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Substitution Reactions of Oxalato Complex Ions. V. Kinetics of Aquation of $Rh(C_2O_4)_3{}^{3-}$ in Solvent Mixtures of H_2O and D_2O

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The kinetics of aquation of the ion $Rh(C_2O_4)_3{}^{3-}$ have been studied in solvent mixtures of H_2O and D_2O using a spectrophotometric method. In ~ 1 *M* H^+ the half-time for aquation in H_2O at 50° is 47 hr. Other rate data obtained over the range 50 to 80° lead to the rate constant expression $k = 8.0 \times 10^{12} \exp(-27{,}000/RT)$ M^{-1} sec.$^{-1}$. The acceleration of rate in solutions containing D_2O enabled evaluation of the solvent deuterium isotope effect, $k_D/k_H = 3.68$. The cubic and the linear forms of the Gross-Butler equation and a medium effect equation have been applied in an attempt to interpret the experimental k_n/k_H ratios.

Introduction

In Part II of this series,[1] a study of the kinetics of aquation of $Cr(C_2O_4)_3{}^{3-}$ in H_2O, H_2O–D_2O, and D_2O solvent systems was reported. The rate of aquation was found to increase as a function of deuterium atom fraction of the solvent in agreement with the Gross–Butler equation, suggesting a plausible pre-equilibrium protonation step. This postulation was consistent with the experimental data on (1) the aquation of $Cr(C_2O_4)_3{}^{3-}$ to form *cis*-$Cr(C_2O_4)_2(H_2O)_2{}^-$ and (2) the exchange of $^{14}C_2O_4{}^{2-}$ with the bound oxalate in $Cr(C_2O_4)_3{}^{3-}$.

Since Purlee's critical reexamination[2] of the Gross–Butler theory of the solvent isotope effect for H_2O–D_2O mixtures, several other papers of this type have appeared in the literature.[3-10] Gross–Butler predictions concerning the solvent isotope effect hitherto have been applied to mostly organic systems and the acid-catalyzed aquation of $Cr(C_2O_4)_3{}^{3-}$ was the first inorganic complex ion reaction to be studied from this point of view.

Substitution reactions of octahedral rhodium(III) complexes are exceedingly slow, as recently shown in studies of the exchange of $^{14}C_2O_4{}^{2-}$ with the bound oxalate in $Rh(C_2O_4)_3{}^{3-}$,[11] and the exchange of H_2O^{18} with $Rh(H_2O)_6{}^{3+}$.[12a] For example, at 130° the half-time for the oxalate exchange is between 4 and 16 hr., depending on *p*H and other conditions, while the half-time for the aquo exchange is $\sim$50 hr. at 65°. As a worthwhile sequel to these investigations the aquation of $Rh(C_2O_4)_3{}^{3-}$ in H_2O–D_2O mixtures now has been studied to provide further evidence concerning the mechanism of oxalate exchange, and to allow a comparison with the closely-related chromioxalate reactions.

Experimental

A. **Reagents.**—Crystalline $K_3Rh(C_2O_4)_3 \cdot 4.5H_2O$ was prepared from $RhCl_3 \cdot 4H_2O$ supplied by Engelhard Industries, Newark, N. J., by first precipitating the hydrated rhodium(III) oxide and dissolving it in a stoichiometric quantity of KHC_2O_4 prior to crystallization. The large orange-red efflorescent crystals obtained were checked for purity by chemical analysis. On standing in air at room temperature there was a weight loss of *ca.* 10.7%, corresponding to the formation of a stable monohydrate, $K_3Rh(C_2O_4)_3 \cdot H_2O$. Formation of the monohydrate was confirmed by an experiment on a sample dried over anhydrous $CaCl_2$ which showed approximately the same weight loss over a long period. The monohydrate was analyzed for Rh and C_2O_4 content by Werner and Poupardin's method[12b]; Rh by hydrogen reduction (%Rh found, 20.1; calcd., 20.5); and C_2O_4 permanganometrically (%C_2O_4 found, 52.1; calcd., 52.6). G. F. Smith reagent grade $HClO_4$ and anhydrous $NaClO_4$ were used without further purification. All other chemicals were of reagent grade. D_2O (99.5%) was obtained from Stuart Oxygen Company, California.

B. **Aquation Studies.**—Preliminary studies indicate that the aquation reaction

$$Rh(C_2O_4)_3{}^{3-} + 2H_3O^+ \longrightarrow Rh(C_2O_4)_2(H_2O)_2{}^- + H_2C_2O_4$$

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[1] K. V. Krishnamurty and G. M. Harris, *J. Phys. Chem.*, **64**, 346 (1960).

[2] E. L. Purlee, *J. Am. Chem. Soc.*, **81**, 263 (1959).

[3] F. A. Long and J. Bigeleisen, *Trans. Faraday Soc.*, **55**, 2077 (1959).

[4] V. Gold, *ibid.*, **56**, 255 (1960).

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[8] C. A. Bunton and V. J. Shiner, Jr., *ibid.*, **83**, 42, 3207, 3214 (1961).

[9] E. A. Halevi, F. A. Long, and M. A. Paul, *ibid.*, **83**, 305 (1961).

[10] A. V. Willi, *Z. Naturforsch.*, **16a**, 162 (1961).

[11] D. Barton and G. M. Harris, IV of this series, *Inorg. Chem.*, **1**, 251 (1962).

[12] (a) W. H. Plumb and G. M. Harris, manuscript in preparation; (b) A. Werner and J. Poupardin, *Ber.*, **47**, 1955 (1914).

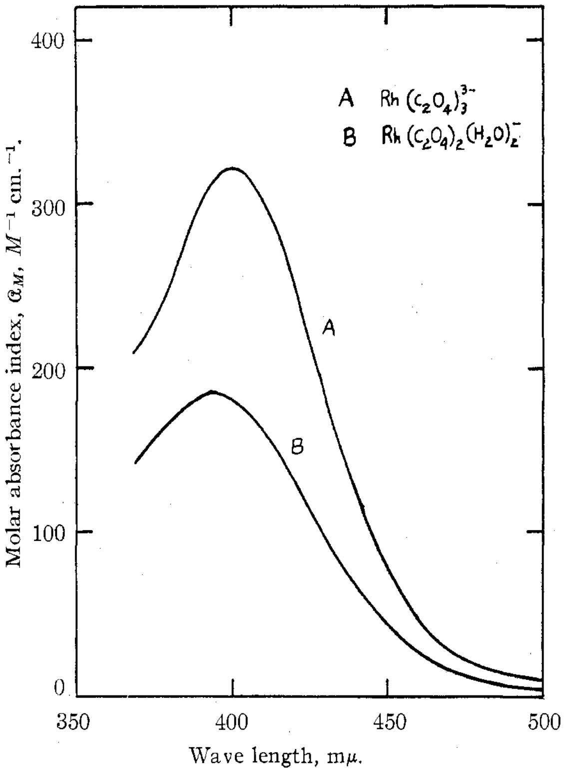

Fig. 1.—Absorption spectra of $Rh(C_2O_4)_3^{3-}$ and $Rh(C_2O_4)_2(H_2O)_2^-$ ions: 2.5 × 10^{-3} *M* each in H_2O and run in a Beckman Model DU spectrophotometer.

is extremely slow at room temperature and at low acidities. However, at temperatures ≥50°, and acidities ≥1 *M* the reaction can be followed spectrophotometrically. Figure 1 illustrates the absorption spectra of the two rhodium species: $Rh(C_2O_4)_3^{3-}$ and $Rh(C_2O_4)_2(H_2O)_2^-$. It is not known if the product of aquation is *cis* or *trans*, although analysis of the reaction mixture in a kinetic run indicates one mole of free oxalate and two moles bound as in the ion $Rh(C_2O_4)_2(H_2O)_2^-$. The latter is assumed to be predominantly in the *cis* form analogous to the aquation product of $Cr(C_2O_4)_3^{3-}$.

Kinetic runs were made in a Beckman Model DU spectrophotometer as described earlier.[1,11] Calculated volumes of standardized solutions of $HClO_4/DClO_4$ and $NaClO_4$ diluted with necessary amounts of H_2O/D_2O were thermostated in a 25-ml. volumetric flask and mixed with the required volume of a similarly thermostated solution of 2.5 × 10^{-2} *M* $K_3Rh(C_2O_4)_3$ in H_2O/D_2O. A portion of the reaction mixture (~3 ml.) immediately was transferred to the spectrophotometric cell and the absorbance of the mixture at 400 mμ was determined at frequent intervals. The rate constants were determined from the absorbance data in the usual way. Series of experiments were carried out to determine the effects of variation of the concentration of rhodium complex ion, acidity, temperature, and the deuterium atom fraction of the solvent.

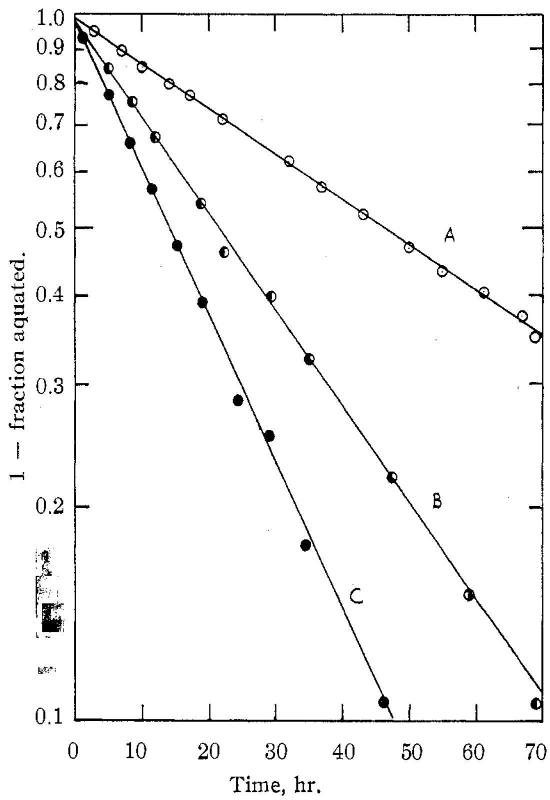

Fig. 2.—Typical aquation runs at conditions: 50.0°, 2.5 × 10^{-3} *M* $Rh(C_2O_4)_3^{3-}$, 0.97 *M* H^+, 7.5 × 10^{-3} *M* K^+, 0.97 *M* ClO_4^-, ionic strength adjusted to 1.00 adding $NaClO_4$. Curve A: pure water, $t_{1/2}$ = 47.0 hr.; curve B: 51% heavy water, $t_{1/2}$ = 22.0 hr.; curve C: 92% heavy water, $t_{1/2}$ = 14.0 hr.

Results

For individual runs, plots of ln (1 − *F*) against time give good straight lines (see Fig. 2) as expected for the known first order dependence on the trisoxalato complex ion concentration. The temperature dependence of the rate in H_2O at 0.97 *M* H^+ ion concentration was studied at three different temperatures: 50, 65, and 80°. The over-all activation energy calculated from the slope of the curve (see Fig. 3) is 27.0 kcal./mole.[13] The experiments carried out in H_2O–D_2O solvent mixtures resulted in the data shown in Table I.

Discussion

The mechanism already proposed[11] for the aquation is

$$Rh(C_2O_4)_3^{3-} + H_3O^+ \rightleftharpoons Rh(C_2O_4)_2OC_2O_3H\cdot H_2O^{2-}$$

$$Rh(C_2O_4)_2OC_2O_3H\cdot H_2O^{2-} + H_2O \longrightarrow Rh(C_2O_4)_2(H_2O)_2^- + HC_2O_4^-$$

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[13] (a) Some recent unpublished experiments by L. Casali[13b] and K. V. Krishnamurty show that the experimental activation energy for $Rh(C_2O_4)_3^{3-}$ aquation in ~1 *M* H^+ decreases linearly with increase in the deuterium atom fraction of the solvent according to the equation: $E_n = E_H - 2.07n$. The difference between the activation energies in H_2O and in D_2O, $E_H - E_D$, is ~2.1 kcal./mole. The ratio between the frequency factors, A_H/A_D, calculated from the equation $k_H/k_D = A_H/A_D\cdot\exp\{(-E_H + E_D)/RT\}$ is ~6.6. The estimated difference between the entropies of activation, $\Delta S_H^* - \Delta S_D^*$, is ~3.7 e.u. It is not known at the present time whether any significance can be attached to these calculations; (b) National Science Foundation Research Participant, 1961.

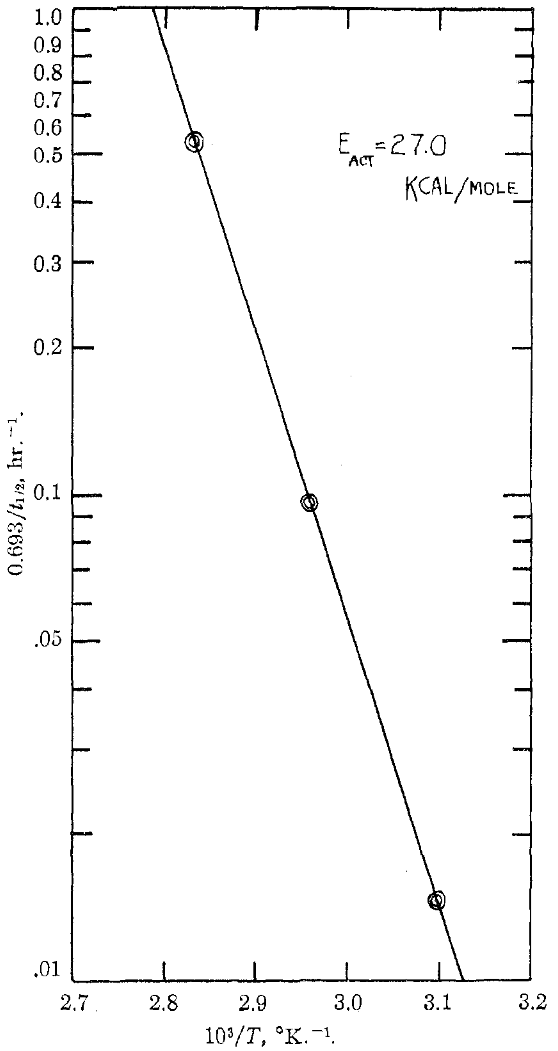

Fig. 3.—Temperature dependence of rate at conditions: 2.5×10^{-3} *M* $Rh(C_2O_4)_3^{-3}$, 0.97 *M* H^+, 7.5×10^{-3} *M* K^+, 0.97 *M* ClO_4^-, ionic strength adjusted to 1.00 by adding $NaClO_4$.

Table I

Solvent Deuterium Isotope Effect on the Aquation of $Rh(C_2O_4)_3^{3-}$; 50.0°, 2.5×10^{-3} *M* $Rh(C_2O_4)_3^{3-}$, 0.97 *M* H^+, ionic strength 1.0

$n =$ (D)/(H + D)	$t_{1/2}$, hr.	$k =$ $0.693/t_{1/2}$, hr.$^{-1}$ × 10^3	k_n/k_H expt.
0.000	47.0	14.7	1.00
.248	30.0	23.1	1.57
.506	22.0	31.5	2.14
.747	17.5	39.6	2.69
.914	14.0	49.5	3.36
1.000	12.8[a]	54.3[a]	3.68[a]

[a] Independently extrapolated values obtained from curves of best fit.

This is the type of proton pre-equilibration acid-catalysis mechanism for which deuterium solvent isotope effects are likely to be diagnostically valuable.

The following solvent–isotope-effect equations[9] are relevant to the discussion here

"Cubic" equation

$$k_n/k_H = \frac{1 - n + (k_D/k_H)nl^3}{(1 - n + nl)^3} \qquad (I)$$

"Linear" equation

$$k_n/k_H = \frac{1 - n + (k_D/k_H)nl^3}{1 - n + nl^3} \qquad (II)$$

"Medium effect" equation

$$k_n/k_H = (k_D/k_H)^{n\gamma} \qquad (III)$$

In these, k_H, k_n, and k_D are the rate constants in pure H_2O, in H_2O–D_2O of deuterium atom fraction n, and in pure D_2O, respectively. The ratio k_D/k_H is the solvent deuterium isotope effect and l is defined as $L^{-1/6}$, where L represents the equilibrium constant of the exchange reaction $2D_3O^+ + 3H_2O = 2H_3O^+ + 3D_2O$. The exponent γ in the medium effect equation is an arbitrarily adjustable parameter and generally is taken as unity.

Using the Gross–Butler equations I and II the k_n/k_H ratios were calculated for several values of l and a comparison made with those obtained experimentally at different deuterium atom fractions of the solvent. The results of the calculation, adopting the "best-fit" value of $l = 0.90$, are shown in Fig. 4, curve 3. The experimentally obtained k_n/k_H ratios agree reasonably well with either of the Gross–Butler equations. From $Rh(C_2O_4)_3^{3-}$ aquation data alone, it thus is not possible to discriminate between the two forms of the Gross–Butler equation. However, the medium effect equation (III), also illustrated in Fig. 4, is not satisfactory.

In using the cubic (I) or the linear (II) equations is must not be overlooked that the constant L is the equilibrium constant for the complete exchange of D's in D_3O^+ with H_2O. The cubic form (I) of the equation, in fact, is a direct consequence of the assumption of the conventional hydronium ion (H_3O^+) with all the hydrogens equivalent.[4] Also the linear form (II) of the Gross–Butler equation can be claimed to be applicable only to a system with a proton of unspecified hydration undergoing the exchange reaction $2D_{aq}^+ + H_2O = 2H_{aq}^+ + D_2O$. It is not clear at the present time which concept of the hydrated proton is correct. The state of protons in aqueous solution has been discussed at length by Khomutov[14] and Conway, Bockris, and

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[14] N. Khomutov, *Russ. J. Phys. Chem.*, **34**, 177 (1960).

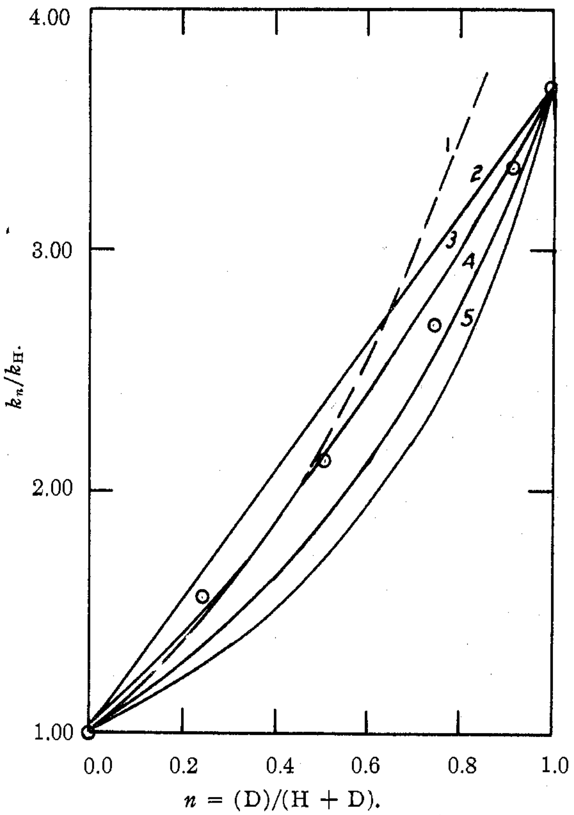

Fig. 4.—Comparison of cubic, linear, and medium effect equations for $Rh(C_2O_4)_3^{3-}$ aquation: curve 1: (III), $\gamma = 1.20$; curve 2: (I) or (II), $l = 1.00$; curve 3: (I) or (II), $l = 0.90$; curve 4: (III) $\gamma = 1.00$, (I) $l = 0.70$, (II) $l = 0.75$; curve 5: (II), $l = 0.70$; experimental points indicated by circles.

Linton.[15] However, evidence from other sources, particularly from the relaxation methods used by Eigen and co-workers,[16] supports the special stability of the tetrahydrated proton, $H(H_2O)_4^+$ or $H_9O_4^+$.

The exchange equilibria given by the general equation

$$2D(D_2O)_x^+ + (2x + 1)H_2O = 2H(H_2O)_x^+ + (2x + 1)D_2O$$

therefore must be examined in the light of alternate structures for the hydrated proton. If $x = 1$, then this is the case of the conventional monohydrated proton with all three hydrogens exchangeable for deuterium atoms. This results in the equilibrium constant L already discussed. The "best-fit" value for L from the data of the present work at 50° is 1.89, corresponding to $l = 0.90$. The high k_D/k_H ratio of 3.68 in the aquation of $Rh(C_2O_4)_3^{3-}$ makes the treatment more sensitive to the choice of L than the lower value of 2.62 found for $Cr(C_2O_4)_3^{3-}$ aquation. In the latter case the calculated k_n/k_H ratios agreed quite satisfactorily for any value of $1.89 < L < 22$.

The half-times, over-all activation energies, and k_D/k_H ratios for the acid-catalyzed aquation of $Cr(C_2O_4)_3^{3-}$ and $Rh(C_2O_4)_3^{3-}$ are much different under comparable conditions, as shown below (data obtained at 50°). It is obvious that the slower reaction has a larger isotope effect. The activation energies also bear the usual relationship; the reaction of lower activation energy having the smaller isotope effect.[17]

	$t_{1/2}$	E_a, kcal./mole	k_D/k_H
Cr	17 min.	22	2.62
Rh	47 hr.	27	3.68

In conclusion it is shown here that for $k_D/k_H = 3.68$ the choice of L is important and the calculated k_n/k_H ratio is sensitive to values of L. It has not been proven[4] unequivocally that the aquation of $Cr(C_2O_4)_3^{3-}$ and $Rh(C_2O_4)_3^{3-}$ proceed *via* pre-equilibrium protonation rather than *via* a slow proton transfer mechanism. However, the former seems to be the most logical mechanism for the aquation of these complex ions, as the existence of a relatively stable protonated species of similar complexes containing a basic anion chelate ligand is well established.[18]

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