it is not surprising that Al(acac)$_3$ is most highly hydrated. Also as expected Rh(acac)$_3$ with the greatest number of electrons is least hydrated. The ionic radii of Co^{3+} and Cr^{3+} are the same (0.65 Å.), so that the complexes differ only in atomic number and the number of d-electrons. Since Co(acac)$_3$ (d^6) has twice as many outer shell electrons as Cr(acac)$_3$ (d^3) in the octahedral faces, it might be expected that Co(acac)$_3$ would be hydrated to a lesser extent than Cr(acac)$_3$. However, the $\Delta H°$ values indicate that the opposite order of hydration is true. That Co(acac)$_3$ should be hydrated more than Cr(acac)$_3$ can be explained by reference to the molar electron polarizations ($_{\mathrm{E}}P$) of metal acetylacetonates.[24] Although Fe(acac)$_3$ contains thirteen more electrons than Al(acac)$_3$, the molar electron polarizations are nearly identical (91.5 and 91.1 cm.^{3}, respectively). The 3d^5-electrons of Fe(acac)$_3$ have spherical symmetry and are not concentrated in the octahedral faces. The added polarization of Co(acac)$_3$ (99.4 cm.^{3}) or Cr(acac)$_3$ (95.3 cm.^{3}) might be attributed to the nonspherically symmetric d-electrons. As a water molecule approaches an octahedral face of the complex, these d-electrons are displaced, reducing the screening of the cation. Since the molar electron polarization of Co(acac)$_3$ is greater than that for Cr(acac)$_3$ and the nuclear charge of Co is higher, the Co(acac)$_3$ becomes more highly hydrated than Cr(acac)$_3$.

The data for the distributions of Co(prac)$_3$ and Cr(meac)$_3$ support the assumption that hydration occurs through the octahedral faces. Addition of a methyl group to the 3-carbon of the acetylacetonate ion [as in Cr(meac)$_3$] causes a shift in the free energy, $\Delta F°$, of 1.3 kcal./mole toward the CCl_4 layer, while addition of the methyl group to the end of the chain [Co(prac)$_3$] causes a shift of 2.2 kcal./mole. The addition of the methyl group to the end of the acetylacetonate ion increases the shielding of the octahedral face so that hydration is less favorable. Addition to the 3-carbon would not affect hydration since this methyl group would not shield the central ion at all; it points directly away from the central ion.

The diffusion coefficients, which were calculated from the Ilkovic equation using polarographic data, were found to be 6.2×10^{-6} cm.^{2} sec.$^{-1}$ for Co(acac)$_3$ and 7.0×10^{-6} cm.^{2} sec.$^{-1}$ for Cr(acac)$_3$. The $E_{1/2}$ values (-0.1 and -1.45 v., respectively) are only approximate because of irreversibility. The value of n (number of electrons involved in the reduction) was determined by noting that there was a second wave for Co(acac)$_3$ at about -1.4 v. which was twice as high as the first one, indicating one and two electron reductions. These two molecules, which are identical in size, have slightly different values of D, indicating that the effective radii in solution are different. The more highly hydrated Co(acac)$_3$ would be expected to diffuse more slowly.

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The Kinetics of Formation of the Nickel Monooxalate Complex in Solution[1]

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The rate of formation of the monooxalate complex of nickel(II) both in neutral and in acid solution has been studied by the use of a flow technique. The results are interpreted in terms of the reactions $\text{Ni}^{2+} + \text{A}^{2-} \underset{k_{1\text{d}}}{\overset{k_{1\text{f}}}{\rightleftharpoons}} \text{NiA}$ and $\text{Ni}^{2+} + \text{HA}^- \underset{k_{2\text{d}}}{\overset{k_{2\text{f}}}{\rightleftharpoons}} \text{NiA} + \text{H}^+$ where A^{2-} represents the oxalate ion. At 25.0° and ionic strength 0.10 M, $k_{1\text{f}} = 7.5 \times 10^4\ M^{-1}\ \text{sec.}^{-1}$, $k_{2\text{f}} = 5 \times 10^3\ M^{-1}\ \text{sec.}^{-1}$, $k_{1\text{d}} = 3.6\ \text{sec.}^{-1}$, and $k_{2\text{d}} = 1.5 \times 10^3\ M^{-1}\ \text{sec.}^{-1}$. Studies at various temperatures between 5 and 35° give $\Delta H_{1\text{f}}^* = 14$ kcal. mole^{-1}, $\Delta H_{2\text{f}}^* = 14$ kcal. mole^{-1}, $\Delta S_{1\text{f}}^* = 12$ cal. deg.$^{-1}$ mole^{-1}, and $\Delta S_{2\text{f}}^* = 7$ cal. deg. mole^{-1}. The results are consistent with a model in which the rate-determining step is the elimination of a water molecule from the inner hydration shell of the nickel ion.

The question of complex and ion pair formation in electrolyte solutions has been much discussed. In cases such as the bivalent metal sulfates where the association is only moderately strong, conductance and other data give definite indication of ion pair formation. It has been suggested that the derived association constants are merely artifacts arising from the breakdown of the Debye–Hückel theory.[3] Such arguments, however, disregard the strong kinetic evidence in

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(3) E. A. Guggenheim, *Discussions Faraday Soc.*, **24**, 53 (1957).

favor of the existence of discrete species or ion pairs in the solutions.[4]

A number of complex-formation reactions have now been characterized by the determination both of thermodynamic association constants and their variation with temperature.[5] Studies of nickel oxalate yielding free energies, enthalpies, and entropies of association have been made over a range of temperature using cells incorporating hydrogen and silver–silver chloride electrodes.[6] It has been shown that the following equilibria exist in solutions containing nickel ions in the presence of lower concentrations of oxalate ions

$$\mathrm{Ni^{2+} + A^{2-} \rightleftharpoons NiA} \qquad K_1$$

$$\mathrm{H_2A \rightleftharpoons H^+ + HA^-} \qquad K_{1a}$$

$$\mathrm{HA^- \rightleftharpoons H^+ + A^{2-}} \qquad {}_aK_2$$

where A^{2-} represents the oxalate ion. The heat of formation of NiA has also been obtained with some precision by a calorimetric method[7] and it has been shown that temperature coefficient data over a sufficiently wide range of temperature are capable of giving reliable ΔH values.

Although the determination of thermodynamic properties can give much information about the type of ion association, it is clearly desirable to have kinetic data in order to be able to discuss the mechanism of the process. A knowledge of the rate constants enables comparisons to be made with other similar complex-formation reactions, and the energies and entropies of activation are of importance in the elucidation of the mechanism.

We have studied the rate of formation of nickel monooxalate both in neutral and in acid solutions. The rates are compared with those of similar reactions and with the rates of exchange of water molecules between the bulk of the solution and the inner coordination shell of the nickel ion.

Experimental

Nickel perchlorate solutions were made by dissolving nickel carbonate (Baker Analyzed Reagent) in a solution of perchloric acid prepared from the J. T. Baker Chemical Company (70%) reagent. Stock solutions were analyzed gravimetrically for nickel. Sodium perchlorate was prepared by dissolving sodium carbonate (Baker Analyzed Reagent) in concentrated perchloric acid and salting out with excess acid. Stock solutions were made from this solid with the addition of further sodium carbonate to neutralize the excess perchloric acid and were analyzed gravimetrically after evaporation. The sodium oxalate was Mallinckrodt Analyzed Reagent.

The kinetics was studied at an ionic strength of 0.10 *M* using the rapid-mixing and flow apparatus described previously[8]; absorption spectra were obtained with a Beckman DU spectrophotometer. Two series of experiments were made in which nickel perchlorate solutions were mixed with sodium oxalate solutions. In the first, sodium perchlorate was added to bring the ionic strength to the required value, and in the second, part of the sodium perchlorate was replaced by perchloric acid. Although the addition of oxalate ions produces an appreciable intensification of the color of nickel perchlorate solutions at 400 mμ, the effect was too small to be useful at the low concentrations of the present work. It was required to keep the concentration of oxalate ions as small as possible in order to limit complex formation to the mono complex. Absorbance changes in the ultraviolet in the presence of oxalate were very much larger, and the reactions were followed at wave lengths between 220 and 250 mμ and at temperatures between 5 and 35°. Stopped-flow techniques were used to study reactions with half-lives greater than 5–6 msec., and continuous-flow was used in faster reactions.

Results

The kinetic data are consistent with the assumption that the formation of NiA occurs *via* two paths

$$\mathrm{Ni^{2+} + A^{2-} \underset{k_{1d}}{\overset{k_{1f}}{\rightleftharpoons}} NiA} \qquad (1)$$

$$\mathrm{Ni^{2+} + HA^- \underset{k_{2d}}{\overset{k_{2f}}{\rightleftharpoons}} NiA + H^+} \qquad (2)$$

The rate of formation of NiA is given by

$$\frac{\mathrm{d(NiA)}}{\mathrm{d}t} = k_{1f}(\mathrm{Ni^{2+}})(\mathrm{A^{2-}}) - k_{1d}(\mathrm{NiA}) + k_{2f}(\mathrm{Ni^{2+}})(\mathrm{HA^-}) - k_{2d}(\mathrm{NiA})(\mathrm{H^+})$$

If it is assumed that the protolytic reactions reach equilibrium much faster than the metal complex reactions, then the following relations hold throughout the course of the reaction

$$(\mathrm{A^{2-}}) = \frac{K_{2a}(\mathrm{HA})}{(\mathrm{H^+})}$$

and

$$(\mathrm{H_2A}) = \frac{(\mathrm{H^+})(\mathrm{HA^-})}{K_{1a}}$$

where K_{1a} and K_{2a} are the dissociation constants of oxalic acid at an ionic strength of 0.10 *M*. At equilibrium, $\mathrm{d(NiA)}/\mathrm{d}t = 0$ and the corresponding concentrations are expressed by the equation

$$k_{1f} = \frac{(\mathrm{H^+})_{eq}[k_{1d}(\mathrm{NiA})_{eq} + k_{2d}(\mathrm{NiA})_{eq}(\mathrm{H^+})_{eq} - k_{2f}(\mathrm{Ni^{2+}})_{eq}(\mathrm{HA^-})_{eq}]}{K_{2a}(\mathrm{Ni^{2+}})_{eq}(\mathrm{HA^-})_{eq}}$$

If $(\mathrm{Ni^{2+}}) >> T_A$, where T_A is the total oxalate concentration, and $(\mathrm{H^+})$ is effectively constant, we may apply the mass balance condition

$$T_A = (\mathrm{A^{2-}}) + (\mathrm{HA^-}) + (\mathrm{H_2A}) + (\mathrm{NiA}) = (\mathrm{A^{2-}})_{eq} + (\mathrm{HA^-})_{eq} + (\mathrm{H_2A})_{eq} + (\mathrm{NiA})_{eq}$$

and the rate of complex formation becomes

$$\frac{\mathrm{d(NiA)}}{\mathrm{d}t} = \left[k_{1d}\left\{1 + \beta^{-1}\frac{(\mathrm{NiA})_{eq}}{(\mathrm{HA^-})_{eq}}\right\} + k_{2d}(\mathrm{H^+})\left\{1 + \beta^{-1}\frac{(\mathrm{NiA})_{eq}}{(\mathrm{HA})_{eq}}\right\}\right][(\mathrm{NiA})_{eq} - (\mathrm{NiA})]$$

where $\beta = 1 + K_{2a}/(\mathrm{H^+}) + (\mathrm{H^+})/K_{1a}$. The observed first-order rate constant under these conditions is therefore given by

$$k_{obsd} = \frac{0.693}{t_{1/2}} = k_{1d}\left\{1 + \frac{K_1K_{2a}(\mathrm{Ni^{2+}})}{(\mathrm{H^+})\beta}\right\} + k_{2d}(\mathrm{H^+})\left\{1 + \frac{K_1K_{2a}(\mathrm{Ni^{2+}})}{(\mathrm{H^+})\beta}\right\} \qquad (3)$$

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TABLE I

THE RATE OF FORMATION OF NiA IN NEUTRAL SOLUTIONS
Ionic strength = 0.10 M

Temp., °C.	$(Ni^{2+}) \times 10^4$, M	$T_A \times 10^5$, M	$t_{1/2}$, msec.	k_{1d}, sec.$^{-1}$
5	5.22	7.50	85	0.68
5	13.05	10.0	34	0.71
10	5.22	7.50	55	1.1
10	13.05	10.0	20	1.2
15	5.22	7.50	32	1.9
15	13.05	10.0	11	2.3
20	5.22	7.50	27	2.4
25	2.48	2.50	30	3.7
25	2.48	3.75	30	3.7
25	2.48	5.00	28	4.0
25	4.95	2.50	17	3.6
25	4.95	3.75	17	3.6
25	4.95	5.0	15	4.1
25	5.22	7.50	17	3.4
25	52.20	5.00	2.0	3.2
25	52.20	10.0	1.9	3.3
25	104.4	5.0	1.0	3.2
25	13.05	10.0	6.6	3.7
35	13.05	10.0	2.9	8.4

TABLE II

THE RATE OF FORMATION OF NiA IN ACID SOLUTIONS
Ionic strength = 0.10 M

Temp., °C.	$(Ni^{2+}) \times 10^3$, M	$T_A \times 10^3$, M	$(H^+) \times 10^2$, M	$t_{1/2}$, msec.	$k_{2d} \times 10^{-2}$, l. mole^{-1} sec.$^{-1}$
5	8.41	1.00	4.97	35	2.7
5	8.74	1.00	7.40	35	2.1
5	15.00	1.00	5.40	29	2.6
10	8.41	1.00	4.97	21	4.3
10	8.74	1.00	7.40	24	3.1
10	15.00	1.00	5.40	20	3.9
10	16.82	1.00	4.97	18	4.3
15	8.41	1.00	4.97	15	6.5
15	8.74	1.00	7.40	12	6.3
15	15.00	1.00	5.40	12	6.6
20	8.41	1.00	4.97	10	10
20	8.74	1.00	7.40	9.4	8.8
20	15.00	1.00	5.40	7.0	11
25	7.83	1.00	5.00	6.6	15
25	7.83	0.50	5.00	6.6	15
25	8.41	1.00	4.97	6.5	15
25	8.74	1.00	7.40	5.5	14
25	10.00	0.10	5.00	5.8	16
25	12.40	0.50	4.50	5.5	17
25	12.40	1.23	4.40	5.5	17
25	12.40	2.50	4.00	5.5	17
25	15.00	1.00	5.40	5.0	16
25	12.12	1.23	4.97	5.5	16

TABLE III

KINETIC PARAMETERS FOR THE FORMATION OF NiA AT 25.0° AND IONIC STRENGTH 0.10

	$Ni^{2+} + A^{2-} \rightleftharpoons NiA$	$Ni^{2+} + HA^- \rightleftharpoons NiA + H^+$
k_f[a]	7.5×10^4 l. mole^{-1} sec.$^{-1}$	5×10^3 l. mole^{-1} sec.$^{-1}$
k_d[a]	3.6 sec.$^{-1}$	1.5×10^3 l. mole^{-1} sec.$^{-1}$
E_f, kcal. mole^{-1}	15	15
E_d, kcal. mole^{-1}	12	13
ΔG_f^*, kcal. mole^{-1}	11	12
ΔH_f^*, kcal. mole^{-1}	14	14
ΔS_f^*, cal. deg.$^{-1}$ mole^{-1}	12	7
K_0, l. mole^{-1}	13	2.0
k_{10}, sec.$^{-1}$	6×10^3	3×10^3
ΔG_0, kcal. mole^{-1}	−1.5	−0.4
ΔS_0, cal. deg.$^{-1}$ mole^{-1}	15	7.8
ΔH_0, kcal. mole^{-1}	3.1	1.9
ΔH_{10}^*, kcal. mole^{-1}	11	12
ΔS_{10}^*, cal. deg.$^{-1}$ mole^{-1}	−3	−0.8

[a] Subscripts f and d refer to formation and decomposition reactions, respectively.

where K_1 is the association constant for reaction 1 at $I = 0.10\ M$. Experiments in which sodium oxalate solutions were mixed with perchloric acid in the flow apparatus confirmed the validity of the assumption that the protolytic equilibria were maintained throughout the reaction.

In neutral solutions, calculation of the concentrations of ionic species from the measured pH values shows (HA^-) to be only about 1% of (A^{2-}), and eq. 3 becomes

$$\frac{0.693}{t_{1/2}} = k_{1d}[1 + K_1(Ni^{2+})] \qquad (4)$$

The results are summarized in Table I in which $t_{1/2}$ values were obtained from the excellent first-order rate plots of the experimental data. Activity coefficients, f_z, of z-valent ions at $I = 0.10\ M$ were calculated from the Davies equation[9]

$$\log f_z = -Az^2[I^{1/2}/(1 + I^{1/2}) - 0.2I]$$

with the appropriate Debye–Hückel constant A and were used to correct the thermodynamic equilibrium constants K_{1a}, K_{2a}, and K_1 at each temperature. Values of the rate constant k_{1d} are given in Table I and it is seen that eq. 4 is closely obeyed over a range of (Ni^{2+}), the rate being independent of T_A under these conditions.

A number of experiments were also made in the presence of perchloric acid and the results are summarized in Table II. Potentiometric measurements showed the pH to be constant to within 0.01 unit during the reactions, and under these conditions the results were analyzed using eq. 3 and the k_{1d} values of Table I. $t_{1/2}$ values were obtained from first-order rate plots, and in Table II k_{2d} is probably accurate to ±10%. The last experiment of Table II at 25° refers to a rate of dissociation in which the nickel oxalate solution was mixed with a perchloric acid–sodium perchlorate solution and, once again, the k_{2d} value is in good agreement. The concentration range available for these experiments was limited by the high rate of the reaction.

Values of E_a, ΔG^*, ΔH^*, and ΔS^* calculated from the slopes of plots of log k_{1d} and log k_{2d} against $1/T$, and the equations

$$k = \frac{RT}{Nh} e^{-\Delta G^*/RT} \text{ and } \Delta G^* = \Delta H^* - T\Delta S^*$$

are shown in Table III. k_{1f} and k_{2f} were obtained from the relationships $k_{1f} = K_1 k_{1d}$ and $k_{2f} = K_1 K_{2a} k_{2d}$. The net heat change for reaction 2 is given by $\Delta H_1 - \Delta H_{2a}$ where ΔH_1 is the heat of association [reaction 1] and ΔH_{2a} that of the second dissociation step of oxalic

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(9) C. W. Davies, *J. Chem. Soc.*, 2093 (1938).

acid at $I = 0.10\ M$. ΔH_1 (3.0 kcal. mole^{-1}) was calculated from that at zero ionic strength, 0.15 kcal. mole^{-1},[3] using the expression

$$\Delta H_1 = \Delta H_0 - 3RT^2\left[\frac{1}{D}\frac{\partial D}{\partial T} + \frac{1}{T}\right]\ln f_z$$

The value of $1/D\ \partial D/\partial T$ where D is the dielectric constant of the solvent was obtained from the data of Åkerlöf.[10] ΔH_{2a} (1.0 kcal. mole^{-1}) was obtained from a plot of log K_{2a} against $1/T$ using the data of Pinching and Bates[11] corrected to an ionic strength of 0.10 M.

Discussion

There is considerable evidence supporting the view that the rates of complex-formation reactions are controlled primarily by the rate of loss of a water molecule from the inner coordination shell of the cation.[4,12] For example, Hamm and co-workers[13] have shown that the activation energies for complex formation of $Cr(H_2O)_6^{3+}$ with acetate, oxalate, malonate, citrate, and *o*-phthalate were all similar and not too different from the activation energy for water exchange on $Cr(H_2O)_6^{3+}$.[14] They proposed that the common slow step in these reactions was the loss of a water molecule from the inner coordination shell of the chromium(III) and that in the case of the bidentate ligands the subsequent steps leading to the chelated structures were relatively rapid. It has also been found that the rates at which $Fe(H_2O)_6^{3+}$ forms complexes with a number of inorganic ligands are similar, and it has been proposed that in these systems, too, the common slow step involved the loss of a coordinated water molecule.[15] Very striking evidence for this model of complex formation has been presented by Connick and co-workers.[16] They have shown that the rates of exchange of water molecules between the bulk of the solution and the inner coordination shells of Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+} correlated well with the rates of formation of the sulfate complexes of the cations determined by Eigen and Tamm.[17]

For purposes of discussing our results we shall adopt the reaction scheme used by Hammes and Steinfeld[18,19] in their studies of the complex formation of Ni(II) and Co(II) with ligands containing nitrogen atoms. The reaction of Ni(II) with oxalate may be considered to occur in the following steps

$$Ni(H_2O)_6^{2+} + A^{2-} \rightleftharpoons (H_2O)_5Ni(H_2O)A \qquad K_0$$

$$(H_2O)_5Ni(H_2O)A \underset{k_{01}}{\overset{k_{10}}{\rightleftharpoons}} (H_2O)_5NiA + H_2O \qquad K_{10}$$

$$(H_2O)_5NiA \underset{k_{02}}{\overset{k_{20}}{\rightleftharpoons}} (H_2O)_4NiA + H_2O \qquad K_{20}$$

where $(H_2O)_5NiA$ represents a half-bonded intermediate, the hydration of A^{2-} is omitted, and it is assumed that equilibrium in the first step is attained rapidly. The rate of formation of $(H_2O)_4NiA$ is given by

$$\frac{d[(H_2O)_4NiA]}{dt} = k_{20}[(H_2O)_5NiA] - k_{02}[(H_2O)_4NiA]$$

If the steady-state assumption for the concentration of $(H_2O)_5NiA$ is made, it follows that

$$k_{1f} = \frac{k_{20}k_{10}K_0}{k_{01} + k_{20}} \text{ and } k_{1d} = \frac{k_{02}k_{01}}{k_{01} + k_{20}}$$

If $k_{20} >> k_{01}$, then $k_{1f} = k_{10}K_0$ and $k_{1d} = k_{01}/K_{20}$. It is seen that under these conditions the formation of $(H_2O)_4NiA$ is determined primarily by the loss of a coordinated water molecule. Following Hammes and Steinfeld[18,19] we have calculated values of K_0 using the Debye–Hückel interaction potential, and these values together with the derived parameters for the nickel oxalate reactions are presented in Table III. ΔS_0 was assumed equal to $-19.4z_1z_2/a$ with a, the distance of closest approach of the ion-pair partners, equal to 5 Å.; the other parameters are defined by $\Delta H_0 = \Delta G_0 - T\Delta S_0$, $\Delta H_{10}^* = \Delta H_f^* - \Delta H_0$, and $\Delta S_{10}^* = \Delta S_f^* - \Delta S_0$.

The values of k_{10} determined in this work are compared with other estimates in Table IV. It will be seen that the various determinations of k_{10} agree within one order of magnitude, which is rather remarkable in view of the large differences in the natures of the ligands and the assumptions made in calculating K_0.

The heats and entropies of activation may be compared with the corresponding quantities for water exchange on Ni^{2+} determined by Swift and Connick.[16] These workers established that the rate constant for the exchange of water molecules between the bulk of the solution and the inner coordination shell of Ni^{2+} is 2.7×10^4 sec.$^{-1}$ at 25.0° and that the heats and entropies of activation for the exchange are 11.6 kcal. mole^{-1} and 0.6 cal. deg.$^{-1}$ mole^{-1}, respectively. It

TABLE IV

CALCULATED FIRST-ORDER RATE CONSTANTS FOR THE FORMATION OF MONO COMPLEXES OF NICKEL(II) AT 25.0°

Ionic strength = 0.10–0.15 M

Ligands	$10^{-3}k_{10}$, sec.$^{-1}$
Monodentate	
Imidazole[a]	16
Thiocyanate[b,c]	~6
Sulfate[d]	10
Bidentate	
Oxalate	6
Bioxalate	3
Glycine[a]	9
Diglycine[a]	12
Triglycine[e]	4.6

[a] Reference 18. [b] A. G. Davies and W. M. Smith, *Proc. Chem. Soc.*, 380 (1961). [c] Ionic strength = 0.5 M. The value of k_{10} is uncertain because of the large ionic strength correction made in the calculation of K_{10}. [d] Reference 17. [e] Reference 19.

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can be seen that these values are very similar to k_{10}, ΔH_{10}^*, and ΔS_{10}^*, respectively, given in Table III, providing additional evidence for the view that the rates of complex formation are controlled primarily by the rate of loss of a coordinated water molecule from the cation.[4,12,16]

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Oxalate Exchange in the Bisoxalatoplatinate(II) Ion

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The kinetics of the exchange between bisoxalatoplatinate(II) ion and free oxalate have been examined in weakly acidic aqueous medium. Under the conditions employed (25°, pH 3.6–6.8, ionic strength = 0.17–0.55) the exchange proceeds very slowly according to the two-term rate law: oxalate exchange rate = $k_1[Pt(C_2O_4)_2^{-2}] + k_2[Pt(C_2O_4)_2^{-2}][\text{oxalate}]$. Both rate constants are essentially independent of hydrogen ion concentration; k_1 is also independent of ionic strength while k_2 increases with increasing ionic strength. Typical values for the constants at 25° are: pH 4.7 (oxalate buffer), ionic strength = 0.170, $k_1 = 1.6\ (\pm 0.2) \times 10^{-9}$ sec.$^{-1}$, $k_2 = 4.6\ (\pm 0.3) \times 10^{-7}\ M^{-1}$ sec.$^{-1}$. The results are interpreted in terms of a mechanism involving intermediates containing monodentate oxalate ligands.

Many workers[3] have investigated substitution reactions of monodentate ligands in square complexes. In general these reactions have been found to exhibit a combination of first- and second-order rate behavior, considerable evidence existing to imply that the first-order term involves solvent participation. Also, exchange reactions between free and coordinated oxalate have been reported for various metal complexes.[4–9] To the best of our knowledge, however, this is the first reported kinetic study of oxalate exchange in a square complex.

Experimental

(A) **Materials.**—Potassium bisoxalatoplatinate(II) dihydrate was prepared by the reaction of potassium hexachloroplatinate(IV) (J. Bishop and Co.) with excess oxalate.[10] The resultant salt was recrystallized three times from distilled water, washed with absolute alcohol, and dried at 70°. Portions of the salt were analyzed for carbon and hydrogen by the usual procedure, the residue being heated in a stream of carbon dioxide and weighed as platinum plus potassium carbonate.[11] The potassium content of a solution of the salt was estimated by passing measured volumes through Dowex 50W-X8 ion-exchange resin in the H^+ form and titrating the effluent solution with standard sodium hydroxide using methyl red as an indicator. A typical analysis is given. *Anal.* Calcd. for $K_2Pt(C_2O_4)_2 \cdot 2H_2O$: K, 16.11; Pt, 40.20; C, 9.89; H, 0.82. Found: K, 15.89; Pt, 40.6; C, 10.12; H, 0.94. For the exchange experiments the potassium salt was quantitatively converted into the more soluble sodium salt by treatment of an aqueous solution at 80° with Dowex 50W-X8 cation-exchange resin in the sodium form.

Sodium oxalate with a carbon-14 activity of ~1.7 μcuries per mg. was obtained from International Chemical and Nuclear Corporation. Water was obtained by heating ordinary distilled water with $KMnO_4$ and NaOH and redistilling in a Barnstead S-1 apparatus. All other materials employed were of reagent grade.

(B) **Preparation of Exchange Solutions.**—Reactant solutions were prepared by mixing appropriate volumes of sodium bisoxalatoplatinate(II) solution, 0.050 *M* oxalate solution[12] with a carbon-14 activity of ~0.5 μcurie per ml., sodium nitrate solution (for ionic strength adjustment), and distilled water. In some cases inactive oxalate solution and/or a phosphate buffer solution was also added. The reaction was studied at three different pH values, namely, 3.6, 4.7, and 6.8. In the first two cases it was possible to use the active oxalate solution as a buffer, and it was ascertained by pH measurements on similar but inactive solutions that variation of the uncomplexed oxalate concentration (from 1×10^{-3} to 2×10^{-2} *M*) in the various exchange solutions did not change the pH by more than ±0.1 unit. For the highest pH it was necessary to buffer the exchange solutions by the addition of an appropriate phosphate solution. For more strongly acidic conditions (pH <3) we were unable to obtain consistent kinetic results, and it was also visually apparent that a reaction other than oxalate exchange was taking place; possibly polymerization of the bisoxalatoplatinate(II) ion.[13] Reactant solutions were stored in the dark at a temperature of 25.00 ± 0.05°.

(C) **Exchange Procedure and Calculations.**—In a given experimental run the amount of exchange was determined by duplicate determinations after three periods of time, usually ~100, 200, and 300 hr. Quenching was achieved by adding an aliquot of the reactant solution to an equal volume of 10% potassium chloride solution and cooling to 0°. Under these conditions potassium bisoxalatoplatinate(II) dihydrate is precipitated in 2–3 hr.[14] The precipitate was filtered and washed with ice-cold

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[1] Supported by the National Science Foundation under Grant G11283.

[2] Presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

[3] See, for example: (a) R. L. Rich and H. Taube, *J. Phys. Chem.*, **58**, 1 (1954); (b) D. Banerjea, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **79**, 4055 (1957); (c) A. A. Grinberg, *Russ. J. Inorg. Chem.*, **4**, 139 (1959); (d) H. B. Gray, *J. Am. Chem. Soc.*, **84**, 1548 (1962); (e) S. J. Lokken and D. S. Martin, Jr., *Inorg. Chem.*, **2**, 562 (1963).

[4] F. A. Long, *J. Am. Chem. Soc.*, **61**, 570 (1939).

[5] D. R. Llewellyn and A. L. Odell, *Proc. Australian At. Energy Symp.*, 623 (1958).

[6] D. Barton and G. M. Harris, *Inorg. Chem.*, **1**, 251 (1962).

[7] F. A. Johnson and E. M. Larsen, *ibid.*, **1**, 159 (1962).

[8] F. D. Graziano and G. M. Harris, *J. Phys. Chem.*, **63**, 330 (1959).

[9] K. V. Krishnamurty and G. M. Harris, *ibid.*, **64**, 346 (1960).

[10] P. Pascal, "Traité de Chemie Minérale," Masson et Cie., Paris, 1928, p. 672.

[11] Analyses by S. M. Nagy, Microchemical Laboratory, Massachusetts Institute of Technology, Cambridge, Mass.

[12] Oxalate concentrations refer to the total concentrations of all uncomplexed oxalate species in solution.

[13] K. Krogmann and P. H. Dodel, Proceedings of the 7th International Conference on Coordination Chemistry, 1962, p. 67.

[14] Analysis of a carefully dried precipitate confirmed the formula $K_2Pt(C_2O_4)_2 \cdot 2H_2O$. This result and observations that spectra of solutions of the platinum complex remain essentially constant for 1 or 2 weeks, both in the presence and absence of phosphate buffer, support the view that aquation is unimportant and that no significant amounts of phosphate become incorporated in the coordination sphere of the platinum.