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## Substitution Reactions of Oxalato Complex Ions. IV. Oxalate Exchange and Aquation Reactions of the Trisoxalatorhodium(III) Complex

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The oxalate exchange and aquation reactions of  $\text{Rh}(\text{C}_2\text{O}_4)_3^{-3}$  ion were studied in water solutions of controlled acidity. Both reactions are first order in (complex ion). The exchange reaction was studied over the range  $2 < \text{pH} < 8$ . Its pseudo-first-order rate constant is given by the expression:  $k_{\text{ex}} = k_{\text{H}_2\text{O}} + k_{\text{H}^+}(\text{H}^+) + k_{\text{OH}^-}(\text{OH}^-)$ . At  $133.2^\circ$ , the values of the constants are  $6 \times 10^{-6} \text{ sec.}^{-1}$ ,  $1.5 \times 10^{-2} M^{-1} \text{ sec.}^{-1}$ , and  $1.3 \times 10^2 M^{-1} \text{ sec.}^{-1}$ , respectively. The pseudo-first-order rate constant of aquation was determined within the range  $0.25 M < (\text{HClO}_4) < 2.5 M$ . It obeys the relation  $k_{\text{aq}} = k_{\text{H}^+}(\text{H}^+)$  at low acidity, but  $k_{\text{H}^+}$  increases somewhat at high acidity, in the manner typical of an activity effect. The product of aquation is the anion  $\text{Rh}(\text{C}_2\text{H}_4)_2(\text{H}_2\text{O})_2^-$ , and in  $1 M \text{ HClO}_4$  at  $79.5^\circ$ ,  $k_{\text{H}^+} = 1.5 \times 10^{-4} M^{-1} \text{ sec.}^{-1}$ . At  $\text{pH} > 8$ , the trisoxalato complex decomposes into oxalate and hydrated rhodium(III) oxide, there being no oxidation-reduction involved. Possible mechanisms of the various reactions are discussed.

Earlier work<sup>2-4</sup> has shown that the very slow ligand displacement reactions of inner orbital oxalato complexes of Co(III) and Cr(III) may under suitable conditions be subjected to detailed kinetic study. The investigation of the trisoxalato-cobalt(III) compound<sup>2</sup> was complicated by its well known intramolecular electron-transfer process.<sup>5,6</sup> A study now has been made of a second  $d^6$ -type trisoxalato complex ion,  $\text{Rh}(\text{C}_2\text{O}_4)_3^{-3}$ , in which the central metal ion has no readily accessible lower oxidation state. The oxidation-reduction complication thus avoided, a detailed comparison with the ligand substitution kinetics of the  $d^3$ -species,  $\text{Cr}(\text{C}_2\text{O}_4)_3^{-3}$ , now is possible.

Previous reaction rate studies of Rh(III) complexes have indicated the great resistance of these compounds to ligand replacement. For example, the acid hydrolysis rate of  $\text{Rh}(\text{NH}_3)_5\text{Br}^+$  is at least an order of magnitude slower than that of the corresponding Cr(III) or Co(III) reactions.<sup>7</sup> The unusual stability to racemization of optically active  $\text{K}_3\text{Rh}(\text{C}_2\text{O}_4)_3$  is further evidence of the barrier to ligand-metal bond breakage in this class of compounds, although racemization and

ligand exchange need not necessarily proceed by identical or even closely related mechanisms.<sup>8</sup>

The preceding kinetic studies of the reactions of the  $\text{Cr}(\text{C}_2\text{O}_4)_3^{-3}$  ion showed<sup>2,3</sup> that several types of oxalate displacement were involved, including acid- and base-catalyzed reactions. Also observed were zero- and first-order dependences of the oxalate exchange reaction on total free oxalate concentration. This partial dependence of the rate on the free basic ligand concentration is of special significance, since this complex is one for which a simple conjugate-base mechanism is not possible. In this it contrasts with the octahedral diamine complexes, concerning which there has been such a vigorous controversy.<sup>9,10</sup> The present work indicates that the  $\text{Rh}(\text{C}_2\text{O}_4)_3^{-3}$  species does not exhibit a variation of exchange rate with free oxalate concentration. Its characteristic resistance to any kind of ligand substitution is demonstrated, and possible mechanisms of the reactions observed are discussed.

### Experimental

**A. Preparation and Analysis of Compounds.**—Potassium trisoxalatorhodium(III) was prepared by Werner's method,<sup>11</sup> starting with water-soluble  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ . The rhodium(III) complex was freed of excess potassium acid oxalate by repeated precipitation with alcohol, followed by several recrystallizations from cold water. The red

(1) Work done by D. Barton as part of the Ph.D. requirement of University of Buffalo, 1959. Complete report available from University Microfilms, Ann Arbor, Michigan.

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

(3) K. B. Krishnamurty and G. M. Harris, *ibid.*, **64**, 346 (1960).

(4) S. Sheel, D. Meehan, and G. M. Harris, *Inorg. Chem.*, **1**, 170 (1962).

(5) A. W. Adamson, H. Ogata, J. Grossman, and R. Newbury, *J. Inorg. & Nuclear Chem.*, **6**, 319 (1958).

(6) F. S. Dainton, G. S. Lawrence, W. Schneider, D. R. Stranks, and M. S. Vaidya, Proc. Intern. Conf. on Radioisotopes in Sci. Research, Paris, 1957, No. UNESCO/NS/RIC211.

(7) J. Lewis and R. G. Wilkins (Editors), "Modern Co-ordination Chemistry." Interscience Publishers, Inc., New York, N. Y., 1960, p. 127 *et seq.*

(8) K. B. Krishnamurty and G. M. Harris, *Chem. Revs.*, **61**, 229 (1961).

(9) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions." John Wiley and Sons, Inc., New York, N. Y., 1958, Ch. III.

(10) C. K. Ingold, "Substitution of Elements Other Than Carbon." Weizmann Science Press of Israel, Jerusalem, 1959, Ch. I.

(11) A. Werner and J. Poupardin, *Ber.*, **47**, 1955 (1914).

crystals thus obtained (reported<sup>12</sup> to be  $K_3Rh(C_2O_4)_3 \cdot 4.5H_2O$ ) disintegrate in the atmosphere at room temperature, losing about 10% of their weight. Over  $CaCl_2$  at room temperature the weight loss is 11.8%, yielding a yellow stable monohydrate as the final product. This was the material used in all subsequent experiments. It was analyzed for rhodium by hydrogen reduction<sup>11</sup> and for  $C_2O_4^{2-}$  by two alternative procedures: (A) heating a sample of the salt with 0.1 *N* NaOH to precipitate the rhodium as hydrated oxide, centrifuging, and titrating the filtrate with standardized acidic  $KMnO_4$  solution; (B) direct slow titration of a solution of the salt in sulfuric acid with standard  $KMnO_4$ . Carbon was determined by standard semi-micro combustion procedure. *Anal.* for  $K_3Rh(C_2O_4)_3 \cdot H_2O$ : Rh, 20.5;  $C_2O_4$ , 52.6; C, 14.3. Found: Rh, 20.6;  $C_2O_4$ , 52.0 (A), 52.6 (B); C, 14.0. High-activity C-14 oxalic acid obtained from a commercial source was diluted with inactive  $K_2C_2O_4$  to produce a 0.120 *M* stock solution of convenient activity for the experiments.

**B. Apparatus and Technique.** (1) **Exchange Reactions.**—The procedure used to follow the progress of the oxalate exchange was similar to that reported previously for analogous ligand exchange studies.<sup>2-4</sup> Thin samples of solid calcium oxalate monohydrate were used for the radioassays, which served to follow the loss of radioactivity by the uncomplexed oxalate. Sample weights throughout a given experiment were sufficiently close to one another to make self-absorption and self-scattering corrections unnecessary. Since the exchange reaction is exceedingly slow at room temperature, stock solutions of the required reaction mixtures could be prepared and used at leisure. The ionic strength of all such solutions was adjusted to 0.12 with  $NaClO_4$ . Samples of about 5 ml. of stock solution were placed in cylindrical Pyrex vessels (*ca.* 1.2 × 13 cm.), frozen at Dry Ice temperature, pumped down to high vacuum, and sealed off before placing in the constant temperature bath. Acidity determinations were made at room temperature on a Beckman Model G *pH* meter, and absorption spectra were measured using Beckman Models DU and DK2 spectrophotometers.

(2) **Acid-Catalyzed Aquation Reactions.**—Complex ion solutions containing any other needed reagents and, separately, perchloric acid solutions, were heated to the reaction temperature, then rapidly mixed. The course of the reaction was followed by means of the change in *D*, the optical density at 400 *mμ*, the wave length of the maximum in the absorption curve of  $K_3Rh(C_2O_4)_3$ . Samples were withdrawn at appropriate intervals from the stoppered reaction vessels, cooled to room temperature, and placed in the spectrophotometer cell for measurement. The pseudo-first-order rate constants were computed in the usual manner from the linear plots of the function  $\log [(D_\infty - D_0)/(D_\infty - D_t)]$  vs. time.

## Results

**A. Stability Studies of Exchange Systems.**—Trisoxalatorhodium(III) cation is remarkably resistant to decomposition at 133° in aqueous solution near *pH* 4. No change in its absorption spectrum between 230 and 400 *mμ* was detectable

in a typical exchange solution after 90 hr. at the elevated temperature. There was, however, a slight increase in *pH*; in a 0.1 *M* oxalate solution containing complex ion and perchlorate, the drift was from 3.74 to 3.86 in 42 hr. But the same acidity change occurred in oxalate solutions containing no complex ion, so it could be ascribed to slow thermal decomposition of  $K_2C_2O_4$  itself. The approximate rate of this decomposition, determined by precipitation of residual oxalate as calcium oxalate and titration with  $KMnO_4$ , was such that not more than 2.5% of the oxalate present would decompose during the longest exchange half-times. Corrections for this fact therefore were ignored, as were those for the *pH* drift. Near *pH* 4, the exchange rate will be seen to be nearly independent of acidity in any case. A final check in this *pH* range was made by running duplicate exchange experiments except that one was preheated for 24 hr. at 133° prior to addition of radioactive oxalate. Identical exchange rates were obtained.

In the weakly buffered solutions above *pH* 5, the acidity changes were on occasion large and erratic, varying from zero to as much as 0.9 *pH* unit in successive experiments. However, no changes in the visible spectrum of the complex ion were observable, and potassium oxalate solutions not containing complex ion were subject to the same type of erratic *pH* behavior. The acidity changes in this *pH* region also are ascribable, therefore, to oxalate decomposition. Around *pH* 7, these changes are not appreciable and their effect on the exchange could be ignored, but when the *pH* is maintained at 8.4 with borax buffer slow decomposition of the complex itself occurs, as evidenced by a growth of turbidity and a change in the spectrum. In more strongly basic solution, such as in 0.1 *N* NaOH, the decomposition of complex is rapid, yielding as products alkali oxalate and hydrated rhodium(III) oxide precipitate.

Near *pH* 2, oxalate solutions again undergo slow decomposition accompanied by *pH* changes. In the presence of the complex ion, however, the acidity changes are of a different type, as illustrated in these data, taken at 133° ((complex) =  $5.3 \times 10^{-3}$  *M*; (oxalate) =  $9.6 \times 10^{-3}$  *M*)

Time, hr.	0.00	1.08	2.33	4.00
<i>pH</i>	2.06 <sup>a</sup>	2.16	2.16	2.16
Optical density (400 <i>mμ</i> )	0.84	0.76	0.75	0.76

<sup>a</sup> Adjusted with perchloric acid.

(12) M. Delépine, *Anales fis. y quim.* (Madrid), **27**, 490 (1929).

It is clear that a relatively rapid pre-equilibration takes place, accompanied by parallel  $pH$  and optical density shifts. This undoubtedly is the result of partial acid-catalyzed aquation of the trisoxalato ion, to be considered in greater detail below. In the present example, the ratio of  $Rh(C_2O_4)_3^{-3}$  to  $Rh(C_2O_4)_2(H_2O)_2^-$  at equilibrium was estimated to be about 7:2. Similar acidity and spectrum changes were found in the other "acid" exchange experiments ( $2 < pH < 3$ ), but in these the fraction of diaquo species present was much smaller and could be ignored in the exchange rate calculations.

**B. Oxalate Exchange Experiments.**—The exchange data were analyzed in the conventional way,<sup>2</sup> employing the equation<sup>13</sup>

$$R = \left( \frac{0.693}{t_{1/2}} \right) \times \left( \frac{3ab}{3a + b} \right) \quad (a)$$

The results are given in Table I. The  $pH$  values quoted are the average of the room tem-

TABLE I  
RATE OF EXCHANGE OF FREE OXALATE WITH  $Rh(C_2O_4)_3^{-3}$   
ION AT 133.2°

$pH$	(Complex) $M \times 10^3$	(Free oxalate) $M \times 10^3$	$10^3 R/a$ (obsd.) sec. <sup>-1</sup>	$10^3 R/a$ (calcd.) sec. <sup>-1</sup>
2.11	5.3	9.6	16 <sup>a</sup>	13
2.71	5.3	4.8	3.2	3.6
2.71	5.3	9.6	3.5	3.6
2.73	10.6	9.6	3.2	3.4
2.74	4.85	7.2	3.1	3.3
3.69	5.3	2.4	0.5	0.6
3.70	5.3	4.8	.5	.6
3.82	5.3	9.6	.5	.6
3.69	5.3	14.4	.6	.6
3.64	5.3	24.0	.7	.6
3.75	10.6	9.6	.6	.6
3.65	16.2	9.6	.6	.6
4.18	4.85	7.2	.6	.6
(5-6?)	4.85	7.2	(1.3)	<sup>b</sup>
(6-7?)	4.85	7.2	(2.6)	<sup>b</sup>
7.00	10.6	9.6	1.9	1.9
7.15	5.3	4.8	2.3	2.4
7.25	5.3	9.6	2.9	2.9
7.30	4.85	7.2	3.3	3.4
7.40	5.3	19.2	3.5	3.8
8.40	4.85	7.2	>10 <sup>c</sup>	(35)

<sup>a</sup> Corrected for equilibrium decomposition of trisoxalato to bisoxalato diaquo complex at this  $pH$ .<sup>13</sup> <sup>b</sup>  $pH$  determinations very unsatisfactory in these two experiments so no calculation attempted. <sup>c</sup> Only a lower limit possible since heterogeneous decomposition at this  $pH$  obscured the result.

(13) The symbols  $a$  and  $b$  refer to the total equilibrium concentrations of the exchanging species (complex ion and free oxalate ion, respectively), corrected for any changes from their initial values due to chemical equilibration.

perature readings made initially and at the exchange half-time of each experiment. They are not necessarily a true measure of the acidity at reaction temperature, nor are they strictly comparable in different buffer regions at different temperatures. In a given narrow  $pH$  range, however, it may be reasonably assumed that the recorded  $pH$  values give a good indication of the relative acidities of the reaction solutions. The figures in the last column of the table were calculated using a rate law of the form

$$\text{Rate} = (\text{complex}) [k_{H_2O} + k_{H^+}(H^+) + k_{OH^-}(OH^-)] \quad (b)$$

The "best-fit" values of the constants used in calculating  $R/a$  were  $k_{H_2O} = 6.0 \times 10^{-6} \text{ sec.}^{-1}$ ,  $k_{H^+} = 1.5 \times 10^{-2} M^{-1} \text{ sec.}^{-1}$ , and  $k_{OH^-} = 1.3 \times 10^2 M^{-1} \text{ sec.}^{-1}$ .

**C. Acid-Catalyzed Aquation Experiments.**—In strong perchloric acid solution the loss of one mole of oxalate per formula weight of trisoxalatorhodium(III) complex was established by means of oxalate precipitation and permanganate titration. The aquated product is undoubtedly a *cis-trans* equilibrium mixture of  $Rh(C_2O_4)_2(H_2O)_2^-$  ions, as is found on similar treatment of the analogous chromium(III) salt.<sup>3</sup> Separation and identification of the diaquorhodium species was not attempted in this research. The consistent linearity of the rate-determination plots proves that the reaction is simple first order in parent complex ion concentration. This was confirmed by the fact that the slope of the plots is independent of the initial concentration of complex under constant acidity conditions. Separate experiments showed that the rate is unaffected by addition of excess sodium perchlorate or oxalic acid. The variation of the rate as a function of perchloric acid concentration at 79.5° is shown in Fig. 1, expressed as the pseudo-first-order rate constant  $k_{aq} = k_{H^+}(H^+)$ . In 1  $M$   $HClO_4$ ,  $k_{H^+} = 1.5 \times 10^{-4} M^{-1} \text{ sec.}^{-1}$ .

## Discussion

The interpretation of the observed rate data is subject to the usual ambiguities concerning the role of the solvent and the exact identity of the rate-determining bond-ruptures. A mechanism similar in some respects to that used to discuss the trisoxalatochromium(III) reactions<sup>2,3</sup> is proposed, in reactions 1-5.

Reaction 1 probably goes well over toward completion in aqueous solution, since there is

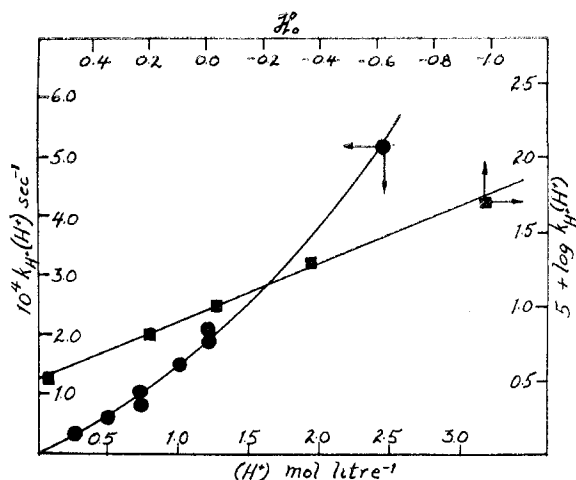
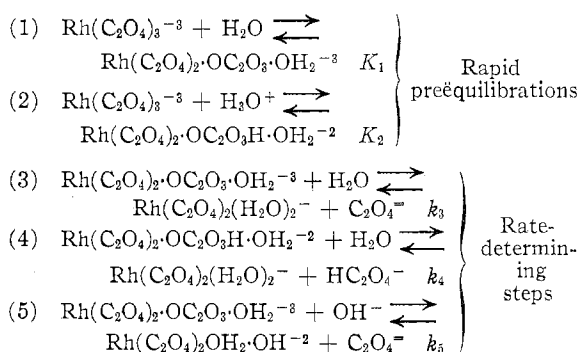


Fig. 1.—Variation of pseudo-first-order rate constant of aquation of  $\text{Rh}(\text{C}_2\text{O}_4)_3^{-3}$  ion with acid concentration: circles, plot of  $k_{\text{H}^+}(\text{H}^+)$  vs.  $(\text{H}^+)$ ; squares, plot of  $\log k_{\text{H}^+}(\text{H}^+)$  vs.  $\mathcal{H}_0$  (the Hammett acidity function).



evidence from a recent n.m.r. study<sup>14</sup> that even in the solid crystalline hydrate,  $\text{K}_3\text{Rh}(\text{C}_2\text{O}_4)_3\cdot 4.5\text{H}_2\text{O}$ , half of the trisoxalatorhodium(III) ions are mono-aquated, with one end of the oxalate group displaced. The mechanism allows for the same kind of proton-pre-equilibration acid dependence as proposed for the trisoxalatochromium(III) analog.<sup>3</sup> Support for this view comes from a recent study<sup>15</sup> of the deuterium solvent isotope effect on the aquation of the rhodium(III) complex, in which the expected large  $k_{\text{D}}/k_{\text{H}}$  ratio is observed (3.7 at 50° in 0.97 M  $\text{HClO}_4$ ). On the other hand, the present mechanism omits the second proton-catalyzed step found necessary to explain the trisoxalatochromium(III) data. This step is excluded because the observed upward curvature of the plot of rhodium(III) complex aquation rate vs.  $(\text{H}^+)$  (Fig. 1) cannot be fitted satisfactorily by a simple  $k_{\text{aq}} = k'(\text{H}^+) + k''(\text{H}^+)^2$  assumption. It is noteworthy, however,

that a linear Hammett function plot<sup>16,17</sup> is obtainable, as shown in Fig. 1. This is, of course, the expected behavior for a proton-pre-equilibration mechanism of acid catalysis in strongly acid solutions.

Rate-determining reactions 3, 4, and 5 are considered to be completely reversible<sup>18</sup> under all conditions not leading to precipitation of rhodium oxide. Assuming that reactions 1 and 2 shift only slightly to the right, the experimental rate constants are identifiable as:  $k_{\text{H}_2\text{O}} = k_3K_1$ ,  $k_{\text{H}^+} = k_4K_2$ , and  $k_{\text{OH}^-} = k_5K_1$ . The mechanism requires that  $k_{\text{H}^+}$  for the exchange reaction should be identical with  $k_{\text{H}^+}$  obtained in the aquation study. A temperature-dependence study of the latter<sup>15</sup> within the range 50 to 80° leads to the rate constant expression:  $k_{\text{H}^+} = 8.0 \times 10^{12} \exp(-27,000/RT)$ . Extrapolation of this to 133° predicts a value for  $k_{\text{H}^+}$  at unit acidity of  $2.3 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ , in good agreement with the experimental exchange figure of  $1.5 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ , considering the wide temperature gap, the uncertainties in the acidity measurements at the high temperature, and the activity effect on  $k_{\text{H}^+}$  as determined by aquation in strongly acid solution.

A noteworthy feature of the present study is the apparent lack of dependence of the oxalate exchange reaction on free oxalate ion concentration, a sharp contrast with the findings for the trisoxalatochromium(III) complex, particularly in acid solution.<sup>2</sup> A possible explanation is that the ligand-dependent process necessitates a concerted reaction with participation of a six-coördinate intermediate of the form:  $\text{M}(\text{C}_2\text{O}_4)_2(\text{OC}_2\text{O}_3\text{H})(\text{OC}_2\text{O}_3)^{-4}$ . When  $\text{M} = \text{Rh}(\text{III})$ , substitution of  $\text{C}_2\text{O}_4^{=}$  for  $\text{H}_2\text{O}$  to produce this intermediate may be completely inhibited due to the great stability of the aquorhodate resulting from reaction 1 or 2. This view accords with the finding that the rate of water exchange of hexaaquorhodium(III) ion is hundreds of times slower than that of the corresponding Cr(III) ion under comparable conditions.<sup>19</sup> An alternative hypothesis

(16) F. A. Long and M. A. Paul, *Chem. Revs.*, **57**, 935 (1957).

(17) The function used is  $H_0$  when it should in fact have been  $H^-$ , at present an undetermined function. Recent work (M. W. Fuller, private communication) suggests that  $H^-$  values differ from  $H_0$  in the acidity range shown by a relatively constant intercept, thus not greatly affecting the slope. The deviation of the observed slope (0.8) from unity is in the expected direction for reaction at elevated temperature.<sup>16</sup>

(18) An experiment was done in which the "infinite time" product of an acid-catalyzed aquation run was neutralized with NaOH to pH 4. The reverse of reaction 4 occurred rapidly and completely, as evidenced spectrophotometrically.

(19) W. Plumb and G. M. Harris, manuscript in preparation.

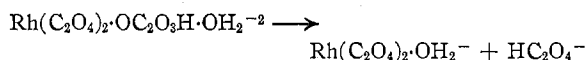
(14) A. L. Porte, H. S. Gutowsky, and G. M. Harris, *J. Chem. Phys.*, **34**, 66 (1961).

(15) K. V. Krishnamurty, *Inorg. Chem.*, **1**, in press (1962).

is that the  $d^3$  Cr(III) compound reacts *via* the seven-coördinate activated complex  $M(C_2O_4)_2(OC_2O_3H)(OC_2O_3)(OH_2)^{-4}$  at a rate comparable to that of the other exchange paths available, which the  $d^6$  Rh(III) analog is not able to do because of the higher energy requirement. Crystal field theory, for example, predicts for strong field octahedral complexes an increased activation energy of about 4 kcal./mole for  $d^6$  displacement substitutions,<sup>20</sup> as compared to  $d^3$ . In the present case the comparison is not entirely valid since Cr and Rh are in different series of the periodic table.

A second point of contrast between these two trisoxalato complexes lies in the hydrogen ion concentration dependence of the acid-catalyzed aquation reactions, which is first-order for the rhodiate but is clearly second-order for the chromium(III) complex. One order is ascribable to the proton pre-equilibration common to both species. It is conceivable that participation of a second proton in the rhodiate reaction is inhibited by a considerably weaker basicity of the  $M(C_2O_4)_2 \cdot OC_2O_3H \cdot OH_2^{-2}$  intermediate when  $M = Rh(III)$  but this seems unlikely in view of the closely parallel acidities of the aquopentammines of the two ions.<sup>21</sup> Alternatively, it may be simply a second demonstration of the suppression of a displacement substitution mechanism in the  $d^6$  rhodium complex, as suggested above. This implies that aquation proceeds through a dis-

sociative mechanism,<sup>21</sup> such that a five-coördinate activated complex intervenes in reaction 4, *viz.*



But against this must be set the fact that the activation energy for aquation of the rhodiate is 5 kcal./mole greater than for the chromiate, a somewhat larger difference than expected for the dissociative mechanism.

The strongly basic substituent,  $OH^-$ , is seen to promote second-order ligand replacement of the rhodiate, in keeping with the usual behavior of hydroxyl. Unfortunately, the hoped-for unequivocal choice between possible  $SN1CB$  and  $SN2$  mechanisms is not possible, due to the participation of the aquo-ion  $Rh(C_2O_4)_2 \cdot OC_2O_3 \cdot OH_2^{-3}$ , which undoubtedly is acidic in nature. The divergence in magnitude of  $k_{OH^-}$  and  $k_{H_2O}$  is not unusual, factors as great as  $10^4$  having been frequently observed for rate constant ratios of this type.<sup>7</sup> It is of interest that the substituent  $CO_3^-$ , between  $OH^-$  and  $C_2O_4^-$  in basicity, does promote partial second-order ligand displacement in the carbonato-bis-(diamine)-cobalt(III) series of complexes.<sup>22</sup> A study of the analogous carbonato-rhodium(III) compounds should prove of considerable significance.

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(20) Reference 9, p. 108 *et seq.*

(21) Reference 9, p. 387.

(22) J. E. Boyle and G. M. Harris, *J. Am. Chem. Soc.*, **80**, 782 (1958).