BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 93—96 (1971)

Dissociation Constants of the Oxalato-Titanium(III) Complex as Determined from Spectrophotometric Measurements

Kuan Pan, Chin Chan Lai, and Teh-Shoon Huang
Chemistry Research Center, National Taiwan University, Teipei, Taiwan, China

(Received August 25, 1970)

The dissociation constant of $Ti(C_2O_4)_2^-$ ions in hydrochloric acid media was evaluated from the data obtained by spectrophotometric measurements at 25°C. The average value of p*K* for the reaction, $Ti(C_2O_4)_2^- = Ti(III) + 2C_2O_4^{2-}$, at an infinite dilution was estimated as 9.0, while that for the $Ti(C_2O_4)_2^- = Ti^{3+} + 2C_2O_4^{2-}$ reaction was evaluated as 8.7_4.

The preparation of the oxalato-titanium(III) complex, $MTi(C_2O_4)_2 \cdot 2H_2O$ (M=K, Rb, NH_4), has been reported by Stahler.[1] The composition of the oxalato-titanium(III) ion in an aqueous solution was spectrophotometrically determined as $Ti(C_2O_4)_2^-$ by Pecsok,[2] while Subbanna, Rao, and Bhattacharya[3] asserted the molar ratio to be 1 : 1, corresponding to the formula, $H(TiOC_2O_4)$ from their spectrophotometric and conductometric measurements, however, they did not give an detailed data or the observed pH range. Afterwards, Jϕrgensen[4] suggested that the complexes $M^ITi(C_2O_4)_2 \cdot 2H_2O$ contain a tetrahedral, $Ti(C_2O_4)_2^-$ anion, while Eve and Fowles[5] proposed the polymetric structure for $M^ITi(C_2O_4)_2 \cdot 10H_2O$ on the basis of the diffuse reflectance spectra.

The present investigation was undertaken in order to redetermine the composition and to evaluate the dissociation constants of the oxalato-titanium(III) complex in a hydrochloric acid solution on the basis of spectrophotometric measurements at 25°C.

Experimental

Titanium(III) chloride was prepared by heating titanium sponge (99.9% purity, Alfa Inorganics, Inc., U. S. A.) with a 3N hydrochloric acid solution. Additional hydrochloric acid was added as the reaction progressed to prevent the hydrochloric acid concentration from falling below the point where hydrolysis could occur. The solution was then cooled and maintained under an atmosphere of nitrogen to prevent the formation of any appreciable quantity of Ti(IV). The Ti(III) content was determined by addition to an excess of ceric sulfate in a sulfuric acid solution, followed by potentiometric back-titration with a standard solution of ferrous sulfate. The chloride ion content was determined by potentiometric titration with silver nitrate. Hydrochloric acid, sodium chloride, and sodium hydroxide were used to adjust the H_3O^+ ion concentration and the ionic strength of the solution.

The oxalato-titanium(III) complex was prepared by the rapid addition of Ti(III) chloride to an aqueous solution of oxalic acid, according to Eve and Fowles,[5] and dried in a vacuum.

A Bausch & Lomb recording spectrophotometer, model 505, equipped with a constant temperature holder controlled to ±0.2°C was used.

For the spectrophotometric determination of the oxalato-titanium(III) complex, calibration curves for a series of solutions in an excess of oxalate at various H_3O^+ ion concentrations and ionic strengths were prepared. All the solutions were prepared from deaerated water and were kept in an atmosphere of nitrogen. All the reactants and their mixtures were kept in a thermostat whose temperature was controlled within ±0.2°C.

Since no time effect on the absorbance of the mixture of Ti(III) and oxalate ions in hydrochloric acid was observed in this pH range, and since the mixture of Ti(III) and oxalate as well as $KTi(C_2O_4)_2 \cdot 2H_2O$ in oxalic acid has the same absorption band at 440 mμ, a mixture containing a known content of Ti(III) in a HCl solution and a desired amount of a slight excess of oxalate was for the spectrophotometric measurements. The absorbance at 440 mμ was taken for the calculation of the dissociation constants.

Results and Discussion

Extinction Coefficients of Ti(III) Ions in Hydrochloric Acid Media. The titanium(III) ion has been known to form chloro-complexes such as $[TiCl(H_2O)_5]^{2+}$ and

---

[1] A. Stahler, *Ber.*, **37**, 4405 (1904).

[2] R. L. Pecsok, *J. Amer. Chem. Soc.*, **73**, 1304 (1951).

[3] V. V. Subbanna, G. S. Rao, and Bhattacharya, *J. Sci. Ind. Res.*, **18B**, 127 (1959).

[4] C. K. Jϕrgensen, "Inorganic Complexes," Academic Press, New York (1963).

[5] D. J. Eve and G. W. A. Fowles, *J. Chem. Soc.*, **1966**, 1183.

$[TiCl_2(H_2O)_4]^+$ [6] even if the formation of the hydrolysis products, *e. g.* $[Ti(OH)(H_2O)_5]^{2+}$ and $[Ti(OH)_2 \cdot (H_2O)_4]^+$, is neglegible in strong acid media. As a first degree of approximation, however, we may assume only the coexistence of $[Ti(H_2O)_6]^{3+}$ and $[TiCl(H_2O)_5]^{2+}$ (abbreviated as Ti^{3+} and $TiCl^{2+}$) in chloride media at pH 1—2.5 after the independence of the H_3O^+ ion concentration of the absorbance of the Ti(III) ions has been confirmed. Since no detailed data on the extinction coefficients of these ions is available, a series of spectrophotometric measurements were conducted for the determination of the extinction coefficients (ε_1) of Ti(III) ions in a mixture of 0.2—0.6N HCl and KCl solutions at 25°C.

TABLE 1. THE EXTINCTION COEFFICIENTS OF Ti (III) IN HCl AND KCl AT 25°C
(ε_1 in l mol^{-1} cm^{-1})

$[Cl^-]/\lambda$ mμ	0.2	0.3	0.4	0.5	0.6	Average
400	1.1	1.3	1.4	1.5	1.5	1.4
420	2.5	2.5	2.4	2.7	2.7	2.6
440	3.7	3.9	4.1	4.3	4.2	4.1
460	5.2	5.4	5.5	5.8	5.7	5.5
500	5.9	6.0	6.1	6.2	6.2	6.1
520	5.5	5.6	6.8	6.7	6.7	6.7
550	4.7	4.8	4.8	4.7	4.8	4.8

Since the extinction coefficient of Ti(III), ε_1, in the presence of a large excess of Cl^- ions was found to be practically independent of the H_3O^+ and Cl^- ion concentrations in the H_3O^+ ion concentration range mentioned above, we took the average value of 4.1 l mol^{-1} cm^{-1} for ε_1 at 440 mμ.

Extinction Coefficients of Oxalato-Titanium(III) Complexes. Since, even in the acid media of pH 1.5—2.5, the mole ratio of the oxalato-titanium(III) complex was found to be 1 : 2 by the continuous variation plot (Fig. 1), the formation of the $Ti(C_2O_4)_2^-$ ion in the presence of HCl at pH 1.5 to 2.5 was assumed. The extinction coefficient of the complex was determined by plotting the absorbance against the total concentration of Ti(III) in a large excess of oxalate ions over this pH range at a constant ionic strength. The extinction coefficient of the oxalato-titanium(III) complex, ε_2, was found to be practically independent of the H_3O^+ and Cl^- ion concentrations, or of the ionic strength over the pH range of 1.5—2.5. We therefore, also took the average value of 320 l mol^{-1} cm^{-1} for ε_2 in the calculation of this investigation.

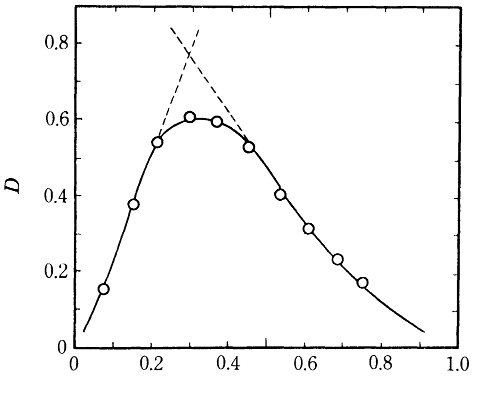

Fig. 1. Continuous variation plot for the Ti(III)-oxalate system. $[Ti(III)]+[H_2C_2O_4]=0.062$M $[Cl^-]=0.254$M, pH 1.5

Dissociation Constants of the Oxalato-Titanium(III) Complex. When the $Ti(C_2O_4)_2^-$ ion is in equilibrium with Ti(III) and $HC_2O_4^-$ ions in a 10^{-3}—10^{-1}N hydrochloric acid solution, the stoichiometric equilibrium constants for the dissociation of $Ti(C_2O_4)_2^-$ and $HC_2O_4^-$ ions (denoted as TiX_2^- and HX^-),

$$TiX_2^- + 2H_3O^+ = Ti(III) + 2HX^- + 2H_2O \qquad (I)$$

and $HX^- + H_2O = H_3O^+ + X^{2-}$

at a constant ionic strength are given by

$$K_1 = \frac{[Ti(III)][HX^-]^2}{[TiX_2^-][H^+]^2} \qquad (1)$$

and
$$k_2 = \frac{[H^+][X^{2-}]}{[HX^-]} \qquad (2)$$

where k_2 is the secondary ionization constant of the $HC_2O_4^-$ ion.

From Eq. (1) and Eq. (2), the apparent dissociation constant of $Ti(C_2O_4)_2^-$;

$$TiX_2^- = Ti(III) + 2X^{2-} \qquad (II)$$

is given by

$$K_2 = K_1 k_2^2 = \frac{[Ti(III)][X^{2-}]^2}{[TiX_2^-]} \qquad (3)$$

where Ti(III) represents a mixture of Ti(III) ions other than the oxalate complexes.

The molar concentration of the unchelated oxalate ions is represented by

$$[X]_0 - 2[TiX_2^-] = [H_2X] + [HX^-] + [X^{2-}] \qquad (4)$$

and that of the free $C_2O_4^{2-}$ ion concentration is given by

$$[X^{2-}] = \frac{[X]_0 - 2[TiX_2^-]}{1 + \frac{[H^+]}{k_2} + \frac{[H^+]^2}{k_1 k_2}} \qquad (5)$$

where $[X]_0$ is the total concentration of oxalate ions and $[TiX_2^-]$ is the concentration of oxalato-titanium(III) ion as estimated from the spectrophotometric data.

When the absorption of the solution at 440 mμ is assumed to be associated with the equilibrium between the Ti(III) and TiX_2^- ions, the absorbance of the solution, D, can be expressed by;

$$D = \varepsilon_1(a-x) + \varepsilon_2 x \qquad (6)$$

where a is the total molarity of the Ti(III) ions, x is that of the complexes, and ε_1 and ε_2 are the extinction coefficients of the unchelated and chelated ions respectively in a mixture of HCl and NaCl solutions.

From Eq. (6), therefore, the molar concentrations of TiX_2^- and Ti(III) ions can be given by;

$$x = [TiX_2^-] = \frac{D - D_0}{\varepsilon_2 - \varepsilon_1} \qquad (7)$$

and;
$$a - x = [Ti(III)] = \frac{D_c - D}{\varepsilon_2 - \varepsilon_1} \qquad (8)$$

where $D_0 = \varepsilon_1 a$ for $x=0$ in the absence of oxalate ions and $D_c = \varepsilon_2 a$ for $x=a$ in a large excess of oxalate ions.

---

[6] H. Hartmann and H. L. Schläfer, *Z. Phys. Chem.*, **197**, 116 (1951).

Thus, by substituting the ratio of Eq. (8) to Eq. (7) into Eq. (3), the apparent dissociation constant of the complex can be given by;

$$K_2 = \frac{(D_c - D)[X^{2-}]^2}{D - D_0} \tag{9}$$

The substitution of Eq. (5) into Eq. (9) gives;

$$K_2 = \frac{(D_c - D)\{[X]_0 - 2[TiX_2^-]\}^2}{(D - D_0)\left(1 + \frac{[H^+]}{k_2} + \frac{[H^+]^2}{k_1 k_2}\right)^2} \tag{10}$$

where k_1 and k_2 are the step-by-step ionization constants of oxalic acid, given by $k_1 = 5.38 \times 10^{-2}$ [7] and $k_2 = 5.18 \times 10^{-5}$ [8] at 25°C.

Taking the average values of the extinction coefficients, $\varepsilon_1 = 4.1$ and $\varepsilon_2 = 320\ l\ \mathrm{mol^{-1}\ cm^{-1}}$ for the unchelated Ti(III) ions and the chelate ion, $Ti(C_2O_4)_2^-$, the values of D_0 and D_c at a specified total titanium(III) ion concentration, a, were evaluated. The substitution of the values of $[TiX_2^-]$ calculated by means of Eq. (7), and that of $[C_2O_4^{2-}]$ calculated by means of Eq. (5), into Eq. (10), the apparent dissociation constant of $Ti(C_2O_4)_2^-$ ion was evaluated. The results are summarized in Table 2.

TABLE 2. SPECTROPHOTOMETRIC DATA FOR THE Ti (III)-OXALATE SYSTEM AT 25°C ($[KHC_2O_4] = 0.02$ M)

I	$10^3\ a$	D	$[Cl^-]_0$	$10^2\ [H^+]$	$10^5\ [C_2O_4^{=}]$	$10^9\ K_2$	pK_2
0.1	0.656	0.1331	0.0844	1.244	6.480	2.457	8.61
	1.312	0.2798	0.0848	1.089	7.235	2.640	8.58
	4.868	0.9872	0.0939	0.933	6.537	2.520	8.59
	2.624	0.6308	0.0857	0.778	9.345	2.917	8.54
0.2	1.312	0.2604	0.1848	1.089	7.273	3.139	8.50
	4.868	0.9355	0.1939	0.933	6.691	3.042	8.52
	2.624	0.6021	0.1857	0.778	9.460	3.556	8.45
	3.280	0.8041	0.1861	0.622	11.192	3.824	8.42
0.3	0.679	0.1113	0.2850	1.656	6.251	3.826	8.42
	1.540	0.2596	0.2795	1.177	6.619	4.032	8.40
	3.079	0.5901	0.2751	0.954	7.501	3.856	8.41
	1.510	0.3468	0.2842	0.765	10.509	4.421	8.36
0.4	1.540	0.2496	0.3864	1.177	6.642	4.412	8.36
	1.588	0.2933	0.3823	1.147	6.770	4.579	8.34
	2.566	0.4498	0.3781	1.028	7.252	4.674	8.33
	0.927	0.1403	0.3853	0.656	13.390	4.989	8.30

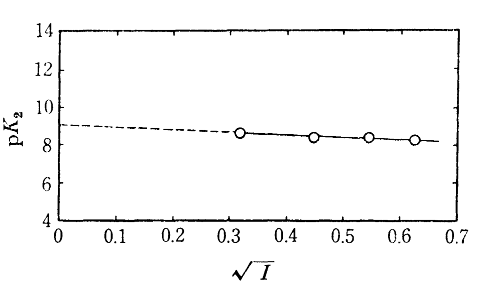

Fig. 2. Plot of pK_2 vs. $\sqrt{I}$ at 25°C.

TABLE 3. DEPENDENCE OF AVERAGE pK_2 VALUES *vs.* IONIC STRENGTH

I (M)	0.1	0.2	0.3	0.4
$[Cl^-]_0$ (average) (M)	0.0872	0.1876	0.2809	0.3830
pK_2 (average)	8.58	8.47	8.40	8.33

By plotting the average values of pK_2 at each ionic strength against $\sqrt{I}$, as is shown in Fig. 2, and by extrapolating to zero ionic strength, the limiting value of $pK^\circ = 9.0$ at 25°C was obtained. Since the value of K_2 varies slightly with the H_3O^+ and Cl^- ion concentrations, as is shown in Table 2, however, we must also take into consideration the hydrolysis and the formation of chloro-complexes of Ti^{3+} ions;

$$Ti^{3+} + 3H_2O \overset{K_3}{\rightleftharpoons} TiO^+ + 2H_3O^+ \tag{III}$$

$$Ti^{3+} + Cl^- \overset{K_4}{\rightleftharpoons} TiCl^{2+} \tag{IV}$$

and;

$$TiO^+ + Cl^- \overset{K_5}{\rightleftharpoons} TiOCl \tag{V}$$

and represent the stoichiometric equilibrium constants as;

$$K_3 = \frac{[TiO^+][H^+]^2}{[Ti^{3+}]} \tag{11}$$

$$K_4 = \frac{[TiCl^{2+}]}{[Ti^{3+}][Cl^-]} \tag{12}$$

and;

$$K_5 = \frac{[TiOCl]}{[TiO^+][Cl^-]} \tag{13}$$

respectively, at a constant ionic strength. Thus, the total concentration of Ti(III) ions other than the oxalato chelate may be given by;

$$[Ti(III)] = [Ti^{3+}]\left\{(1 + K_4[Cl^-]) + K_3(1 + K_3[Cl^-])\frac{1}{[H^+]^2}\right\} \tag{14}$$

and the apparent dissociation constant for the reaction (II) may be given by;

$$K_2 = \frac{[Ti^{3+}][X^{2-}]^2}{[TiX_2^-]}\left\{(1 + K_4[Cl^-]) + K_3(1 + K_5[Cl^-])\frac{1}{[H^+]^2}\right\} \tag{15}$$

by substituting Eq. (14) into Eq. (3). Therefore, when the true dissociation constant of $Ti(C_2O_4)_2^-$;

$$TiX_2^- = Ti^{3+} + 2X^{2-} \tag{VI}$$

is represented by;

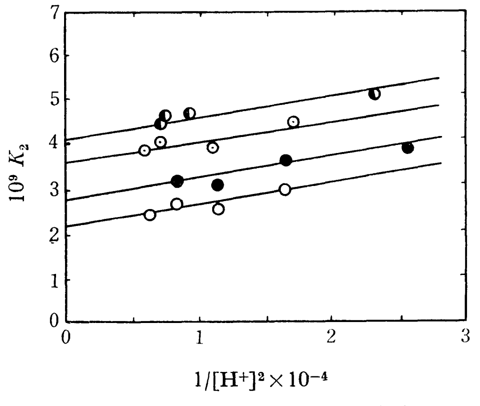

Fig. 3. Plots of K_2 vs. $1/[H^+]^2$ at various Cl^- ion concn. $[Cl^-]_0$(average): ○ 0.085M, ● 0.184M, ⊙ 0.278M, ◑ 0.385M.

---

[7] W. J. Harned and L. D. Fallon, *J. Amer. Chem. Soc.*, **61**, 3111 (1939).

[8] L. S. Darken, *ibid.*, **63**, 1007 (1941).

$$K_6 = \frac{[\mathrm{Ti}^{3+}][\mathrm{X}^{2-}]^2}{[\mathrm{TiX}_2^{-}]} \qquad (16)$$

the observed value of K_2 is related to that of K_6 by;

$$K_2 = K_6\left\{(1+K_4[\mathrm{Cl}^-]) + K_3(1+K_5[\mathrm{Cl}^-])\frac{1}{[\mathrm{H}^+]^2}\right\} \qquad (17)$$

By plotting the K_2 values against $1/[\mathrm{H}^+]^2$ at a constant ionic strength and Cl^- ion concentration, as is shown in Fig. 3, a series of straight lines was obtained. The slope (S_1) corresponds to the value of $K_6K_3(1+K_5[\mathrm{Cl}^-])$, and the intercept ($A$), to that of $K_6(1+K_4[\mathrm{Cl}^-])$.

Since the slopes of these lines are practically independent of the Cl^- ion concentration, we may estimate that the value of K_4 is smaller than 0.1, and that the product, K_6K_3, corresponds to the slope of $S_1=5\times10^{-4}$. On the other hand, by plotting the value of the intercept, (A), obtained from Fig. 3, against the Cl^- ion concentration, a straight line was obtained (Fig. 4). From the intercept, $B=1.8\times10^{-9}$, and the slope, $S_2=6.4\times10^{-9}$, the values of K_6, K_4, and K_3 were evaluated to be 1.8×10^{-9}, 3.6, and 3×10^{-5} respectively. The formation constant of the TiCl^{2+} ion, $K_4=3.6$, obtained in this experiment is in fair agreement with that of 2.18 estimated by Duke and Quinney[9] in their kinetic study of the reduction of the perchlorate ion by Ti(III).

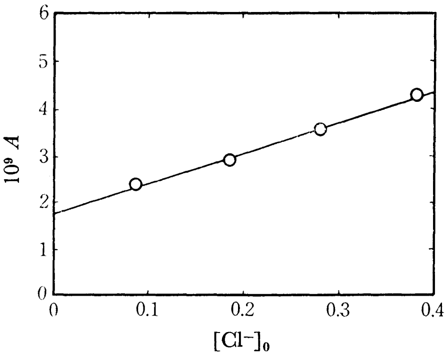

Fig. 4. Dependence of intercept (A) upon total Cl^- ion concn.

Though there was some inevitable under-estimation of the $\mathrm{H_3O^+}$ ion concentration, which caused some deviation in the evaluation of the K_2 values, the fact that the value of K_2 thus calculated decreases with an increase in the $\mathrm{H_3O^+}$ ion concentration and increases with an increase in the Cl^- ion concentration seems to support the reaction mechanism proposed.

This work was carried out as a part of the research projects of Chemistry Research Center, National Taiwan University, CRC-5802 which was supported by the National Council on Science Development.

---

[9] P. R. Duke and J. D. Quinney, *J. Amer. Chem. Soc.*, **76**, 3800 (1954).