(6) I. Oonishi, S. Sato, and Y. Saito, *Acta Crystallogr., Sect. B*, **30**, 2256 (1974).
(7) B. Bosnich and J. MacB. Harrowfield, *Inorg. Chem.*, **14**, 861 (1975).
(8) B. Bosnich and J. MacB. Harrowfield, *J. Am. Chem. Soc.*, **94**, 3425 (1972); *Inorg. Chem.*, **14**, 828, 847 (1975).
(9) A. M. Sargeson, *Transition Metal Chem.*, **3**, 303 (1967), and references therein.
(10) R. J. Geue and M. R. Snow, *J. Chem. Soc. A*, 2981 (1971).
(11) There is general agreement on the names of two of the basic conformations of the trimethylenediamine chelate ring, namely, the chair and the boat, but the one shown in Figure 1 has been called either skew or twist or skew boat or twist boat. The cyclohexane analogy notwithstanding, it seems to us that either of the last two names is better reserved for the conformation which is intermediate between the skew (twist) and the boat. This conformation becomes important when two or more six-membered chelate rings are (linearly) linked (see, D. A. House, P. R. Ireland, I. E. Maxwell, and W. T. Robinson, *Inorg. Chim. Acta*, **5**, 397 (1971)).
(12) C. J. Dippel and F. M. Jaeger, *Recl. Trav. Chim. Pays-Bas*, **50**, 547 (1931).
(13) F. Mizukami, H. Ito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, **45**, 2129 (1972); R. Kuroda, J. Fujita, and Y. Saito, *Chem. Lett.*, **225** (1975).
(14) W. Moffitt, *J. Chem. Phys.*, **25**, 467 (1956).
(15) C. J. Hawkins, "Absolute Configuration of Metal Complexes", Interscience, New York, N.Y., 1971.
(16) S. F. Mason and B. J. Norman, *Proc. Chem. Soc. London*, 339 (1964).
(17) H. L. Smith and B. E. Douglas, *J. Am. Chem. Soc.*, **86**, 3885 (1964).
(18) S. F. Mason and B. J. Norman, *J. Chem. Soc. A*, 307 (1966).
(19) B. E. Douglas, *Inorg. Chem.*, **4**, 1813 (1965); S. F. Mason, A. M. Sargeson, R. Larsson, B. J. Norman, A. J. McCaffery, and G. M. Searle, *Inorg. Nucl. Chem. Lett.*, **2**, 333 (1966); *J. Chem. Soc.*, 1304, 1310 (1968); K. Ogino, K. Murano, and J. Fujita, *Inorg. Nucl. Chem. Lett.*, **4**, 351 (1968).
(20) F. Mizukami, H. Ito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, **46**, 2410 (1973).
(21) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).
(22) T. Aoki, K. Matsumoto, S. Ooi, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **46**, 159 (1973).

Contribution from the Department of Chemistry,
Boston University, Boston, Massachusetts 02215

Oxygen Exchange and Acid Hydrolysis Reactivity of Bis(ethylenediamine)oxalatorhodium(III) Ion[1]

NANCY S. ROWAN, RONALD M. MILBURN,*[2] and TARA P. DASGUPTA

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The reactivity of $Rh(en)_2C_2O_4^+$ toward oxygen exchange with solvent and aquation to *cis*-$Rh(en)_2(H_2O)_2^{3+}$ has been examined in aqueous $HNO_3/NaNO_3$ media at ionic strength 0.50 M. There are two kinetically distinct types of coordinated oxygen, the slower exchange being attributed to inner/outer oxygen interchange which we presume must occur before inner oxygens can exchange with solvent. Over the temperature range studied, rate constants for inner/outer oxygen interchange and for exchange of outer oxygens with solvent differ only slightly. Both processes are first order in $[H^+]$. Rate parameters, calculated on the basis that there are two outer oxygens and two inner oxygens, are as follows: for inner/outer oxygen interchange, per mole of complex, k_{i2} $(=k_{i1}/[H^+]) = 4.5 \times 10^{-5}$ M^{-1} s^{-1} at 35.0 °C, $\Delta H^\ddagger_{i2} = 26.0$ (± 1.2) kcal mol^{-1}, $\Delta S^\ddagger_{i2} = +5.8$ (± 4.0) cal mol^{-1} K^{-1}; for outer oxygen exchange with solvent, per mole of complex, k_{o2} $(=k_{o1}/[H^+]) = 9.6 \times 10^{-5}$ M^{-1} s^{-1} at 35.0 °C, $\Delta H^\ddagger_{o2} = 17.1$ (± 0.3) kcal mol^{-1}, $\Delta S^\ddagger_{o2} = -21.6$ (± 1.0) cal mol^{-1} K^{-1}. $Rh(en)_2C_2O_4^+$ also equilibrates in acidic solution in accord with the stoichiometry: $Rh(en)_2C_2O_4^+ + 2H_3O^+ \rightleftharpoons$ *cis*-$Rh(en)_2(H_2O)_2^{3+} + H_2C_2O_4$. Thermodynamic parameters for this reaction are $K = 2.1$ $(\pm 0.2) \times 10^{-3}$ M^{-1} at 35.0 °C, $\Delta H^\circ = 4.5$ (± 0.4) kcal mol^{-1}, and $\Delta S^\circ = 2.4$ (± 1.2) cal mol^{-1} K^{-1}. The forward hydrolysis rate proceeds according to a two-term rate law: $R = \{k_{a2}[H^+] + k_{a3}[H^+]^2\}[Rh(en)_2C_2O_4^+]$. At 35.0 °C, $k_{a2} = 4.3 \times 10^{-6}$ M^{-1} s^{-1} and $k_{a3} = 8.8 \times 10^{-6}$ M^{-2} s^{-1}; also $\Delta H^\ddagger_{a2} = 24.1$ (± 2.0) kcal mol^{-1}, $\Delta S^\ddagger_{a2} = -5.0$ (± 6.0) cal mol^{-1} K^{-1}, $\Delta H^\ddagger_{a3} = 18.0$ (± 2.5) kcal mol^{-1}, and $\Delta S^\ddagger_{a3} = -23.4$ (± 8.0) cal mol^{-1} K^{-1}. Rate and equilibrium data for the hydrolysis reaction provide values of the kinetic parameters for the anation reaction. Mechanistic interpretations for the oxygen-exchange, hydrolysis, and anation data are provided. The behavior of $Rh(en)_2C_2O_4^+$ is contrasted to that of $Co(en)_2C_2O_4^+$, which in acidic solution is notably less reactive toward inner oxygen exchange and hydrolysis.

Introduction

The reactivities of $Co(en)_2C_2O_4^+$,[3,4] $Co(C_2O_4)_3^{3-}$,[5-7] and $Rh(C_2O_4)_3^{3-}$ [8-10] in aqueous acidic solution have all been examined in some detail. Results obtained for these complexes indicated that a study of the reactivity of $Rh(en)_2C_2O_4^+$ would be of interest. Substitution at the Rh(III) center generally occurs at comparable or lower rates than substitution in corresponding Co(III) complexes.[11] Comparison between $Rh(C_2O_4)_3^{3-}$ and $Co(C_2O_4)_3^{3-}$ is complicated, however, by the relatively rapid internal redox decomposition reaction of the latter complex in acidic solution.[5-7] On the other hand, $Co(en)_2C_2O_4^+$ shows no tendency to undergo internal redox decomposition in aqueous solution; further, this complex is notably unreactive toward exchange of inner oxygens with solvent water[3] and toward aquation.[4] These observations on $Co(en)_2C_2O_4^+$ might lead one to suppose that $Rh(en)_2C_2O_4^+$ would also be extremely unreactive toward the inner oxygen exchange and aquation reactions. Contrary to this simplistic view, we find $Rh(en)_2C_2O_4^+$ to be moderately reactive toward these processes.

Experimental Section

Materials. Bis(ethylenediamine)oxalatorhodium(III) nitrate was prepared as described earlier[12] from cis or cis/trans mixtures of $[Rh(en)_2Cl_2]NO_3$.[13] The purity of a sample was checked by elemental analysis. Anal.[14] Calcd for $[Rh(N_2C_2H_8)_2C_2O_4]NO_3 \cdot H_2O$: C, 18.4; H, 4.64; N, 17.9. Found: C, 18.6; H, 4.52; N, 18.0. Other samples were checked by comparison of visible–uv spectra with that for the analyzed sample (λ_{max} 325 nm, ϵ 260 M^{-1} cm^{-1}).[12]

cis-Bis(ethylenediamine)dihydroxorhodium(III) ion was prepared in solution by reaction of *cis*-$Rh(en)_2Cl_2^+$ with potassium or sodium hydroxide.[15,16] *cis*-Diaquobis(ethylenediamine)rhodium(III) ion was prepared in solution by acidifying, with perchloric or nitric acid, solutions containing *cis*-$Rh(en)_2(OH)_2^+$, prepared as described above.

All solutions for kinetic and equilibrium studies utilized water, obtained from ordinary distilled water which was refluxed with alkaline potassium permanganate in a Barnstead S-1 water still and redistilled.

A nitric acid/sodium nitrate aqueous medium was chosen for the studies because of the very low solubility of the oxalato complex in perchlorate media. Nitrate absorbs in the uv region; at the complex absorption maximum at 325 nm, ϵ is $\simeq 2.5$ M^{-1} cm^{-1} for nitrate which was too large for us to handle in spectrophotometric studies of the hydrolysis. However, such studies could be carried out at 340 nm where for nitrate ϵ is $\simeq 0.1$ M^{-1} cm^{-1}. A stock 2 M nitric acid solution was prepared from reagent grade acid which had been boiled for 20 min to remove oxides of nitrogen.[17] After standardization the stoppered solution was stored in the dark. A stock 2 M sodium nitrate solution, prepared from recrystallized reagent grade material, was standardized and stored in a refrigerator.

Acid Hydrolysis Studies. In acidic solution $Rh(en)_2C_2O_4^+$ slowly releases coordinated oxalate. The stoichiometry and equilibrium for the release were studied quantitatively by the following two methods.

Reaction of $\mathrm{Rh(en)_2C_2O_4^+}$ (2×10^{-3} M) in 1.00 M $\mathrm{HNO_3}$ at 55.0 °C was allowed to proceed to equilibrium (>10 half-lives, as determined spectrally at 340 nm using a method similar to that described below). To avoid spectral interference the nitrate was now replaced with chloride by passing the cooled solution through a cold Dowex 1-X8 anion-exchange column in the chloride form.[18] The spectrum of the resulting solution (280–400 nm) was attributable to a mixture of $\mathrm{Rh(en)_2C_2O_4^+}$ and $\mathrm{Rh(en)_2(H_2O)_2^{3+}}$. In a separate experiment the concentration of released oxalate in a similarly equilibrated solution was determined quantitatively by precipitation and separation as $\mathrm{CaC_2O_4}$ and by titration with potassium permanganate. Check analyses were performed with oxalic acid under comparable conditions.

Kinetic and equilibrium studies on the hydrolysis reaction were carried out in aqueous $\mathrm{HNO_3/NaNO_3}$ media at ionic strength 0.50.

For each kinetic run, a freshly prepared solution of $\mathrm{[Rh(en)_2C_2O_4]NO_3{\cdot}H_2O}$ in water was mixed with solutions of $\mathrm{HNO_3}$ and $\mathrm{NaNO_3}$ of appropriate volumes and concentrations. An initial sample was examined spectrally, and other samples were withdrawn for spectral examination until equilibrium had been established. A Cary 16 uv–vis spectrophotometer was used for these measurements, with all kinetic measurements made at 340 nm. At this wavelength the absorbancy coefficients for $\mathrm{Rh(en)_2C_2O_4^+}$, $\mathrm{Rh(en)_2(H_2O)_2^{3+}}$, and $\mathrm{NO_3^-}$ are respectively 219, 123, and 0.12 $\mathrm{M^{-1}\ cm^{-1}}$. To compensate for the absorbance by $\mathrm{NO_3^-}$, a blank solution, which was 0.500 M in $\mathrm{NO_3^-}$, was used in each of two reference cells. One of these cells was used in the reference beam; the other was used in the sample beam to zero the instrument, if necessary, before each reading.

Oxygen-Exchange Studies. The exchange of oxygen between $\mathrm{Rh(en)_2C_2O_4^+}$ and solvent water was studied using procedures which were in general similar to those described earlier for $\mathrm{Rh(C_2O_4)_3^{3-}}$ and $\mathrm{Pt(C_2O_4)_2^{2-}}$ ions.[8,22]

As with the acid hydrolysis work, all kinetic runs utilized a $\mathrm{HNO_3/NaNO_3}$ medium at ionic strength 0.50 M. To conserve ^{18}O-enriched water (a need arising because of the low solubility of $\mathrm{Rh(en)_2C_2O_4^+}$ in the medium), the starting condition for kinetic runs was ^{18}O-enriched complex and normal water (rather than normal complex and enriched water). Enriched complex was prepared from *cis*-$\mathrm{Rh(en)_2Cl_2^+}$ and ^{18}O-enriched $\mathrm{Na_2C_2O_4}$ using procedures already described. The ^{18}O-enriched $\mathrm{Na_2C_2O_4}$ was prepared by equilibrating oxalic acid with enriched water at 35 °C for >10 half-lives, cooling and neutralizing with sodium carbonate, and recovering by rotatory evaporation. The enrichment of the labeled oxalate was determined by precipitation and separation of $\mathrm{Ag_2C_2O_4}$, and mass spectral analysis of the $\mathrm{CO_2}$ obtained by thermal decomposition of the silver salt.

To determine the enrichment of complexed oxalate, it was found convenient to precipitate the $\mathrm{Rh(en)_2C_2O_4^+}$ with $\mathrm{I_3^-}$. Thus, for the conditions of experiment it was found that $\mathrm{I_3^-}$ precipitates $\mathrm{Rh(en)_2C_2O_4^+}$ under conditions where it precipitates neither *cis*-$\mathrm{Rh(en)_2(H_2O)_2^{3+}}$ nor $\mathrm{H_2C_2O_4}$ and $\mathrm{HC_2O_4^-}$ freed by hydrolysis. In the kinetic runs, aliquots from the reaction solution were transferred into a solution cooled in an ice bath which contained NaI together with resublimed $\mathrm{I_2}$. The brown precipitate, obtained on rapid stirring, was filtered, washed successively with cold water, ethanol, and diethyl ether, and air-dried before transferring to a vacuum line. After further drying with a vacuum pump, the precipitate was decomposed in a closed tube with a microburner until the solid became shiny black and there was no further sign of gas evolution. A dry ice/acetone trap was now placed around the decomposition tube to retain the $\mathrm{I_2}$ and easily condensable products such as ethylenediamine, while the $\mathrm{CO_2}$ was distilled into a sample tube held in liquid $\mathrm{N_2}$. The $\mathrm{CO_2}$ was then redistilled before analysis against standard $\mathrm{CO_2}$ on the mass spectrometer (Nuclide 6-60-RMS2).

The decomposition of the solid appears to proceed according to the stoichiometry

$$\mathrm{2[Rh(en)_2C_2O_4]I_3 \xrightarrow{\Delta} 2Rh(s) + 3I_2 + 4CO_2 + 4NH_2CH_2CH_2NH_2} \tag{1}$$

Product scans of samples on the mass spectrometer showed the primary gaseous product collected to be $\mathrm{CO_2}$. There were some impurities at *m/e* 25–27. In samples which were not opened to the vacuum pump, several mass spectral scans showed that CO was not an important product.

Where interest included the earlier to middle stages of exchange, reaction was initiated by quickly mixing, at the thermostat temperature, a freshly prepared solution of complex in water with solutions containing appropriate amounts of $\mathrm{NaNO_3}$ and $\mathrm{HNO_3}$. For studies concentrating on the later stages of the exchange, solutions were usually prepared at room temperature from appropriate amounts of complex, $\mathrm{NaNO_3}$ and $\mathrm{HNO_3}$, and these were thermostated at 25 °C until completion of 6–8 half-lives for the more rapidly exchanging oxygens. The reaction flask was then transferred to a thermostat at the new (higher) reaction temperature. For this further reaction the beginning time was arbitrary, and a "time 0" aliquot was neither taken nor required.

For each kinetic run, values of N_t (atom fraction of oxygen-18) were calculated from the isotope ratio for $\mathrm{CO_2}$ as described elsewhere.[8,23] The enrichment of the coordinated oxygen at infinite time (N_f) could be taken as 2.039×10^{-3}, because the only enriched species in solution was the complex which had an oxygen concentration of $\sim 1 \times 10^{-2}$ M in comparison to the concentration of water oxygens of ~55 M.

Results

Acid Hydrolysis. Our stoichiometric and equilibrium studies demonstrated that $\mathrm{Rh(en)_2C_2O_4^+}$ in acidic solution releases oxalate in accord with the overall reaction

$$\mathrm{Rh(en)_2C_2O_4^+ + 2H_3O^+ \rightleftarrows \mathit{cis}\text{-}Rh(en)_2(H_2O)_2^{3+} + H_2C_2O_4} \tag{2}$$

accompanied by the rapidly established equilibrium

$$\mathrm{H_2C_2O_4 + H_2O \rightleftarrows HC_2O_4^- + H_3O^+} \tag{3}$$

For the acidic range examined (0.08–1.00 M $\mathrm{H^+}$) reaction 2 does not proceed to completion; rather, an equilibrium is established in which various amounts of $\mathrm{Rh(en)_2C_2O_4^+}$ remain.

For 1.00 M $\mathrm{HNO_3}$ and 55.0 °C, the determinations by spectra showed that at equilibrium 70 ± 2% of the oxalate had been released from the complex; the determinations by titrimetry indicated that 75 ± 5% of the oxalate had been released.

The kinetic studies and further equilibrium studies were carried out in the acid range 0.08–0.50 M $\mathrm{H^+}$. For these conditions one needs to give consideration to equilibrium reaction 3. Reaction 2 was allowed to proceed in the absence of added oxalate; hence the stoichiometry defines the equality (since $\mathrm{C_2O_4^{2-}}$ will be present at negligible concentrations)

$$[\mathit{cis}\text{-}\mathrm{Rh(en)_2(H_2O)_2^{3+}}] = [\mathrm{H_2C_2O_4}] + [\mathrm{HC_2O_4^-}] = x \tag{4}$$

For conditions of *constant acidity* (which applied for each experimental run) the simplest rate law, which takes into account the reversibility of reaction 2 and which is consistent with our results, is

$$\mathrm{d}x/\mathrm{d}t = k'_1(a_0 - x) - k'_{-1}x^2 \tag{5}$$

where x is defined by eq 4 and a_0 is the initial concentration of $\mathrm{Rh(en)_2C_2O_4^+}$.

If we make the substitution $k'_{-1} = k'_1(a_0 - x_e)/x_e^2$ as discussed by Laidler,[20] where x_e is the value of x at equilibrium, then

$$k'_1 t = \frac{x_e}{2a_0 - x_e} \ln\left(\frac{a_0 x_e - x(a_0 - x)}{a_0(x_e - x)}\right) \tag{6}$$

Equation 6 may now be converted to a form which uses absorbance data. Thus

$$k'_1 t = \left(\frac{e_2(A_f - A_0)}{A_0(2e_1 - e_2) - e_2 A_f}\right) \times \left\{\ln\left(\frac{A_0 A_f e_1 - 2A_0^2 e_1 + A_0^2 e_2 + e_1 A_t A_0 - e_2 A_f A_t}{(e_1 - e_2)A_0(A_f - A_t)}\right)\right\} \tag{7}$$

where e_1 = absorbancy coefficient for *cis*-$\mathrm{Rh(en)_2(H_2O)_2^{3+}}$ = 123 (±1) $\mathrm{M^{-1}\ cm^{-1}}$ at 340 nm; e_2 = absorbancy coefficient for $\mathrm{Rh(en)_2C_2O_4^+}$ = 219 (±2) $\mathrm{M^{-1}\ cm^{-1}}$ at 340 nm; A_0 =

Table I. Pseudo-First-Order Rate Constants for Forward Reaction 2 at Constant Acidity (k'_1), Concentration Equilibrium Constants for Reaction 2 (K), and Apparent Second-Order Rate Constants for Back Reaction 2 at Constant Acidity (k'_{-1})[a]

Expt no.	Temp, °C	[H⁺], M	$10^5k'_1$,[b] s⁻¹	10^3K,[c,d] M⁻¹		$10^2k'_{-1}$, M⁻¹ s⁻¹
1	64.85	0.504	10.0 (0.2)	3.6	av 4.0 (±0.3)	9.2
2	64.85	0.403	7.98 (0.20)	4.0		9.8
3	64.85	0.302	5.33 (0.07)	4.3		10.5
4	64.85	0.169	2.83 (0.17)	4.3		15.2
5	64.85	0.085	1.30 (0.12)	(4.5)		19.3
6	55.3	0.504	4.76 (0.10)	3.4	av 3.5 (±0.3)	4.8
7	55.3	0.403	3.22 (0.23)	3.2		5.2
8	55.3	0.302	2.32 (0.05)	3.6		5.5
9	55.3	0.202	1.48 (0.08)	3.9		6.7
10	55.3	0.101	0.63 (0.08)	(4.3)		8.0
11	45.0	0.504	1.14 (0.03)	2.9	av 2.9 (±0.1)	1.30
12	45.0	0.403	0.958 (0.35)	2.9		1.73
13	45.0	0.403	0.932 (0.010)	2.8		1.75
14	45.0	0.302	0.677 (0.042)	(3.6)		1.66
15	45.0	0.202	0.373 (0.020)	2.9		2.3
16	45.0	0.101	0.167 (0.010)	3.1		3.0
17	35.0	0.504	0.452 (0.013)	2.3	av 2.1 (±0.2)	0.66
18	35.0	0.504	0.388 (0.025)			
19	35.0	0.403	0.302 (0.030)	2.2		0.73
20	35.0	0.403	0.265 (0.025)			
21	35.0	0.302	0.202 (0.013)	1.8		1.02
22	35.0	0.202	0.127 (0.020)			

[a] Ionic strength 0.50 M. [b] Errors in parentheses from the least-squares program. [c] Values from expression 9, with K_1 values of 9.0×10^{-2}, 8.0×10^{-2}, 7.5×10^{-2}, and 7.0×10^{-2} for the respective temperatures 68.85, 55.3, 45.0, and 35.0 °C, as obtained from data in ref 21. [d] Values in parentheses not included in the average.

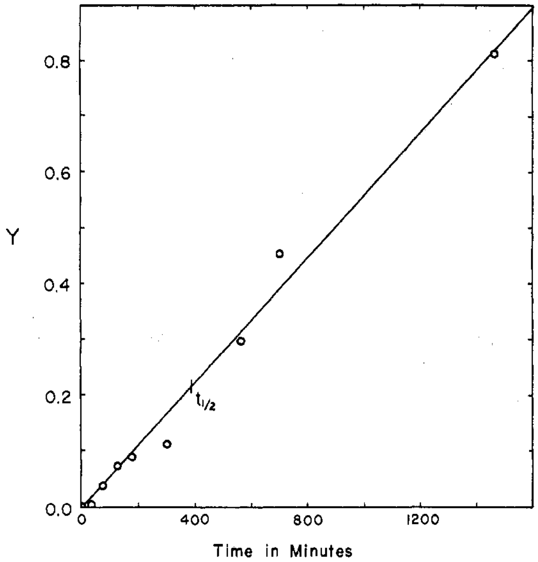

Figure 1. Plot of right side of eq 7 (represented here as "Y") against time, for a representative acid hydrolysis kinetic run. Data are for run no. 13 (Table IV) for which [total rhodium] = 2.60×10^{-3} M, [H⁺] = 0.403 M, and T = 45.0 °C.

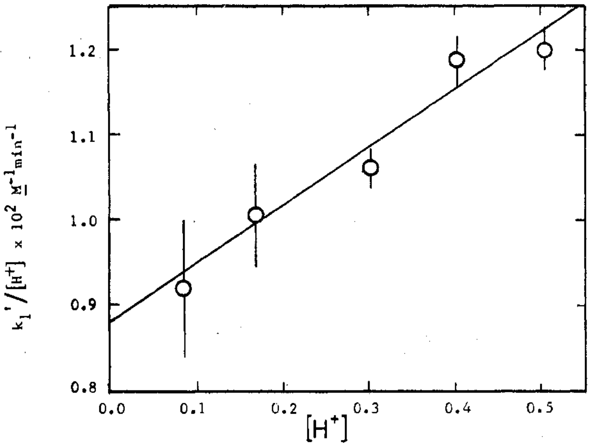

Figure 2. Acid dependence of k'_1 (the pseudo-first-order hydrolysis rate constant) at 64.9 °C.

initial absorbance at 340 nm = e_2a_0; A_t = absorbance at 340 nm at time t; A_f = absorbance at 340 nm at equilibrium. Values of the right side of eq 7 were evaluated and used with the corresponding value of t in a linear least-squares program to obtain values of k'_1. The linearity expected from eq 6 and 7 is in fact found. A representative plot of eq 7 is shown in Figure 1. Values of k'_1, the pseudo-first-order acid hydrolysis rate constant, are given in Table I.

The concentration equilibrium constant (equilibrium quotient) expression for reaction 2 may be written in the form

$$K = \frac{[cis\text{-Rh(en)}_2(H_2O)_2{}^{3+}][Ox_T]}{[Rh(en)_2C_2O_4{}^{+}]([H^+]^2 + [H^+]K_1)} \tag{8}$$

where $[Ox_T] = [H_2C_2O_4] + [HC_2O_4^-]$ and K_1 is the first acid dissociation constant for oxalic acid ($K_1 = [H^+]\cdot[HC_2O_4^-]/[H_2C_2O_4]$). In terms of absorbances and absorbancy coefficients, eq 8 becomes

$$K = \frac{(A_0 - A_f)^2}{(A_f - e_1a_0)(e_2 - e_1)([H^+]^2 + [H^+]K_1)} \tag{9}$$

Values of K, calculated from expression 9 with use of K_1 values extrapolated from the data of Bauer and Smith,[21] are included in Table I. From a plot of ln K vs. $1/T$(K) we obtain, for reaction 2, $\Delta H°$ = 4.5 (±0.4) kcal mol⁻¹ and $\Delta S°$ = 2.4 (±1.2) cal mol⁻¹ K⁻¹.

For the conditions of constant acidity which apply to each experimental run in this work, the equilibrium constant expression 8 can be further rearranged to a form which corresponds to the conditions defined by eq 5

$$K([H^+]^2 + [H^+]K_1) = \frac{x_e[Ox_t]}{a_0 - x_e} = \frac{k'_1}{k'_{-1}} \tag{10}$$

This rearrangement enables one to calculate, for each condition of acidity and temperature, a value of k'_{-1} from the corresponding values of k'_1, K, K_1, and [H⁺]. Results for these calculations are also given in Table I.

Table II. Rate Constants and Activation Parameters for Acid Hydrolysis of $Rh(en)_2C_2O_4^+$

Temp, °C	10^5k_{a2}, M^{-1} s^{-1}	10^5k_{a3}, M^{-2} s^{-1}
64.85	14.7 (±0.5)	11.3 (±1.5)
55.3	5.77 (±0.35)	6.63 (±1.05)
45.0	1.57 (±0.15)	1.80 (±0.43)
35.0	0.43 (±0.07)	0.88 (±0.17)
Rate const[a]	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}
k_{a2}	24.1 (±2.0)	−5.0 (±6.0)
k_{a3}	18.0 (±2.5)	−23.4 (±8.0)

[a] k_{a2} and k_{a3} defined by eq 11.

Table III. Rate Constants and Activation Parameters for Oxalate Anation of *cis*-$Rh(en)_2(H_2O)_2^{3+}$

Temp, °C	10^2k_{-a2}, M^{-1} s^{-1}	10^2k_{-a3}, M^{-2} s^{-1}
64.85	3.0 (±0.2)	4.5 (±0.7)
55.3	1.13 (±0.05)	3.3 (±0.2)
45.0	0.48 (±0.08)	0.70 (±0.22)
35.0	0.35 (±0.08)	*a*
Rate const[b]	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}
k_{-a2}	18.9 (±2.0)	−7.6 (±6.0)
k_{-a3}	13.5 (±3.0)	−26 (±9)

[a] Insufficient data to determine this value. [b] k_{-a2} and k_{-a3} defined by eq 12 and 13.

A plot of k'_1 against $[H^+]$ is not linear, within the limits of error in the k'_1 values, while the plot of $k'_1/[H^+]$ is linear within error limits (Figure 2) and demonstrates that k'_1 is of the form

$$k'_1 = k_{a2}[H^+] + k_{a3}[H^+]^2 \tag{11}$$

Values of k_{a2} and k_{a3} and activation parameters obtained from plots of ln k_{a2} and ln k_{a3} vs. $1/T$(K) are presented in Table II.

The forward reaction path corresponding to the term $k_{a2}[H^+]$ (path I) implies a transition state involving $Rh(en)_2C_2O_4^+$ and one proton (and an unspecified amount of water); similarly, the forward path corresponding to the term $k_{a3}[H^+]^2$ (path II) implies a transition state involving $Rh(en)_2C_2O_4^+$ and two protons (and an unspecified amount of water). According to the principle of microscopic reversibility, for each of these forward reaction paths there will be a corresponding reverse path. For the purpose of evaluating the anation rate constants, we can represent each of the forward reaction paths as if it preceded in a single step. Thus

path II

$$Rh(en)_2C_2O_4^+ + 2H_3O^+ \underset{k_{-a3}}{\overset{k_{a3}}{\rightleftharpoons}} Rh(en)_2(H_2O)_2^{3+} + H_2C_2O_4 \tag{12}$$

path I

$$Rh(en)_2C_2O_4^+ + H_3O^+ + H_2O \underset{k_{-a2}}{\overset{k_{a2}}{\rightleftharpoons}} Rh(en)_2(H_2O)_2^{3+} + HC_2O_4^- \tag{13}$$

For path II at equilibrium

$$K = \frac{k_{a3}}{k_{-a3}} = \frac{x_e[H_2C_2O_4]}{(a_0 - x_e)[H^+]^2} \tag{14}$$

while for path I at equilibrium

$$KK_1 = \frac{k_{a2}}{k_{-a2}} = \frac{x_e[HC_2O_4^-]}{(a_0 - x_e)[H^+]} \tag{15}$$

Values of k_{-a3} ($=k_{a3}/K$) and k_{-a2} ($=k_{a2}/KK_1$) are given in Table III, together with corresponding activation parameters, calculated from differences between the appropriate activation parameters for the forward reaction path and the equilibrium reaction parameters.

Oxygen Exchange. Data, consisting of N_t values vs. time, were obtained for a variety of conditions. For a given temperature and hydrogen ion concentration, the value of N_t diminishes steadily with time as it approaches the natural-abundance value. *All four* oxalate oxygens thus exchange with the solvent. That they do not all undergo exchange at the same rate may be seen by plots of ln $(N_t - N_f)$ vs. time, which deviate from linearity even before the completion of 1 half-life for total exchange.

In total 16 kinetic runs were carried out, covering a range of acidities (0.10–0.50 M) and temperatures (10–65 °C). Analysis of the rate data, in terms of rate constants for specific processes, involves certain intricacies, and it may therefore be useful to give the primary data. These data are provided as supplementary material which lists the number of the run, temperature, hydrogen ion concentration, concentration of complex, times, and values of N_t.

For any given temperature and $[H^+]$, the *observed* rates, as represented by N_t vs. time values, cannot be adequately represented by a single rate constant. However, for each such set of experimental conditions, two rate constants will suffice to represent the data for the entire exchange process. Satisfactory values of such rate constants may be chosen if one considers exchange proceeding according to the consecutive reaction scheme of eq 16. Here, k_{i1} and k_{o1} are specific rate

$$\underset{\text{inner oxygen}}{\mathrm{I}} \underset{k_{i1}}{\overset{k_{i1}}{\rightleftharpoons}} \underset{\text{outer oxygen}}{\mathrm{II}} \underset{k_{o1}}{\overset{k_{o1}}{\rightleftharpoons}} \underset{\text{solvent oxygen}}{\mathrm{III}} \tag{16}$$

constants for exchange between inner and outer oxygen and between outer and solvent oxygen, respectively.[24a]

The relation of these rate constants to changes in the oxygen-18 enrichment may be developed as follows. Let N_I equal the enrichment of inner oxygens at any time *t*, N_{I_0} the enrichment of inner oxygens at time 0, N_{II} the enrichment of outer oxygens at any time *t*, N_{II_0} the enrichment of outer oxygens at time 0, N_f the natural abundance enrichment (i.e., that of the solvent), N'_I ($=N_I - N_f$) excess enrichment of inner oxygens over natural abundance, N'_{II} ($=N_{II} - N_f$) excess enrichment of outer oxygens over natural abundance, N'_{I_0} initial excess enrichment of inner oxygens over natural abundance, and N'_{II_0} initial excess enrichment of outer oxygens over natural abundance. Then, the rate of change of enrichment for outer oxygens will be given by

$$-dN_{II}/dt = k_{o1}N'_{II} - k_{i1}(N'_I - N'_{II}) \tag{17}$$

Similarly, the rate of change of enrichment for inner oxygens will be given by

$$-dN_I/dt = k_{i1}(N'_I - N'_{II}) \tag{18}$$

Solving the coupled differential eq 17 and 18 by the method of Laplace–Carson transforms[25] leads to the equation (F = fraction of exchange)

$$\begin{aligned} 1 - F &= \frac{N'_I + N'_{II}}{N'_{I_0} + N'_{II_0}} \\ &= \frac{N'_{II_0}}{N'_{I_0} + N'_{II_0}} \left[\left(\frac{a_2\left(1 + \frac{N'_{I_0}}{N'_{II_0}}\right) - k_{o1}}{(k_{o1}^2 + 4k_{i1}^2)^{1/2}} \right) e^{-a_1 t} \right. \\ &\quad \left. - \left(\frac{a_1\left(1 + \frac{N'_{I_0}}{N'_{II_0}}\right) - k_{o1}}{(k_{o1}^2 + 4k_{i1}^2)^{1/2}} \right) e^{-a_2 t} \right] \end{aligned} \tag{19}$$

where

$$a_1 = [2k_{i1} + k_{o1} - (k_{o1}^2 + 4k_{i1})^{1/2}]/2 \tag{20}$$

$$a_2 = [2k_{i1} + k_{o1} + (k_{o1}^2 + 4k_{i1}^2)^{1/2}]/2 \tag{21}$$

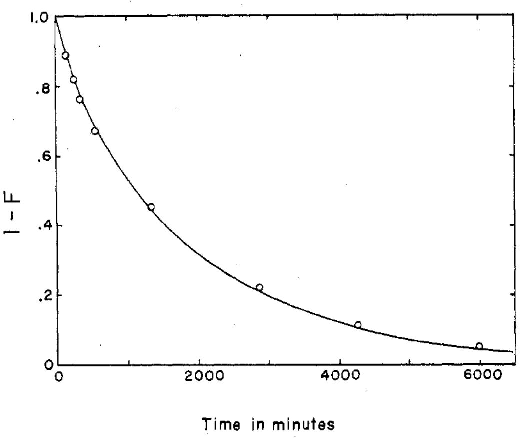

Figure 3. Comparison of calculated and experimental values of 1 − *F* (*F* is fraction of coordinated oxalate oxygens which have exchanged with solvent oxygen). Data are for experiment no. 4 (Table IV). Points are experimental; line is calculated.

Equation 19 enables one to obtain, for any assumed values of k_{i1} and k_{o1}, *calculated* values of 1 − *F* for the coordinated oxalate, which can be compared to the *experimentally* determined values of 1 − *F* $[=(N_t - N_f)/(N_0 - N_f)]$.

For long exchange times, or in experiments where preexchange at 25 °C was allowed, the exponential term in a_2 becomes negligible and only the "a_1 term" of (19) remains important. For this condition eq 19 can be rewritten as

$$\ln (N_t - N_f) = \ln \left[(N_0 - N_f) \left(\frac{N'_{II_0}}{N'_{I_0} + N'_{II_0}} \right) \left(\frac{a_2\left(1 + \frac{N'_{I_0}}{N'_{II_0}}\right) - k_{o1}}{(k_{o1}{}^2 + 4k_{i1}{}^2)^{1/2}} \right) \right] - a_1 t \tag{22}$$

and the slope of a ln $(N_t - N_f)$ vs. time plot is equal to a_1.

For experiments where the whole range of exchange was studied, values of k_{i1} and k_{o1} were varied with the use of a nonlinear least-squares (nlls) program[26] to minimize differences between experimental and calculated values of 1 − *F*. For experiments concentrating on the early stages of exchange only k_{o1} was allowed to vary; the initial values of k_{i1} were obtained as described above and extrapolated to the appropriate temperature and acidity. Experiments emphasizing later exchange were used to determine values of k_{i1} from a_1 values (k_{obsd} values) obtained from plots of ln $(N_t - N_f)$ vs. time at long times (see eq 22 and accompanying text), and k_{o1} values extrapolated to the appropriate experimental conditions. The new k_{i1} values were then used in calculating improved k_{o1} values for experiments concentrating on early exchange. With this procedure, optimized values of k_{i1} and k_{o1} were obtained by recycling until no further changes occurred.

Table IV lists the resulting values of k_{i1} and k_{o1}. Figure 3 compares calculated and experimental values of 1 − *F* for one of the experiments. The degree of agreement in Figure 3 is typical for the other experiments and is within reasonable limits of experimental error. The resulting values of k_{i1} and k_{o1} are both observed to be linearly dependent on [H+]. Second-order rate constants[24b] at 35.0 °C and corresponding activation parameters are as follows: k_{i2} $(=k_{i1}/[H^+])$ = 4.5 × 10^{-5} M^{-1} s^{-1}, $\Delta H^{\ddagger}_{i2}$ = 26.0 (±1.2) kcal mol^{-1}, $\Delta S^{\ddagger}_{i2}$ = +5.8 (±4.0) cal mol^{-1} K^{-1}; k_{o2} $(=k_{o1}/[H^+])$ = 9.6 × 10^{-5} M^{-1} s^{-1}, $\Delta H^{\ddagger}_{o2}$ = 17.1 (±0.3) kcal mol^{-1}, $\Delta S^{\ddagger}_{o2}$ = −21.6 (±1.0) cal mol^{-1} K^{-1}.

The procedure we have described for calculating k_{i1} and k_{o1} presumes the initial oxygen-18 enrichment of the complex is homogeneous between inner and outer oxygens. For experiments where N_0 was measured, the complex was found on the average to be about 5% less enriched than the original oxalate, presumably because some enrichment was lost during synthesis. Nevertheless, our assumption of initial homogeneous enrichment appears reasonable, because under the high-temperature conditions in the synthesis the interchange between outer and inner oxygens in the chelate should be significantly faster than outer oxygen/solvent or free oxalate oxygen/solvent exchange.[27]

Table IV. Values of Pseudo-First-Order Rate Constants for Inner/Outer Oxygen Interchange, k_{i1}, and Outer Oxygen Exchange with Solvent, k_{o1}[a]

Expt no.	Temp, °C	[H+], M	$10^6 k_{i1}$, s^{-1}	$10^6 k_{o1}$, s^{-1}
1	9.8	0.302	0.303[b]	2.20[c,h]
2	15.0	0.302	0.692[b]	3.90[c,h]
3	25.1	0.302	3.15[b]	11.4[c,h]
4	34.9	0.302	13.5[d,h] (11.2[f])	28.5[c,h] (30.0[f])
5	35.0	0.300	15.2[d]	28.5[c,h]
6	45.0	0.302	47.2[d,h] (40.3[f])	72.0[c,h] (74.8[f])
7	45.0	0.299	35.3[d]	70.3[e]
8	55.3	0.298	166[d,h]	168[e]
9	64.9	0.296	663[d,h]	363[e]
10	45.0	0.100	19.7[d]	23.5[e]
11	45.0	0.399	55.8[d]	94.0[e]
12	45.0	0.499	69.2[d]	118[e]
13	45.0	0.499	76.6[d]	118[e]
14	25.0	0.101	1.00[g]	3.88[c]
15	25.1	0.101	1.00[g]	3.52[c]
16	25.0	0.504	4.98[g]	26.8[c]

[a] See ref 24a. [b] Values extrapolated from k_{i1} values for other temperatures and previous round of calculation, with E_a < 1 kcal different from the final value. [c] Value from the nlls program allowing only k_{o1} to vary, with k_{i1} the same or within 2% of value in the k_{i1} column. [d] Value calculated using eq 20, with a_1 $(=k_{obsd})$ obtained by a plot of ln $(N_t - N_f)$ vs. time at long times (see eq 22 and accompanying text) and with k_{o1} equal to the value given in the k_{o1} column. [e] Value calculated from appropriate activation parameters and corrected assuming linear dependence of rate constant on [H+]. [f] Values from the nlls program allowing both k_{i1} and k_{o1} to vary. [g] Calculated from final k_{i1} values at other temperatures and final E_a, with corrections for [H+]. [h] Value used in activation parameter calculation.

The calculations presented above assume that aliquots of complex, isolated during the course of the kinetic run, have maintained two inner and two outer oxygens in the reacting solution. There is a possibility that a species might build up which contains one inner and three outer oxalate oxygens. In the thermal decomposition of $Co(C_2O_4)_3{}^{3-}$ we have seen direct spectral–kinetic evidence for the buildup of a species of this type,[28] although for $Rh(C_2O_4)_3{}^{3-}$ there is no clear indication for a similar situation. In the present case the close similarity in the exchange rates for inner and outer oxygens rules out a distinction on the basis of the oxygen-exchange experiments. Thus, our oxygen-exchange results can also be accommodated, quantitatively, on the basis of a complex with one inner and three outer oxygens,[29] and a situation in which a complex with two inner and two outer oxygens (certainly the initial state[12]) changes to one with one inner and three outer oxygens would therefore also be consistent with the observed oxygen-exchange data. However, we have found *no direct evidence*, spectral and/or kinetic, for the existence of a one-ended oxalato species under the conditions of our experiments.

Discussion

The oxygen-exchange and acid hydrolysis results for $Rh(en)_2C_2O_4{}^+$ are compared to results for related rhodium and cobalt complexes in Table V.

A basic comparison is $Rh(en)_2C_2O_4{}^+$ with $Rh(C_2O_4)_3{}^{3-}$. The temperature dependence of rate constants for oxygen exchange in these two complexes is illustrated in Figure 4; see

Table V. Comparison of Rate Parameters for Rhodium and Cobalt Complexes

Complex	Process	Ionic strength	Rate const[a] at 25 °C	$\Delta H^{\ddagger}$,[b] kcal mol^{-1}	$\Delta S^{\ddagger}$,[b] cal mol^{-1} K^{-1}	Ref
$Rh(C_2O_4)_3^{3-}$	Outer oxygen exchange	0.54	$k_2 = 9.2 \times 10^{-5}$ M^{-1} s^{-1}	16.9 (±2.0)	−20.0 (±6.0)	8
	Inner oxygen exchange	0.54	$k_2 = 1.83 \times 10^{-6}$ M^{-1} s^{-1}	23.4 (±2.0)	−6.3 (±6.0)	8
	Acid hydrolysis	0.54	$k_2 = 2.5 \times 10^{-8}$ M^{-1} s^{-1}	25.5 (±2.0)	−7.8 (±6.0)	8
			$k_3 = 1.49 \times 10^{-7}$ M^{-2} s^{-1}	25.9 (±2.0)	−2.9 (±6.0)	
$Rh(en)_2C_2O_4^+$	Outer oxygen exchange	0.50	$k_{o2} = 3.5 \times 10^{-5}$ M^{-1} s^{-1}	17.1 (±0.3)	−21.6 (±1.0)	This work
	Inner/outer oxygen interchange	0.50	$k_{i2} = 1.0 \times 10^{-5}$ M^{-1} s^{-1}	26.0 (±1.0)	+5.8 (±4.0)	This work
	Acid hydrolysis	0.50	$k_{a2} = 1.08 \times 10^{-6}$ M^{-1} s^{-1}	24.1 (±2.0)	−5.0 (±6.0)	This work
			$k_{a3} = 3.0 \times 10^{-6}$ M^{-2} s^{-1}	18.0 (±2.5)	−23.4 (±8.0)	
$Rh(NH_3)_5OH_2^{3+}$	Oxygen exchange	0.4–0.5	$k_1 = 1.07 \times 10^{-5}$ s^{-1}	24.1 (±0.3)	−0.7[d]	37–39
$Co(C_2O_4)_3^{3-}$	Outer oxygen exchange	1.0	$k_2 = 5.1 \times 10^{-5}$ M^{-1} s^{-1} [c]	15.9[d]	−25[c]	6
		1.3[c]	$k_2 = 4.8 \times 10^{-5}$ M^{-1} s^{-1} [c]	16.6[d]	−23[c]	7
	Inner oxygen exchange	1.0	$k_2 \approx 1.0 \times 10^{-6}$ M^{-1} s^{-1} [c]	~29[d]	+13[c]	6
		1.3[c]	$k_2 = 1.2 \times 10^{-6}$ M^{-1} s^{-1} [c]	41 (±5)		7
	Redox decompn (acid catalyzed)	1.1	$k_2 = 3.3 \times 10^{-5}$ M^{-1} s^{-1}	29.8 (±0.8)	21.0 (±2.0)	28
			$k_3 = 1.3 \times 10^{-5}$ M^{-2} s^{-1}			
$Co(en)_2C_2O_4^+$	Outer oxygen exchange	1.0	$k_2 = 1.2 \times 10^{-5}$ M^{-1} s^{-1}			3
	Inner oxygen exchange	1.0	$k_2 < 2.4 \times 10^{-8}$ M^{-1} s^{-1}			3
	Acid hydrolysis					3, 4
$Co(NH_3)_5OH_2^{3+}$	Oxygen exchange	~0.8	$k_1 = 0.59 \times 10^{-5}$ s^{-1}	26.6 (±0.3)	+6.7 (±1)	40

[a] For rate constants, subscript 1 refers to a first-order constant, subscript 2 to a second-order constant (first order in complex and in [H$^+$]), and subscript 3 to a third-order constant (first order in complex and second order in [H$^+$]). [b] Error limits are those quoted by appropriate authors, unless otherwise indicated. Most values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are quoted to one-tenth of a unit (although uncertainties are larger) to enable calculations for various temperatures of the more precise values of the rate constants. [c] Calculated from data given in the reference. [d] Error limits not given.

also Table V. In most but not all respects the two complexes are similar. As would be anticipated, outer oxygen exchange for the two complexes proceeds at similar rates, with similar values for both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, in accord with observations that the charge on the complex has little influence on the kinetics of this process.[8,22,30,31] Also, for $Rh(C_2O_4)_3^{3-}$ at all temperatures in the normally accessible range (0–100 °C) and for $Rh(en)_2C_2O_4^+$ below ~60 °C, exchange of outer oxygen with solvent ("outer oxygen exchange") proceeds more rapidly than exchange of inner oxygen with solvent ("inner oxygen exchange"). For $Rh(en)_2C_2O_4^+$ at temperatures >60 °C our values of k_{i2} exceed those of k_{o2}, although this does not imply a rate for "inner oxygen exchange" with solvent exceeding that for "outer oxygen exchange" with solvent, for it will be recalled that our k_{i2} and k_{i1} refer to the *interchange* of inner and outer oxygen. As has been described, our interpretation is that an "inner oxygen" must become an "outer oxygen" before it can exchange with solvent. Hence, the rate of inner/outer oxygen interchange can exceed the rate of outer oxygen with solvent (which is undoubtedly the situation for chromium(III) complexes, as well as for $Pt(C_2O_4)_2^{2-}$)[22,30,31] while the rate of "inner oxygen exchange" with solvent can, at most, become equal to the rate of "outer oxygen exchange". For $Rh(C_2O_4)_3^{3-}$, where inner oxygen exchange remains significantly slower than outer oxygen exchange (in the accessible temperature range), the rate constants for the former process apply also to the inner/outer oxygen interchange process. The faster inner/outer oxygen interchange rates for $Rh(en)_2C_2O_4^+$, in comparison to those for $Rh(C_2O_4)_3^{3-}$, appear to be due to a more positive value of $\Delta S^{\ddagger}$, with the difference in rates becoming greater at higher temperatures because of a greater value of $\Delta H^{\ddagger}$ for $Rh(en)_2C_2O_4^+$. For $Rh(en)_2C_2O_4^+$ there is a crossover in the relative values of k_{i2} and k_{o2} at ~60 °C. For $Rh(C_2O_4)_3^{3-}$ a crossover of this type does not occur in the accessible temperature range. For both $Rh(en)_2C_2O_4^+$ and $Rh(C_2O_4)_3^{3-}$, acid hydrolysis proceeds significantly more slowly than inner/outer oxygen interchange for any temperature in the range examined. One notable difference is that the aquation of $Rh(en)_2C_2O_4^+$ does not proceed to completion in the concentration ranges examined ([complex] ≈ 10^{-3} M, [H$^+$] ≈ 0.1–1.0 M), while the acid hydrolysis of $Rh(C_2O_4)_3^{3-}$, under comparable conditions, has been seen as an essentially quantitative stoichiometric process (producing $Rh(C_2O_4)_2(H_2O)_2^-$ and $H_2C_2O_4$).[8b] On statistical grounds one would expect the hydrolysis equilibrium constant (for loss of

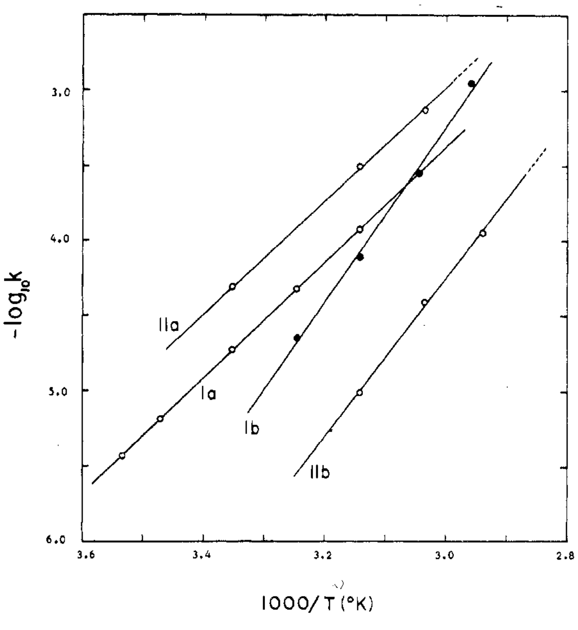

Figure 4. Pseudo-first-order rate constants for [H$^+$] = 0.50 M. $Rh(C_2O_4)_3^{3-}$ (μ = 0.54): IIa, outer oxygen exchange; IIb, inner oxygen exchange.[8] $Rh(en)_2C_2O_4^+$ (μ = 0.50): Ia, outer oxygen exchange; Ib, inner/outer oxygen interchange (refer to Table IV).

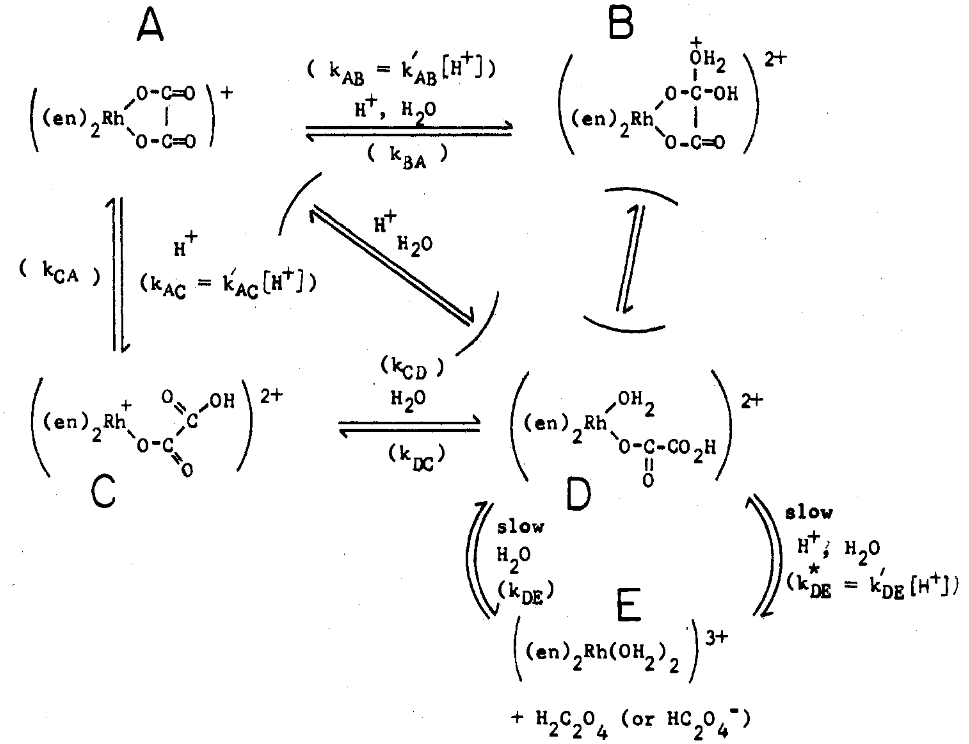

Figure 5. Suggested mechanism for oxygen exchange and aquation.

one oxalate) to be 3 times greater for $Rh(C_2O_4)_3^{3-}$ than for $Rh(en)_2C_2O_4^+$, although this corresponds to a difference in the $\Delta G°$ values for the two processes of only ~0.6 kcal mol^{-1} at 25 °C. More significant contributions toward a more negative value of $\Delta G°$ for the hydrolysis of $Rh(C_2O_4)_3^{3-}$ are likely to arise because of the separating ions being similarly charged, while being oppositely charged for $Rh(en)_2C_2O_4^+$, and because of expected differences, for the two reactions, in changes in solvation. Acid hydrolysis of $Rh(C_2O_4)_3^{3-}$ produces the presumably less hydrated $Rh(C_2O_4)_2(H_2O)_2^-$, and acid hydrolysis of $Rh(en)_2C_2O_4^+$, the presumably more hydrated $Rh(en)_2(H_2O)_2^{3+}$, while hydration changes associated with consumption of H^+ and production of $H_2C_2O_4$ or $HC_2O_4^-$ would be the same for both reactions. The difference in $\Delta S°$ values for the two reactions, arising from these differences in hydration changes, is likely to be of the order of 30 cal mol^{-1} K^{-1} in favor of hydrolysis of $Rh(C_2O_4)_3^{3-}$, corresponding to a difference in the $T\Delta S°$ values of ~11 kcal at 25 °C.[32] The latter contribution to differences in the $\Delta G°$ values may be partially canceled, however, by opposing enthalpy contributions to the hydrational changes.

Our kinetic results for $Rh(en)_2C_2O_4^+$ find their most obvious explanation in mechanistic processes similar to those described[8] for $Rh(C_2O_4)_3^{3-}$. Thus, with reference to Figure 5, exchange of outer oxygen can take place, without the need for ring opening, through the formation of the intermediate species B in a simple A-2 mechanism. A path for inner-oxygen exchange is then available by way of inner/outer oxygen interchange which can arise by Rh–O bond cleavage followed by C–C bond rotation in the short-lived five-coordinate species C. Complete aquation to *cis*-$Rh(en)_2(H_2O)_2^{3+}$ and oxalic acid can be presumed to occur by way of the monodentate oxalato species D, which can be formed by addition of a water molecule to C. The observed pseudo-first-order behavior of all processes at constant [H^+], the observed acid dependency of the processes, the absence of spectral or kinetic evidence for the buildup of intermediate species (particularly D), and the magnitude of *observed* rate constants all fit this scheme where the following rate relationships are indicated over the temperature range investigated ("unprimed" rate constants refer to the first-order or pseudo-first-order constants and incorporate [H^+] where appropriate; refer to Figure 5): $k_{CA} >> k_{BA} > k_{AB} > k_{AC} > k_{DE} \sim k^*_{DE}$; also $k_{CA} >> k_{CD} > k_{DC} > k_{DE} \sim k^*_{DE}$. The reversible arrows in parentheses, specifying direct interconversion between A and D and between B and D, refer to processes which are possible although not required by the data. The possibility that a significant path for exchange of oxygen in the complex could be through reentry of aquated oxalate can be ruled out, for the conditions of our experiments, on the basis of the relative rates of oxygen-exchange, aquation, and anation processes.

The proposal that D forms by way of C implies Rh–O bond cleavage proceeds more readily than O_{inner}–C bond cleavage; it also implies the isotopic composition of the coordinated water in D, at the time of formation, will be that of the solvent. Support for Rh–O bond cleavage in the case of $Rh(C_2O_4)_3^{3-}$ comes from the close similarity in rate laws, rate constants, and activation parameters for inner oxygen exchange and racemization.[8] Metal–oxygen bond cleavage also seems likely for the acid-catalyzed aquation of $(NH_3)_5Rh–OAc^{2+}$ and $(NH_3)_5Co–OAc^{2+}$, where the argument has been presented[3] that the much slower aquation rates found[35] for $(NH_3)_5Ir–OAc^{2+}$ provide upper limits for O–C bond cleavage in the corresponding rhodium and cobalt complexes.

It is noteworthy that $Rh(en)_2C_2O_4^+$ is seen to undergo reversible acid-catalyzed hydrolysis and inner oxygen exchange, whereas $Co(en)_2C_2O_4^+$ is reported to be unreactive.

Thus Sheel et al.[4] observed $Co(en)_2C_2O_4^+$ to be unaffected by prolonged heating at 90 °C in the presence of 1 M mineral acid. These observations are not described in detail. Observations by Brown and Harris[36] on the anation of $Co(en)_2(H_2O)_2^{3+}$ by oxalic acid give further support for the thermodynamic stability of $Co(en)_2C_2O_4^+$, although their data do not allow an estimate of a "stability constant". Certainly under suitably favorable conditions (e.g., at high acidity and *sufficiently low concentration* of complex) $Co(en)_2C_2O_4^+$ *must* undergo acid-catalyzed aquation. In the case of $Rh(en)_2C_2O_4^+$, K for reaction 2 at 90 °C is ~6.5×10^{-3} (i.e.,

$\Delta G° \approx +3.6$ kcal mol^{-1}). The corresponding aquation equilibrium reaction for $Co(en)_2C_2O_4^+$ would be outside the observable range if the fraction which aquates is <5%, which, for 10^{-2} M total cobalt and 1 M H^+, corresponds to $K < 2.4 \times 10^{-5}$ or $\Delta G° \approx 7.7$ kcal mol^{-1} at 90 °C. We then estimate that for acid hydrolysis, $\Delta G°$ (at 90 °C) will be 4 or more kcal mol^{-1} more positive for $Co(en)_2C_2O_4^+$ than for $Rh(en)_2C_2O_4^+$. This circumstance may well account for the lack of reactivity toward acid hydrolysis observed earlier[4] for $Co(en)_2C_2O_4^+$.

The attempt by Andrade et al.[3] to measure exchange between solvent and inner oxygen in $Co(en)_2C_2O_4^+$ was limited by the aquation reaction, which by implication was observed to proceed. For exchange of inner oxygen with solvent, the upper limit for the rate constant at 25 °C is given as $k_c = k_{ex}/[H^+] = 2.4 \times 10^{-8}\ M^{-1}\ s^{-1}$ (where $d[O]/dt = k_{ex}[O] = k_c[H^+][O]$). This limit is then less than $^1/_{400}$th of the inner/outer oxygen interchange rate for $Rh(en)_2C_2O_4^+$ at 25 °C. The lack of more specific information on rate constants and activation parameters for reactions of $Co(en)_2C_2O_4^+$ in acidic solution precludes a detailed comparison with $Rh(en)_2C_2O_4^+$. However, from the information at hand, it seems almost certain that $\Delta H^‡$ for acid hydrolysis of $Co(en)_2C_2O_4^+$ and also for inner oxygen exchange (if the latter process can occur independently of aquation) will be significantly higher than the values found for $Rh(en)_2C_2O_4^+$. This type of situation already appears in the case of $Co(C_2O_4)_3^{3-}$ compared to $Rh(C_2O_4)_3^{3-}$ (see Table V). For $Rh(C_2O_4)_3^{3-}$, the lower values of $\Delta H^‡$ and more negative values of $\Delta S^‡$ for inner oxygen exchange and aquation, in comparison to inner oxygen exchange and acid-promoted redox decomposition for $Co(C_2O_4)_3^{3-}$, suggest more solvent participation in the transition states. This type of situation has already been seen in comparison of other analogous rhodium(III) and cobalt(III) complexes.[15,37,38] As we move from complexes of type $M(C_2O_4)_3^{3-}$ to those of type $M(en)_2C_2O_4^+$, one would expect these differences between rhodium and cobalt to be accentuated. The more positive rhodium center for $Rh(en)_2C_2O_4^+$, compared to $Rh(C_2O_4)_3^{3-}$, is likely to enhance further the associative character of processes involving substitution at the metal center, although this factor would be partially offset by the fact that the separating components are now oppositely charged. But for $Co(en)_2C_2O_4^+$, in comparison to $Co(C_2O_4)_3^{3-}$, the change to the more positive metal center is likely to have much more dramatic consequences because of the presumed greater dissociative character for substitution processes at the cobalt(III) center.[15] A precedent for this type of situation exists in the following behavior: the rates of acid hydrolysis of $Rh(NH_3)_5Cl^{2+}$, *trans*-$Rh(NH_3)_4Cl_2^+$, and $Rh(C_2O_4)_2Cl_2^{3-}$ are all very nearly the same, while *trans*-$Co(NH_3)_4Cl_2^+$ reacts about 10^3 times faster than $Co(NH_3)_5Cl^{2+}$.[15] On this basis, we should not be surprised that $Rh(en)_2C_2O_4^+$ is much more reactive than $Co(en)_2C_2O_4^+$ with regard to substitution at the metal center. Certainly the behavior of $Rh(en)_2C_2O_4^+$ toward inner oxygen exchange and aquation presents a sharp contrast to that of $Co(en)_2C_2O_4^+$, which still appears unique in terms of its kinetic and thermal stability.

Registry No. $Rh(en)_2C_2O_4^+$, 46360-64-9; O_2, 7782-44-7; H_2O, 7732-18-5; $[Rh(en)_2C_2O_4]I_3$, 58944-28-8.

Supplementary Material Available: Listing of the primary data for the oxygen-exchange experiments (N_t values) (2 pages). Ordering information is given on any current masthead page.

References and Notes

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(2) To whom correspondence should be addressed.

(3) C. Andrade, R. B. Jordan, and H. Taube, *Inorg. Chem.*, **9**, 711 (1970).

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

(5) (a) N. S. Rowan, R. M. Milburn, and M. Z. Hoffman, *Inorg. Chem.*, **11**, 2272 (1972); (b) H. G. Kruszyna and R. M. Milburn, *ibid.*, **10**, 1578 (1971); see also references in these papers.

(6) J. A. Broomhead, I. Lauder, and P. Nimmo, *J. Chem. Soc. A*, 645 (1971).

(7) A. L. Odell and D. B. Rands, *J. Chem. Soc., Dalton Trans.*, 749 (1972).

(8) (a) L. Damrauer and R. M. Milburn, *J. Am. Chem. Soc.*, **90**, 3884 (1968); (b) *ibid.*, **93**, 6481 (1971).

(9) (a) D. Barton and G. M. Harris, *Inorg. Chem.*, **1**, 251 (1962); (b) K. V. Krishnamurty, *ibid.*, **1**, 422 (1962).

(10) A. L. Odell, R. W. Olliff, and F. B. Seaton, *J. Chem. Soc.*, 2280 (1965).

(11) See, for example, F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2d ed, Wiley, New York, N.Y., 1967, Chapter 3.

(12) T. P. Dasgupta, R. M. Milburn, and L. Damrauer, *Inorg. Chem.*, **9**, 2789 (1970).

(13) In independent preparations of recrystallized *cis*-$[Rh(en)_2Cl_2]NO_3$, one of us observed absorbancy coefficients of 197 at each of the λ_{max} values of 296 and 350 nm; another of us obtained absorbancy coefficients of 200 at each of these wavelengths. These values do not compare well with the respective values of 180 and 155 reported by S. A. Johnson and F. Basolo, *Inorg. Chem.*, **1**, 925 (1962). It may be relevant that the apparent absorbancy coefficient at 350 nm decreases when a solution containing *cis*-$Rh(en)_2Cl_2^+$ is left overnight.

(14) Analysis by Galbraith Laboratories, Inc., Knoxville, Tenn.

(15) S. A. Johnson, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 1741 (1963).

(16) Johnson et al.[15] found that *cis*-$Rh(en)_2Cl_2^+$ in 0.1 M KOH solution is quantitatively transformed into *cis*-$Rh(en)_2(OH)_2^+$ in 24 h at room temperature, without trace of steric rearrangement. We have observed that this conversion can also be achieved in 2 h at 60 °C.

(17) W. J. Blaedel and V. W. Meloche, "Elementary Quantitative Analysis", 2d ed, Harper and Row, New York, N.Y., 1963, p 302.

(18) In separate experiments it was established that the reactions of Cl^- with $Rh(en)_2C_2O_4^+$ and with *cis*-$Rh(en)_2(H_2O)_2^{3+}$, for the conditions used here, are too slow to be of consequence.

(19) (a) D. A. Skoog and D. M. West, "Fundamentals of Analytical Chemistry", Holt, Reinhart and Winston, New York, N.Y., 1963, pp 434, 444; (b) H. H. Willard, N. H. Furman, and C. E. Bricker, "Elements of Quantitative Analysis", 4th ed, Van Nostrand, Princeton, N.J., 1956, pp 172, 354.

(20) K. J. Laidler, "Chemical Kinetics", McGraw-Hill, New York, N.Y., 1965, pp 19–21.

(21) R. F. Bauer and W. M. Smith, *Can. J. Chem.*, **43**, 2755 (1965).

(22) J. E. Teggins and R. M. Milburn, *Inorg. Chem.*, **4**, 793 (1965).

(23) L. Damrauer, Ph.D. Dissertation, Boston University, 1969.

(24) (a) In the designations k_{i1} and k_{o1} subscript "i" is used to indicate inner/outer oxygen interchange, subscript "o" to indicate outer/solvent oxygen interchange, and subscript "1" to indicate a first-order constant. (b) In the designations k_{i2} and k_{o2}, the subscripts "i" and "o" are as before, while "2" refers to a second-order constant.

(25) N. M. Rodiguin and E. N. Rodiguina, "Consecutive Chemical Reactions", translated from Russian, with English edition edited by R. F. Schneider, Van Nostrand, Princeton, N.J., 1964.

(26) Oak Ridge Gaussian least-squares (ORGLS) program, supplied by Dr. R. H. Mann.

(27) If we recalculate values of k_{i1} and k_{o1} on the basis of maximum conceivable inhomogeneity (i.e., outer oxygens initially 5% less enriched and inner oxygens initially 5% more enriched than N_o), the resulting values of k_{i1} become consistently lower (by ~12%) and the values of k_{o1} consistently higher (by ~11%) than the values presented in Table IV, although the change does not noticeably affect the observed first-order dependence on $[H^+]$, nor does it appreciably change the activation parameters {values recalculated on this basis are as follows: $\Delta H^‡_{i2} = 24.8$ (±1.0) kcal mol^{-1}, $\Delta S^‡_{i2} = 1.7$ (±3.0) cal $mol^{-1}\ K^{-1}$; $\Delta H^‡_{o2} = 16.8$ (±0.3) kcal mol^{-1}, $\Delta S^‡_{o2} = -22.8$ (±1.0) cal $mol^{-1}\ K^{-1}$}.

(28) N. S. Rowan and R. M. Milburn, to be submitted for publication.

(29) A recalculation of rate constants, based on one inner oxygen and three kinetically equivalent outer oxygens, results in k_{i1} values which are in general 40–120% higher and k_{o1} values which are 20–40% lower than the values presented in Table IV. The nlls agreement factors are comparable to those found for the results in Table IV. The activation parameters calculated on the basis of this interpretation would be as follows: $\Delta H^‡_{i2} = 30.5$ (±1.4) kcal mol^{-1}, $\Delta S^‡_{i2} = 19.0$ (±4.0) cal $mol^{-1}\ K^{-1}$; $\Delta H^‡_{o2} = 18.3$ (±0.3) kcal mol^{-1}, $\Delta S^‡_{o2} = -21.0$ (±1.0) cal $mol^{-1}\ K^{-1}$.

(30) S. G. Gourley and R. M. Milburn, *Inorg. Chem.*, **11**, 2262 (1972).

(31) (a) J. A. Broomhead, N. Kane-Maguire, and I. Lauder, *Inorg. Chem.*, **10**, 955 (1971); (b) *ibid.*, **9**, 1243 (1970).

(32) Estimated from the Latimer and Powell equation,[33] taking the crystal radii of $Rh(C_2O_4)_2H_2O_2^-$, $Rh(en)_2C_2O_4^+$, and $Rh(en)_2(H_2O)_2^{3+}$ to be the same as that found[34] for $Rh(C_2O_4)_3^{3-}$ in $K_3Rh(C_2O_4)_3 \cdot 4.5H_2O$.

(33) R. Powell and W. M. Latimer, *J. Chem. Phys.*, **19**, 1139 (1951).

(34) B. C. Dalzell and K. Eriks, *J. Am. Chem. Soc.*, **93**, 4298 (1971).

(35) F. Monacelli, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, **24**, 1241 (1962).

(36) P. M. Brown and G. M. Harris, *Inorg. Chem.*, **7**, 1872 (1968).

(37) (a) F. Monacelli and E. Viel, *Inorg. Chim. Acta*, **1**, 467 (1967); (b) E. Borghi and F. Monacelli, *ibid.*, **5**, 211 (1971).

(38) S. B. Tong and T. W. Swaddle, *Inorg. Chem.*, **13**, 1538 (1974).

(39) H. L. Bott, A. J. Poe, and K. Shaw, *J. Chem. Soc., A*, 1745 (1970).

(40) H. R. Hunt and H. Taube, *J. Am. Chem. Soc.*, **80**, 2642 (1958).