ti(C_2O_4)}]^+ + \mathrm{H^+} \qquad (10)$$

$$\mathrm{Ti^{3+}} + \mathrm{H_2C_2O_4} \xrightleftharpoons[k_{-1c}]{k_{1c}} [\mathrm{Ti(C_2O_4)}]^+ + 2\mathrm{H^+} \qquad (11)$$

equation (12) with (13) and (14) and where $[\mathrm{C_2O_4}]_\mathrm{F} = [\mathrm{C_2O_4^{2-}}] + [\mathrm{HC_2O_4^-}] + [\mathrm{H_2C_2O_4}]$. Similarly, the formation of the bis complex is assumed to occur by the reaction

$$\mathrm{d}[\mathrm{Ti^{3+}}]/\mathrm{d}t = -k_1[\mathrm{Ti^{3+}}][\mathrm{C_2O_4}]_\mathrm{F} + k_{-1}[\mathrm{Ti(C_2O_4)^+}] \qquad (12)$$

$$k_1 = k_{1a}\cdot\frac{1}{\alpha} + k_{1b}\cdot\frac{[\mathrm{H^+}]}{\alpha K_{\mathrm{H1}}} + k_{1c}\cdot\frac{[\mathrm{H^+}]^2}{\alpha K_{\mathrm{H1}}K_{\mathrm{H2}}} \qquad (13)$$

$$k_{-1} = k_{-1a} + k_{-1b}[\mathrm{H^+}] + k_{-1c}[\mathrm{H^+}]^2 \qquad (14)$$

of $[\mathrm{Ti(C_2O_4)}]^+$ with $[\mathrm{C_2O_4}]^{2-}$ (k_{2a}), with $[\mathrm{HC_2O_4}]^-$ (k_{2b}), and with $\mathrm{H_2C_2O_4}$ (k_{2c}). Thus we obtain equations (15)—(17).

$$\mathrm{d}[\mathrm{Ti(C_2O_4)_2^-}]/\mathrm{d}t = k_2[\mathrm{Ti(C_2O_4)^+}][\mathrm{C_2O_4}]_\mathrm{F} - k_{-2}[\mathrm{Ti(C_2O_4)_2}]^- \qquad (15)$$

$$k_2 = k_{2a}\cdot\frac{1}{\alpha} + k_{2b}\cdot\frac{[\mathrm{H^+}]}{\alpha K_{\mathrm{H1}}} + k_{2c}\cdot\frac{[\mathrm{H^+}]^2}{\alpha K_{\mathrm{H1}}K_{\mathrm{H2}}} \qquad (16)$$

$$k_{-2} = k_{-2a} + k_{-2b}[\mathrm{H^+}] + k_{-2c}[\mathrm{H^+}]^2 \qquad (17)$$

The rate equations (12) and (15) which describe our system may be expressed in terms of the reactants' equilibrium concentrations and of the deviations (δ[R]) from these. The hydrogen-ion concentration can be considered as constant to a good approximation under the given conditions. Introducing equilibrium relations and mass-conservation conditions one obtains for a relaxation process ($\delta[\mathrm{R}] \ll [\mathrm{R}]$) the differential equations (18) and (19) (see ref. 12). This

$$\begin{aligned}\mathrm{d}\delta[\mathrm{Ti^{3+}}]/\mathrm{d}t = &-\{k_1([\mathrm{Ti^{3+}}] + [\mathrm{C_2O_4}]_\mathrm{F}) + k_{-1}\}\delta[\mathrm{Ti^{3+}}] \\ &-(k_{-1} - k_1[\mathrm{Ti^{3+}}])\delta[\mathrm{Ti(C_2O_4)_2^-}] \qquad (18)\end{aligned}$$

$$\begin{aligned}\mathrm{d}\delta[\mathrm{Ti(C_2O_4)_2^-}]/\mathrm{d}t = &-k_2([\mathrm{C_2O_4}]_\mathrm{F} - [\mathrm{Ti(C_2O_4)}])\delta[\mathrm{Ti^{3+}}] \\ &-\{k_2([\mathrm{Ti(C_2O_4)^+}] + [\mathrm{C_2O_4}]_\mathrm{F}) + k_{-2}\}\delta[\mathrm{Ti(C_2O_4)_2^-}] \qquad (19)\end{aligned}$$

---

[16] H. McConnell and N. Davidson, *J. Amer. Chem. Soc.*, 1950, **72**, 3164.

system of equations leads to two relaxation-time constants which are of the form[12] (20), with (21)—(24), $k_1/k_{-1} = K_1/\alpha$, and $k_2/k_{-2} = K_2/\alpha$. From equation (20) is obtained (25) and (26). With the relations (21)—(24) we obtain (27)—(29).

$$\frac{1}{\tau_{1,2}} = \frac{1}{2}\left\{(a_{11} + a_{22}) \pm \left[(a_{11} + a_{22})^2 - 4(a_{11}a_{22} - a_{12}a_{21})\right]^{\frac{1}{2}}\right\} \qquad (20)$$

$$a_{11} = k_1\{[\mathrm{Ti}^{3+}] + [\mathrm{C_2O_4}]_\mathrm{F} + (\alpha/K_1)\} \qquad (21)$$

$$a_{12} = k_1\{(\alpha/K_1) - [\mathrm{Ti}^{3+}]\} \qquad (22)$$

$$a_{21} = k_2([\mathrm{C_2O_4}]_\mathrm{F} - [\mathrm{Ti(C_2O_4)^+}]) \qquad (23)$$

$$a_{22} = k_2\{[\mathrm{Ti(C_2O_4)^+}] + [\mathrm{C_2O_4}]_\mathrm{F} + (\alpha/K_2)\} \qquad (24)$$

$$\frac{1}{\tau_1} \cdot \frac{1}{\tau_2} = a_{11}a_{22} - a_{12}a_{21} \qquad (25)$$

$$\frac{1}{\tau_1} + \frac{1}{\tau_2} = a_{11} + a_{22} \qquad (26)$$

$$\frac{1}{\tau_1} \cdot \frac{1}{\tau_2} = k_1k_2B \qquad (27)$$

$$B = \{[\mathrm{Ti}^{3+}] + [\mathrm{C_2O_4}]_\mathrm{F} + (\alpha/K_1)\}\cdot\{[\mathrm{Ti(C_2O_4)^+}] + [\mathrm{C_2O_4}]_\mathrm{F} + (\alpha/K_2)\} - \{(\alpha/K_1) - [\mathrm{Ti}^{3+}]\}\{[\mathrm{C_2O_4}]_\mathrm{F} - [\mathrm{Ti(C_2O_4)^+}]\} \qquad (28)$$

$$\frac{(1/\tau_1) + (1/\tau_2)}{[\mathrm{Ti}^{3+}] + [\mathrm{C_2O_4}]_\mathrm{F} + (\alpha/K_1)} = k_1 + k_2 \cdot \frac{[\mathrm{Ti(C_2O_4)^+}] + [\mathrm{C_2O_4}]_\mathrm{F} + (\alpha/K_2)}{[\mathrm{Ti}^{3+}] + [\mathrm{C_2O_4}]_\mathrm{F} + (\alpha/K_1)} \qquad (29)$$

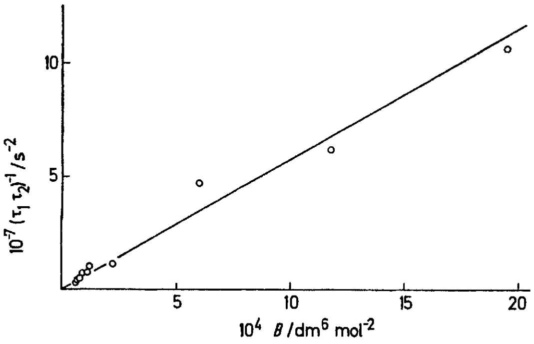

FIGURE 4 Plot of the product of the reciprocal relaxation times against B according to equation (27) at $[\mathrm{H^+}] = 0.4$ mol dm^{-3}

Data which refer to $[\mathrm{H^+}] = 0.4$ mol dm^{-3} have been plotted according to equations (27) and (29) in Figures 4 and 5, respectively. The straight line in Figure 5 has been placed such that a reasonably good fit is obtained and that the product of intercept and gradient agrees with the value of $k_1k_2 = (5.8 \pm 0.6) \times 10^{10}$ dm^6 mol^{-2} s^{-2} which results from Figure 4. From Figure 5 we obtained $k_1 = (5.8 \pm 0.6) \times 10^4$ and $k_2 = (1.0 \pm 0.1) \times 10^6$ dm^3 mol^{-1} s^{-1} (10 °C $I = 1.0$ mol dm^{-3}). It follows with these rate constants that $a_{22} \gg a_{11}$ under our conditions ($a_{22}/a_{11} =$ 12—27). Since $1/\tau_1 \gg 1/\tau_2$, equation (26) simplifies to (30).

$$1/\tau_1 \simeq a_{22} = k_2\{[\mathrm{Ti(C_2O_4)^+}] + [\mathrm{C_2O_4}]_\mathrm{F}\} + k_{-2} \qquad (30)$$

Furthermore, in a first approximation $a_{12}a_{21} \ll a_{11}a_{22}$ and therefore [from (25) and (30)] we obtain (31). Plots according to equations (30) and (31) are shown in Figure 6. The apparent forward rate constants derived from these plots

$$1/\tau_2 \simeq a_{11} = k_1([\mathrm{Ti}^{3+}] + [\mathrm{C_2O_4}]_\mathrm{F}) + k_{-1} \qquad (31)$$

($k_1 = 5.7 \times 10^4$ and $k_2 = 9.8 \times 10^5$ dm^3 mol^{-1} s^{-1}) are very close to those obtained from Figure 4 and 5. Also, the ratios of gradient : intercept from Figure 6 yield values of the stability constants ($K_1 = \alpha k_1/k_{-1} = 2.74 \times 10^6$ and $K_2 = \alpha k_2/k_{-2} = 1.17 \times 10^6$ dm^3 mol^{-1}) which agree very well with those which have been determined spectrophotometrically.

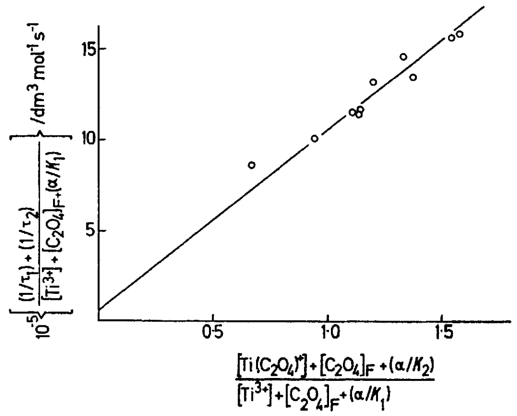

FIGURE 5 Plot according to equation (29) for the evaluation of k_1 and k_2 at $[\mathrm{H^+}] = 0.4$ mol dm^{-3}, 10 °C, and $I = 1.0$ mol dm^{-3}

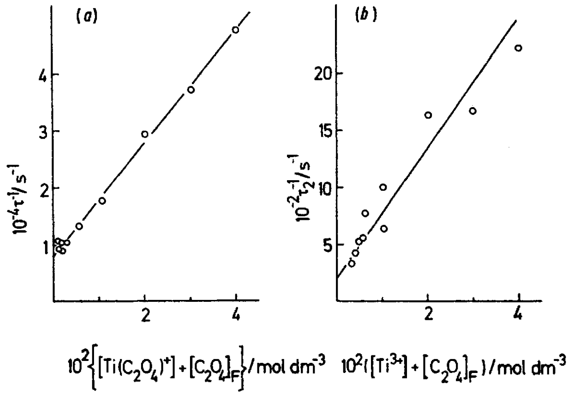

FIGURE 6 Concentration dependence of the reciprocal relaxation times: (*a*) plot according to equation (30); (*b*) plot according to equation (31) at $[\mathrm{H^+}] = 0.4$ mol dm^{-3}

Part of the scatter of the experimental points in Figure 6(*b*) (and in Figure 4) is due to a relatively large error in τ_2; the amplitude of this relaxation effect was rather small in most of the experiments. The fast relaxation effect (time constant τ_1) may to a good approximation be considered as uncoupled from the slower relaxation process and its amplitude was large enough (the relative change in transmitted light intensity $\delta I/I$ varied from 0.0022 to 0.023 at $[\mathrm{H^+}] = 0.4$ mol dm^{-3}, 1-cm path length) to be evaluated with reasonable accuracy. Assuming that the fast effect is due to either the first or the second complex-formation step, the expressions (32)—(35) may be derived,[12,17] where

---

[17] D. Thusius, *J. Amer. Chem. Soc.*, 1972, **94**, 356.

ε_{Ti} = absorption coefficient of Ti^{3+} and $K_1^* = K_1/\alpha$ and $K_2^* = K_2/\alpha$ are the equilibrium constants expressed in

$$\delta I/I = -2.3(\varepsilon_1 - \varepsilon_{Ti})\Gamma_1\delta\ln K_1^* \tag{32}$$

$$\delta I/I = -2.3(\varepsilon_2 - \varepsilon_1)\Gamma_2\delta\ln K_2^* \tag{33}$$

$$\Gamma_1 = \left\{\frac{1}{[Ti(C_2O_4)^+]} + \frac{1}{[Ti^{3+}]} + \frac{1}{[C_2O_4]_F}\right\}^{-1} \tag{34}$$

$$\Gamma_2 = \left\{\frac{1}{[Ti(C_2O_4)_2^-]} + \frac{1}{[Ti(C_2O_4)^+]} + \frac{1}{[C_2O_4]_F}\right\}^{-1} \tag{35}$$

terms of $[C_2O_4]_F$, *e.g.* $K_1^* = [Ti(C_2O_4)^+]/[Ti^{3+}][C_2O_4]_F$. A comparison of the amplitude of the fast effect as well as of its observed concentration dependence with these expressions also indicates unambiguously that the fast effect is due to the second complex-formation step [formation of the bis(oxalato) complex]. To give just one illustration: the amplitude of the fast effect of a reactant solution for which $\Gamma_1 = 1.6 \times 10^{-5}$ and $\Gamma_2 = 1.6 \times 10^{-4}$ mol dm^{-3} was observed to be $\delta I/I = 0.0057$. With $\varepsilon_1 - \varepsilon_{Ti} = 79$ and $\varepsilon_2 - \varepsilon_1 = 410$, this leads to either $\delta\ln K_1^* \sim 2.0$ or to $\delta\ln K_2^* = 0.038$. Only the latter figure represents a reasonable value since $\delta\ln K \simeq \delta K/K \ll 1$. The considerations of the relaxation amplitudes thus confirm the general picture of the kinetics of this two-step system as outlined above.

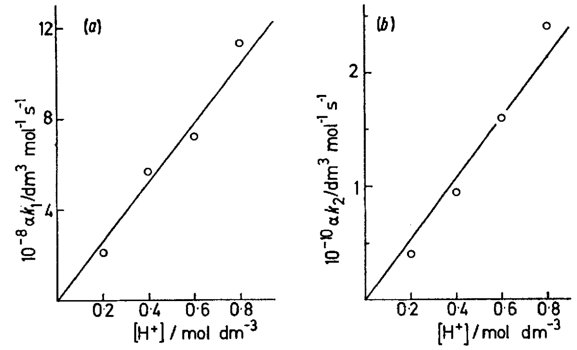

FIGURE 7 [H$^+$] Dependence of (*a*) αk_1 [equation (13)], and (*b*) αk_2 [equation (16)]

Apparent rate constants for the formation of mono-oxalato- and bis(oxalato) titanium(III) at various [H$^+$] (10 °C, I = 1.0 mol dm^{-3}; estimated errors ±10%)

[H$^+$] mol dm^{-3}	$10^{-4}k_1$ dm^3 mol^{-1} s^{-1}	$10^{-5}k_2$ dm^3 mol^{-1} s^{-1}
0.2	7.7	14.7
0.4	5.8	10.0
0.6	3.5	7.8
0.8	3.2	6.8

The data obtained at [H$^+$] = 0.2, 0.6, and 0.8 mol dm^{-3} were evaluated in the same way. A summary of the apparent forward rates for the formation of the mono-oxalato- and bis(oxalato) complexes is given in the Table. Figure 7 shows the dependence of αk_1 and αk_2 on [H$^+$]. Comparisons with equations (13) and (16), respectively, clearly demonstrate that the terms with k_{1a} and k_{2a} do not contribute measurably to the overall reaction (zero intercept) and the same applies apparently to the terms with k_{1c} and k_{2c} (approximate linearity). Actually, the slight curvature of the experimental points in Figure 7(*b*) could indicate some contribution from k_{2c} but the effect is not large enough to be established beyond doubt. Thus complex formation proceeds predominantly *via* reaction with $[HC_2O_4]^-$ under the conditions of this study, and the straight lines in Figure 7 yield the rate constants of this ligand species with Ti^{3+} and with $[Ti(C_2O_4)]^+$: $k_{1b} = (3.9 \pm 0.4) \times 10^5$, $k_{2b} = (8.0 \pm 0.8) \times 10^6$ dm^3 mol^{-1} s^{-1} (10 °C, I = 1.0 mol dm^{-3}). With the equilibrium relations it follows that $k_{-1b} = 460$ and $k_{-2b} = 2.2 \times 10^4$ dm^3 mol^{-1} s^{-1}. The value for k_{-2b} has also been derived from the [H$^+$] dependence of the intercepts ($=k_{-2}$) of plots of the type shown in Figure 6(*a*); the corresponding plot of k_{-2} against [H$^+$] [equation (17)] also showed slight curvature.

DISCUSSION

Titanium(III) in aqueous solution has a fairly strong tendency towards hydrolysis. Pecsok and Fletcher[18] determined values of $K_T = [Ti(OH)^{2+}]/[Ti^{3+}][OH^-]$ at 15, 25, and 35 °C at various ionic strengths. Their data (in potassium bromide solution) lead to an estimate of $K_T = 1.6 \times 10^{12}$ dm^3 mol^{-1} at 10 °C and I = 1.0 mol dm^{-3}. With $[H^+][OH^-] = 0.46 \times 10^{-14}$ mol^2 kg^{-2} at 10 °C and 1.0 mol dm^{-3} KCl,[19] the value for the acid-dissociation constant $K_A = [Ti(OH)^{2+}][H^+]/[Ti^{3+}]$ is *ca.* 7×10^{-3} mol dm^{-3} at 10 °C and I = 1.0 mol dm^{-3}. This value is somewhat larger than the one which has been reported[20] at 25 °C and I = 3.0 mol dm^{-3} (KBr), *i.e.* $K_A = 2.8 \times 10^{-3}$ mol dm^{-3}, and indicates that at the lowest [H$^+$] used in this study *ca.* 3.5% of the Ti^{III} is present in the hydrolyzed form. The small extent of hydrolysis was neglected in the equilibrium determinations.

The extent of complex formation of Ti^{III} with chloride ion is also rather small. It has been reported that in 2 mol dm^{-3} HCl and in up to 5 mol dm^{-3} HCl solutions the Ti^{III} is present predominantly as the hexa-aqua-complex.[9,21] A more recent spectrophotometric study[22] over a wide range of [Cl$^-$] resulted in a stability constant for the monochlorotitanium(III) complex of K_{Cl} = 0.07—0.2 dm^3 mol^{-1}, with some evidence that the lower value is more correct. In the experiments of the present investigation the concentration of Cl$^-$ varied between 0.91 and 0.99 mol dm^{-3}. Thus it is to be expected that not more than a few percent of the Ti^{III} is present as the monochloro-complex. The small extent of inner-sphere complexing with chloride is therefore also considered to be a negligible factor. (No relaxation effect was observed between 3 μs and 0.5 s in the absence of oxalate.)

On the other hand, outer-sphere complexing between Ti^{3+} and Cl$^-$ is certainly appreciable; it may easily involve about half of the Ti^{III} which is not complexed by oxalate since the stability constant for outer-sphere association between reactants of the charge type +3, −1 is often near unity at an ionic strength near 1.0 mol dm^{-3}.[5]

---

[18] R. L. Pecsok and A. N. Fletcher, *Inorg. Chem.*, 1962, **1**, 155.

[19] H. S. Harned and B. B. Owen, ' The Physical Chemistry of Electrolytic Solutions,' 3rd edn., Reinhold, New York, 1958, p. 640.

[20] M. R. Paris and C. L. Gregoire, *Analyt. Chim. Acta*, 1968, **42**, 439.

[21] C. K. Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 73.

[22] H. J. Gardner, *Austral. J. Chem.*, 1967, **20**, 2357.

Under our conditions the concentration of Cl^- is large compared with those of Ti^{III} and oxalate and is approximately constant. Also, outer-sphere complex equilibration is extremely rapid. Therefore, the influence of outer-sphere complex formation between Ti^{3+} and Cl^- on the equilibria and the kinetics of the system titanium(III)-oxalate may be simply considered as a constant effect of the medium.

The strong shielding of electrostatic interactions by the high ionic strength certainly contributes to the observation that the stepwise equilibrium constants for the formation of $[Ti(C_2O_4)]^+$ and $[Ti(C_2O_4)_2]^-$ differ only by a factor of 2.3. Similar small ratios of K_1/K_2 at $I = 0.1$—1.0 mol dm^{-3} have also been reported for the oxalato-complexes of several other trivalent metal ions, *e.g.* for Cr^{3+},[23] Fe^{3+},[24] and In^{3+}.[25] The stability constant K_1 for $[Ti(C_2O_4)]^+$ is about one order of magnitude smaller than that[13] for $[Fe(C_2O_4)]^+$ ($K_1 = 3.9 \times 10^7$ dm^3 mol^{-1} at 25 °C and $I = 1.0$ mol dm^{-3}). Other ligands like $[NCS]^-$, Cl^-, and edta^{4-} (ethylenediaminetetra-acetate) also form more stable complexes with Fe^{3+} (ref. 26) than with Ti^{3+}.[5,22,26] This difference in complex stabilities is apparently due to a somewhat larger radius of the Ti^{3+} ion as compared with Fe^{3+}.[27]

It appears reasonable that complex formation occurs predominantly *via* the reaction of Ti^{III} with $[H_2C_2O_4]^-$ under the conditions of this study. The concentration of $[C_2O_4]^{2-}$ is too low to contribute appreciably to the overall reaction, and the fully protonated ligand, $H_2C_2O_4$, is expected to be a very weak nucleophile. Nucleophilic strength is an important factor in associative substitution reactions and there is some evidence that substitution at the $[Ti(OH_2)_6]^{3+}$ ion proceeds by such a mechanism. For instance, from a consideration of activation parameters an associative reaction path was proposed for the exchange of co-ordinated water.[4] Also, the first-order rate constant for water exchange in $[Ti(OH_2)_6]^{3+}$ at 10 °C is 5.4×10^4 s^{-1} [from k_{ex} at 25 °C and $\Delta H^‡$ (ref. 4)], a value clearly lower than that for inner-sphere substitution by $[HC_2O_4]^-$, which is *ca.* 4×10^5 s^{-1} (with an outer-sphere stability constant $\simeq 1$) according to the present study. On the other hand, inner-sphere substitution by $[NCS]^-$ occurs with a rate constant of only $\simeq 8 \times 10^3$ s^{-1}.[5] These variations in inner-sphere substitution rates are also most conveniently accounted for by an associative mechanism, probably of the type 'associative interchange' (I_a mechanism).[28]

In principle, of course, the rate term attributed to $Ti^{3+} + [HC_2O_4]^-$ could also be due to the reaction path $[Ti(OH)]^{2+} + H_2C_2O_4$, with a rate constant $k' = k_{1b}K_{H2}/K_A = 3.6 \times 10^6$ dm^3 mol^{-1} s^{-1}. If this alternative formulation were correct, however, then one would expect also a contribution from $[Ti(OH)]^{2+} + [HC_2O_4]^-$, with a rate constant at least somewhat higher than k' (because of the electrostatics). This means that the plot in Figure 7(*a*) should show a finite intercept of at least 1×10^8—1.5×10^8 dm^3 mol^{-1} s^{-1}, a value which is considered to be outside the experimental uncertainty. Two conclusions can be drawn from this consideration: first, the assignment of the dominating rate term to the reaction path $Ti^{3+} + [HC_2O_4]^-$ is unambiguous; secondly, the reaction of $[Ti(OH)]^{2+}$ with $[HC_2O_4]^-$ is not much faster (<factor 5) than that of Ti^{3+} with $[HC_2O_4]^-$. The second point contrasts with the behaviour exhibited by the system Fe^{III} + oxalate[13] and by the reactions of various other ligands with Fe^{III},[2] Co^{III},[29] and Cr^{III},[30] but is in accord with previous observations of titanium(III) substitution kinetics.[5] A behaviour similar in this respect to that of Ti^{III} is also shown by V^{III} (refs. 3 and 31) and possibly by Mo^{III}.[32]

For the reaction step $[Ti(C_2O_4)]^+ + [HC_2O_4]^- \longrightarrow [Ti(C_2O_4)_2]^- + H^+$ (rate constant k_{2b}), effects of hydrolysis should be negligible because of the reduction in charge of the titanium(III) species. It is remarkable, however, that the rate constant k_{2b} is larger than k_{1b} by a factor of 20, despite a less favourable electrostatic interaction. A similar enhancement has also been reported for the rate of formation of $[Cr(C_2O_4)_2]^-$ as compared to that for $[Cr(C_2O_4)]^+$.[33] Presumably the incorporation of a dinegative oxalate anion into the first co-ordination sphere of Ti^{III} causes a considerable labilization of the remaining water molecules. Because of the lower positive charge it is possible that substitution of water in $[Ti(C_2O_4)(OH_2)_4]^+$ proceeds by a predominantly dissociative mechanism. The nucleophilic strength of the entering ligand is then a rather unimportant factor. Such a change in mechanism (as compared to the first complex-formation step) would conveniently explain why some evidence for a contribution of $[Ti(C_2O_4)]^+ + H_2C_2O_4$ (rate constant k_{2c}) to the second complex-formation step was noticed. The experimental points in Figure 7(*b*) are actually fitted better by $k_{2b} = 5.3 \times 10^6$ and $k_{2c} = 3.0 \times 10^5$ dm^3 mol^{-1} s^{-1} than by $k_{2b} = 8.0 \times 10^6$ dm^3 mol^{-1} s^{-1} and $k_{2c} = 0$. However, the evidence for the participation of the reaction path denoted by k_{2c} can only be considered as tentative at this moment.

P. C. thanks the Max Planck Society for a postdoctoral fellowship award.

[6/679 *Received, 7th April, 1976*]

---

[23] K. Nagata, A. Umayahara, and R. Tsuchiya, *Bull. Chem. Soc. Japan*, 1965, **38**, 1059.

[24] V. I. Pramonova and S. A. Bartenev, *Russ. J. Inorg. Chem.*, 1963, **8**, 157.

[25] Y. Hasegawa and T. Sekine, *Bull. Chem. Soc. Japan*, 1966, **39**, 2776.

[26] L. G. Sillen and A. E. Martell, 'Stability Constants of Metal-Ion Complexes, *Special Publ.*, The Chemical Society, 1964, No. 17.

[27] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967.

[28] C. H. Langford and H. B. Gray, 'Ligand Substitution Processes,' W. A. Benjamin, New York, 1965.

[29] T. J. Conocchioli, G. H. Nancollas, and N. Sutin, *Inorg. Chem.*, 1966, **5**, 1.

[30] J. H. Espenson, *Inorg. Chem.*, 1969, **8**, 1554.

[31] B. R. Baker, N. Sutin, and T. J. Welch, *Inorg. Chem.*, 1967, **6**, 1948; W. Kruse and D. Thusius, *ibid.*, 1968, **7**, 464.

[32] Y. Sasaki and A. G. Sykes, *J.C.S. Dalton*, 1975, 1048.

[33] C. Schenk, H. Stieger, and H. Kelm, *Z. anorg. Chem.*, 1972, **391**, 1.