Formation Constants of Chromium(III)-Oxalato Complexes

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There have been published a great number of investigations of the syntheses[1] and the properties[2] of oxalato complexes of various metals; the data of the formation constants concerned have been summarized in a review.[3] However, these data concern only the bivalent cations. The formation constants of the oxalato complexes of tervalent metal cations are scarcely known except for a few examples.

In a preceding paper the formation constants of chromium(III) complexes with ethylenediamine were reported;[4] this is the simplest chelating agent which coordinates to the central chromium by means of two nitrogen atoms. In the present study, the formation constants of chromium(III) complexes with oxalate ion, the simplest chelating agent coordinating by two oxygen atoms, have been determined in order to compare them with those published in the previous report.[4] The results found have also been compared with the data of the corresponding complexes of other first-transition metals already known.

Experimental

Hexaaquochromium(III) Perchlorate.—Chromium trioxide was precipitated by adding concentrated sulfuric acid to potassium bichromate. When it was reduced with formic acid[5] in the presence of perchloric acid, the hexaaquochromium(III) perchlorate which was the starting material in the present study was obtained. Since it was very hygroscopic, it was stored in a vacuum desiccator.

The analysis of the chromium in the hexaaquochromium(III) perchlorate prepared as above was carried out by oxidizing the tervalent chromium to bichromate by ammonium persulfate in the presence of a trace of silver nitrate as a catalyst, and by measuring the absorbancy of the solution at 420 mμ with a Hitachi FPW-4 photoelectric photometer after adjusting the pH of the solution to 2. The analysis of the perchlorate ion was made by titrating the elute passed through the cation exchange resin "Amberlite IR-120" with a standard sodium hydroxide solution.

By these analyses it was found that the crystalline hexaaquochromium(III) perchlorate prepared above as the sarting material had the following composition, if the adsorbed water was excluded:

$[Cr(H_2O)_6](ClO_4)_3$	48.66 mol.%
$HClO_4$	51.34 mol.%

Sodium Oxalate.—Salt of the highest commercial grade was further purified by recrystallization.

Procedure.—The determination of the formation constants was carried out by pH measurement. Mixed solutions of various concentrations of hexaaquochromium(III) perchlorate and sodium oxalate, to which some quantities of sodium hydroxide had been added to make the pH of the solution higher and an appropriate amount of sodium perchlorate, to make the ionic strength of the solution 0.1, were kept at 25°C in a thermostat for one or one-and-a-half months. The pH of the solution was measured with a Toa Denpa pH meter, model HM-8, after the equilibrium in the solution had been attained.

Results

Acid Dissociation Constants of Oxalic Acid.—If the oxalic acid is represented as H_2ox, the acid dissociation constants, K_1 and K_2, may be expressed by:

$$K_1 = [H^+][Hox^-]/[H_2ox] \qquad (1)$$

$$K_2 = [H^+][ox^{2-}]/[Hox^-] \qquad (2)$$

where [ ] expresses the concentration in moles per liter. If the total concentration of ionizable hydrogen atoms and that of oxalate ions are expressed by C_H and C_{ox} respectively, $\bar{n}_H$, denoted as the average number of hydrogen atoms attached to each oxalate ion, is given by the following equation:

$$\bar{n}_H = \frac{[Hox^-] + 2[H_2ox]}{[ox^{2-}] + [Hox^-] + [H_2ox]} = \frac{C_H - [H^+]}{C_{ox}} \qquad (3)$$

On the other hand, C_H is expressed by the equation as:

$$C_H = C_{ox} + C_a - C_{OH} \qquad (4)$$

where C_a and C_{OH} are the concentrations of perchloric acid and of sodium hydroxide added respectively.

The determination of the acid dissociation

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constants was carried out by titrating the mixed solution of oxalic acid and sodium oxalate with perchloric acid or with a sodium hydroxide solution. By inserting the values of C_{H} calculated from the titre of perchloric acid or sodium hydroxide and the $[\mathrm{H}^+]$ values obtained from the pH measurement into Eqs. 3 and 4, the value of $\bar{n}_{\mathrm{H}}$ was obtained. The plot of $\bar{n}_{\mathrm{H}}$ vs. pH is shown in Fig. 1.

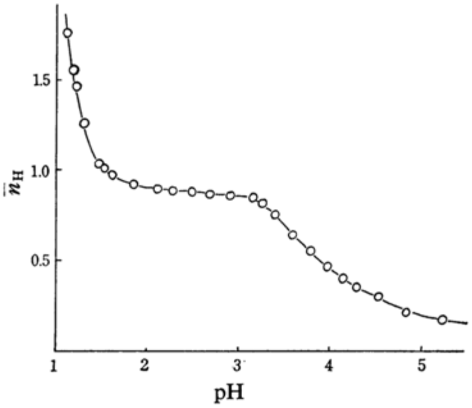

Fig. 1. The relation between $\bar{n}_{\mathrm{H}}$ and pH

The values of the acid dissociation constants of the first and second steps, $\mathrm{p}K_1$ and $\mathrm{p}K_2$, are obtained from Fig. 1 as 1.13 and 3.85 respectively. These values are in good agreement with the $\mathrm{p}K_1=1.14$⁶⁾ ($\mu=0.2$, 25°C) and $\mathrm{p}K_2=3.85$⁶⁾ ($\mu=0.2$, 25°C) already known, although the ionic strength is somewhat different.

Formation Constants of Oxalato-chromium(III) Complexes.—When the total concentration of chromium is expressed by C_{M}, that of the oxalate ion as ligand is given by:

$$C_{\mathrm{ox}}=[\mathrm{ox}^{2-}]+[\mathrm{Hox}^-]+[\mathrm{H_2ox}]+\bar{n}C_{\mathrm{M}} \qquad (5)$$

where $\bar{n}$ is the average number of ligands attached to each chromium. The total concentration of ionizable hydrogen is also given by the following equation:

$$C_{\mathrm{H}}=C_{\mathrm{a}}-C_{\mathrm{OH}} \qquad (6)$$

On the other hand, $\bar{n}$ is expressed as follows:

$$\bar{n}=\left\{C_{\mathrm{ox}}-\frac{C_{\mathrm{H}}-[\mathrm{H}^+]}{\bar{n}_{\mathrm{H}}}\right\}\Big/C_{\mathrm{M}} \qquad (7)$$

where $\bar{n}_{\mathrm{H}}$ is denoted as the number of ionizable hydrogen atoms attached to oxalate ions against the number of oxalate ions which do not coordinate to chromium. It is calculated by using Eqs. 1, 2 and 3 and by applying the values of the acid dissociation constants of oxalic acid and $[\mathrm{H}^+]$.

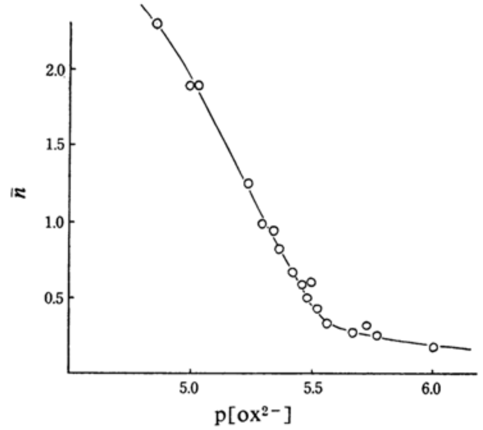

Fig. 2. The formation curve, $\bar{n}$—$p[\mathrm{ox}^{2-}]$, concerning with chromium(III) oxalato complexes.

By measuring the pH in mixed solutions of hexaaquochromium(III) perchlorate and sodium oxalate and by applying Eqs. 1, 2, 5, 6 and 7, the values of $\bar{n}$ and $[\mathrm{ox}^{2-}]$ were calculated. The formation curve, $\bar{n}-\mathrm{p}[\mathrm{ox}^{2-}]$, is plotted in Fig. 2. As the slope of this formation curve is relatively steep, the successive oxalato complexes formed seem to have overlapped each other. Since Bjerrum's simplified method cannot be applied in this case, the calculation of the formation constants was carried out in the following way.⁷⁾

In the successive formation of the complexes, there exists the following relationship:

$$\bar{n}=\sum nK_n[\mathrm{ox}^{2-}]^n/\{1+\sum K_n[\mathrm{ox}^{2-}]^n\} \qquad (8)$$

where $K_n=\Pi k_n$, the products of the successive formation constants. Equation 8 can be rearranged to:

$$\bar{n}=(n-\bar{n})[\mathrm{ox}^{2-}]^nK_n=\sum J_nK_n \qquad (9)$$

where

$$J_n=(n-\bar{n})[\mathrm{ox}^{2-}]^n \qquad (10)$$

By inserting the values of 0.5, 1.5 and 2.3 into $\bar{n}$ and the corresponding values into $[\mathrm{ox}^{2-}]$ in Eqs. 9 and 10, three simultaneous equations are established. By solving these equations, the successive formation constants are obtained as $\log k_1=5.34$, $\log k_2=5.17$ and $\log k_3=4.93$ respectively.

Discussion

The values of the formation constants of chromium(III) oxalato complexes in the first and second steps are compared with the known values of those of the first transition metals in Table I.

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TABLE I. THE FORMATION CONSTANTS OF THE OXALATO COMPLEXES OF THE FIRST TRANSITION METALS

	$\log k_1$	$\log k_2$	$\log k_3$	Ionic strength μ	Temp. °C	Ref.
TiO^+	2.65			—	23	8
Cr^{3+}	5.34	5.17	4.93	0.1	25	Present study
Mn^{3+}	9.98	6.59	2.85	2	25	9
Fe^{3+}	9.4	6.8	4.0	—	—	10
Co^{3+}		$\log k_1k_2k_3 \cong 20$		—	—	11
Al^{3+}	7.25			0	—	12
		$\log k_1k_2$		μ	°C	Ref.
Mn^{2+}		5.25		0	25	13
Fe^{2+}		4.52		0.5	25	14
Co^{2+}		6.7		0.002	25	15
Ni^{2+}		6.51		0.002	25	15
Cu^{2+}		10.32		—	~20	16
Zn^{2+}		7.36		0	25	17

It may be found from Table I that the formation constants of oxalato complexes of tervalent metal ions are remarkably larger than those of the corresponding complexes of bivalent metal ions. This is due to the fact that the ionic radii of the former are smaller than those of the latter; this confirms that the covalencies of the former are much stronger than those of the latter. The bivalent metal ions form four coordinated complexes, whereas the tervalent metal ions form six coordinated complexes.

It is found in the second that the formation constants of oxalato complexes become larger in the order of the tervalent titanium, chromium and manganese, iron or cobalt. That is to say, the formation constants of chromium complexes are smaller than those of manganese, iron and cobalt; they are comparable with those of aluminum complexes.

The formation constants of chromium(III) oxalato complexes are remarkably smaller than those of the corresponding ethylenediamine complexes reported in the preceding paper.[4] This suggests that the chelate group with two nitrogen atoms as the donor forms a more stable complex with chromium than does the chelate group with two oxygen atoms as the donor.

Summary

The formation constants of chromium(III) complexes with the oxalate ion, which is the simplest bidentate ligand coordinating by two oxygen atoms, have been determined by the pH method.

It has been shown that the formation constants of oxalato chromium(III) complexes are larger than those of the corresponding titanium(III) complexes, but smaller than those of the corresponding manganese(III), iron(III) and cobalt(III) complexes in the first transition series.

The formation constants of oxalato chromium(III) complexes have been found to be remarkably smaller than those of the ethylenediamine chromium(III) complexes. This result suggests that two nitrogen atoms form a more stable complex with chromium than do the two oxygen atoms serving as donors in the bidentate chelate.

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