Kinetics of Oxygen Exchange, Racemization, and Aquation in Tris(oxalato)rhodate(III) Ion[1,2]

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Abstract: An earlier study of acid-catalyzed oxygen exchange between $Rh(C_2O_4)_3{}^{3-}$ and solvent water has been extended to a reexamination of the acid-catalyzed racemization and aquation reactions. Racemization over the $[H^+]$ range 0.0–0.4 M requires a two-term rate law: $R = \{k_{r2}[H^+] + k_{r3}[H^+]^2\}[Rh(C_2O_4)_3{}^{3-}]$. At 56.4° and μ (ionic strength) $= 0.54$, $k_{r2} = 4.2 \times 10^{-5}\ M^{-1}\ sec^{-1}$, $k_{r3} = 2.4 \times 10^{-4}\ M^{-2}\ sec^{-1}$, $\Delta H^{\ddagger}{}_{r2} = 23.3 \pm 1.5$ kcal mol^{-1}, $\Delta S^{\ddagger}{}_{r2} = -8.2 \pm 4.0$ eu, $\Delta H^{\ddagger}{}_{r3} = 26.8 \pm 1.5$ kcal mol^{-1}, $\Delta S^{\ddagger}{}_{r3} = 5.8 \pm 4.0$ eu. For inner-oxygen exchange at 56.3° and $\mu = 0.54$, $k_{i2}\ (= k_i/[H^+]) = 8.5 \times 10^{-5}\ M^{-1}\ sec^{-1}$, $\Delta H^{\ddagger}{}_{i2} = 23.4 \pm 2.0$ kcal mol^{-1}, $\Delta S^{\ddagger}{}_{i2} = -6.3 \pm 6.0$ eu. The rate constants and activation parameters, corresponding to rate law terms which are first order in $[H^+]$, are remarkably similar for racemization and inner-oxygen exchange, and the results strongly suggest a parallelism in the mechanisms. The aquation of $Rh(C_2O_4)_3{}^{3-}$ to $Rh(C_2O_4)_2(H_2O)_2{}^{-}$ and free oxalic acid, which was examined over the $[H^+]$ range 0.0–0.5 M, also requires a two-term rate law: $R = \{k_{a2}[H^+] + k_{a3}[H^+]^2\}[Rh(C_2O_4)_3{}^{3-}]$. At 56.3° and $\mu = 0.54$, $k_{a2} = 1.67 \times 10^{-6}\ M^{-1}\ sec^{-1}$, $k_{a3} = 1.16 \times 10^{-5}\ M^{-2}\ sec^{-1}$, $\Delta H^{\ddagger}{}_{a2} = 25.5 \pm 2.0$ kcal mol^{-1}, $\Delta S^{\ddagger}{}_{a2} = -7.8 \pm 6.0$ eu, $\Delta H^{\ddagger}{}_{a3} = 25.9 \pm 2.0$ kcal mol^{-1}, $\Delta S^{\ddagger}{}_{a3} = -2.9 \pm 6.0$ eu. For the conditions under which racemization and inner-oxygen exchange were examined, the aquation is significantly slower. Thus, at 56.3° with $[H^+] = 0.20\ M$ and $\mu = 0.54$, when 50% of the inner oxygens have exchanged, ~4% of the complex has aquated; when 50% of the optically active complex has racemized, ~3% of the complex has aquated. Outer-oxygen exchange is considered to proceed by the previously suggested A2 mechanism without cleavage of rhodium–oxygen bonds. The slower formation of a pentacoordinated intermediate permits the interchange of inner and outer oxygens, hence accommodating inner-oxygen exchange as well as allowing for the possibility of inversion which may receive assistance through additional protonation. Addition of a water molecule to the pentacoordinated intermediate, to form a hexacoordinate intermediate with a monodentate oxalate, provides the path toward aquation.

For resolvable complexes the possibility of relationships between racemization and related reactions has long been a matter of concern.[3,4] Our special interest in this matter developed while we were examining acid-catalyzed exchange of oxygen between $Rh(C_2O_4)_3{}^{3-}$ and solvent water, where marked differences between rates for outer- and inner-oxygen exchange were observed.[5] In particular, the rates of oxygen exchange between inner oxygens and solvent water at ~56° were found to be very similar to the rates of racemization calculated from the data of Odell, *et al.*, for similar conditions of acidity and ionic strength.[6] However, activation parameters measured for inner-oxygen exchange[5] and those reported for racemization[6] were not in particularly close agreement. Because of the possible mechanistic implications, we decided to investigate the racemization reaction further, and also to reexamine the previously studied aquation reaction.[7] We have earlier given summary accounts of our findings;[2,5] we now present the results in detail.

Experimental Section

Materials. Reagent grade materials were used except where otherwise specified. Normal water was obtained from ordinary distilled water which was refluxed with potassium permanganate and sodium hydroxide in a Barnstead S-1 water still, redistilled, and finally passed through the distillation apparatus a second time. Water enriched in ^{18}O was obtained from Yeda Research and Development Co., Inc., Rehovot, Israel.

Perchloric acid and sodium perchlorate solutions were used to control acidity and ionic strength. A stock perchloric acid solution was prepared from about 60% acid and was standardized against dried sodium carbonate. A stock sodium perchlorate solution was prepared from perchloric acid and anhydrous sodium carbonate.

The preparation, analysis, and storage of unresolved $K_3Rh(C_2O_4)_3 \cdot 1.5H_2O$ have been described.[8] Solutions of this complex salt were prepared by dissolving weighed amounts in water. In some cases these solutions were used directly for the preparation of reaction solutions (the complex salt being the only source of potassium ion). In other cases potassium ion was exchanged for sodium ion.

Potassium tris(oxalato)rhodate(III) was resolved following the procedure of Werner.[9] A solution of $K_3Rh(C_2O_4)_3 \cdot 1.5H_2O$ (0.905 g in 50 ml of water at 50°) was added to a solution of strychnine nitrate (2.10 g in 100 ml of water at 85°). After standing for 1 hr, the yellow precipitate of the strychnine salt of $Rh(C_2O_4)_3{}^{3-}$ was separated from solution by suction filtration. Further precipitation continued as water from the solution evaporated at room temperature, and, in all, five fractions were collected. A fivefold weight excess of potassium iodide, dissolved in the minimum amount of water at room temperature, was added to each fraction. Each mixture was ground thoroughly and filtered, and the white solid strychnine iodide was washed with ~2 ml of water. Ethanol (95%) was added to the filtrates to precipitate the yellow potassium tris(oxalato)rhodate(III). The solid was collected by filtration, washed with ~2 ml of ether, dried by pulling air through the funnel, and stored. Solutions of $(-)_{546}$-potassium tris(oxalato)rhodate(III) were prepared as necessary. The optical rotation of solutions measured at 365, 436, 546, and 578 nm with a Perkin-Elmer 141 spectropolarimeter agreed very well with published ORD curves.[10]

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(1) Supported by the National Science Foundation.

(2) Presented at the 12th International Conference on Coordination Chemistry, Sydney, Australia, Aug 1969; *Proc. Int. Conf. Coord. Chem.*, *1969*, 12, 38 (1969).

(3) A. Werner, *Justus Liebigs Ann. Chem.*, **386**, 1 (1912); *Ber.*, **45**, 1228, 3061 (1912).

(4) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, Chapter 4.

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

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(10) A. M. Sargeson in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964, p 221.

Table I. Pseudo-First-Order Rate Constants for the Exchange of Outer Oxygens

Expt no.	[H⁺] × 10², *M*	[Complex], × 10², *M*	Ionic strength	Temp, °C	*k* × 10⁶, sec⁻¹ [a]	% deviation[b]
01	0.978	1.00	0.54	25.1	0.795 (7)	0.4
02	4.89	1.00	0.54	25.1	4.20 (4)	0.6
03	9.78	1.00	0.54	25.1	7.17 (3)	2.6
04	9.78	1.00	0.54	25.1	7.88 (4)	1.3
05	9.78	1.00	0.54	25.1	9.05 (8)	1.0
06	20.4	1.00	0.54	25.1	20.2 (4)	1.8
07	9.78	2.00	0.60	25.1	8.23 (6)	0.2
08	9.78	0.500	0.51	25.1	9.27 (5)	1.4
09	20.4	1.00	0.54	45.0	127 (3)	1.7
010	20.4	1.00	0.54	56.3	302 (3)	0.4
011	0.978	1.00	0.070	25.2	2.28 (5)	0.8

[a] Rate constants calculated from least-squares slopes for plot of eq 1, on the assumption that six oxygens exchange at the same rate and six oxygens do not exchange. Numbers in parentheses give number of points used to compute the least-squares slope. [b] Equal to the standard deviation for the least-squares slope × 100, divided by the least-squares slope.

Table II. Pseudo-First-Order Rate Constants for Exchange of Inner Oxygens

Expt no.	[H⁺] × 10², *M*	$[Rh(C_2O_4)_3{}^{3-}]$ × 10², *M*	Ionic strength	Temp, °C	*k* × 10⁶, sec⁻¹ [a]	% deviation[b]
012	20.4	0.993	0.54	45.0	3.78 (7)	1.9
013	20.4	0.993	0.54	45.0	4.15 (5)	1.4
014	4.83	0.988	0.53	56.3	3.02 (5)	4.1
015	20.3	0.988	0.53	56.3	16.6 (6)	2.0
016	20.3	0.988	0.53	56.3	14.7 (5)	3.2
017	40.6	0.988	0.53	56.3	36.0 (5)	3.3
018	20.2	0.982	0.53	67.0	45.3 (5)	3.4
019	20.8	0.494	0.24	56.3	23.8 (5)	7.6

[a] Rate constants calculated from least-squares slopes for plot of eq 1, using as the initial atom fraction the point when one-half of the oxygens had equilibrated with solvent (in most cases equilibrated at 25°). Thus N_0 for inner-oxygen = N_∞ for outer-oxygen exchange. In fact, the N_0 value is unimportant in determining the least-squares slope, because a plot of log $[(N_\infty - N_0)/(N_\infty - N_t)]$ against *t* gives the same slope as a plot of $-\log (N_\infty - N_t)$ against *t*, since N_0 is a constant. [b] Equal to the standard deviation for the least-squares slope × 100, divided by the least-squares slope.

Table III. Activation Parameters[a]

Process	Rate constant		$\Delta H^\ddagger$, kcal mol⁻¹ [b]	$\Delta S^\ddagger$, eu[b]
	Symbol	Value at 56.3°		
Outer-oxygen exchange	k_{o2}	$1.48 \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$	16.9 ± 2.0	−20.0 ± 6.0
Inner-oxygen exchange	k_{i2}	$8.5 \times 10^{-5}\ M^{-1}\ \text{sec}^{-1}$	23.4 ± 2.0	−6.3 ± 6.0
Racemization	k_{r2}	$4.2 \times 10^{-5}\ M^{-1}\ \text{sec}^{-1}$	23.3 ± 1.5	−8.2 ± 4.0
	k_{r3}	$2.4 \times 10^{-4}\ M^{-2}\ \text{sec}^{-1}$	26.8 ± 1.5	+5.8 ± 4.0
Aquation	k_{a2}	$1.67 \times 10^{-6}\ M^{-1}\ \text{sec}^{-1}$	25.5 ± 2.0	−7.8 ± 6.0
	k_{a3}	$1.16 \times 10^{-5}\ M^{-2}\ \text{sec}^{-1}$	25.9 ± 2.0	−2.9 ± 6.0

[a] All values are for ionic strength 0.54. [b] Values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are quoted to one-tenth of a unit (although the uncertainties are larger) to enable calculation for various temperatures of the more precise values of the rate constants.

The uv and visible spectra also matched spectra of the unresolved starting material.

Oxygen-Exchange Studies. The procedures used to study the exchange of oxygen between $Rh(C_2O_4)_3{}^{3-}$ and solvent water were similar to those described earlier for the $Pt(C_2O_4)_2{}^{2-}$ ion.[11] The essential details of these studies have already been presented.[5]

For each kinetic run values of *N*, the atom fraction of oxygen-18 $(=[^{18}O]/\{[^{18}O] + [^{17}O] + [^{16}O]\})$, were obtained as a function of time from the standard expression $N = R/(R + 2)$, where *R* is the isotope ratio for carbon dioxide $(=[C^{16,18}O_2]/\{[C^{16,16}O_2] + [C^{16,17}O_2]\})$. The left side of eq 1 could then be plotted against time. Values of N_∞ were calculated without inclusion of perchlorate oxygen, which is not considered to exchange under the reaction conditions used.[12]

$$\log [(N_\infty - N_0)/(N_\infty - N_t)] = (k/2.303)t \qquad (1)$$

In using eq 1, linear first-order rate plots are obtained for the early stages of reaction only if N_∞ values are calculated on the basis that very close to one-half of the 12 oxygens have equilibrated with solvent (ref 5, Figure 1A). Plots made on the basis that just one-half of the oxygens are exchanging provide pseudo-first-order rate constants which we associate with exchange of the outer oxygens. The data obtained is summarized in Table I.

After the outer oxygens have equilibrated with solvent, inner-oxygen exchange can be followed. Linear first-order rate plots are obtained now if one takes as the initial time the point when one-half of all oxygens have equilibrated. Thus, N_0 for inner-oxygen exchange is equal to N_∞ for outer-oxygen exchange.[13] A representative rate plot for inner-oxygen exchange has already been presented (ref 5, Figure 1B). Data obtained for inner-oxygen exchange are summarized in Table II. If a modified McKay equation is used for the case where one-half of the atoms exchange at one rate and one-half at a different rate,[14,15] linearity is obtained for exchange of 90% of all oxygens.

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

(12) (a) N. F. Hall and O. R. Alexander, *J. Amer. Chem. Soc.*, 62, 3455 (1940); (b) E. R. S. Winter, M. Carlton, and H. V. A. Briscoe, *J. Chem. Soc.*, 131 (1940); (c) A. I. Brodskii and N. A. Vysotskaya, *Dokl. Akad Nauk SSSR*, **101**, 869 (1955).

(13) Because the activation energy for outer-oxygen exchange was found to be less than that for inner-oxygen exchange, the usual procedure was to equilibrate the outer oxygens with solvent at 25° before following inner exchanges at higher temperatures. At 25° outer oxygens exchange ~60 times more rapidly than inner oxygens; at 56° the difference is ~20-fold.

(14) C. A. Bunton, J. H. Carter, D. R. Llewellyn, C. O'Connor, A. L. Odell, and S. Y. Yih, *J. Chem. Soc.*, 4615 (1964).

Table IV. Pseudo-First-Order Rate Constants for Racemization[a]

Expt no.	[H$^+$]	Ionic strength	Temp, °C	$k_{\text{obsd}} \times 10^5$, sec^{-1} [b]	% deviation[c]
R1	0.104	0.54	45.0	0.175	0.91
R2	0.209	0.54	45.0	0.490	0.74
R3	0.398	0.54	45.0	1.31	0.68
R4	0.104	0.54	50.0	0.318	0.46
R5	0.208	0.54	50.0	0.892	0.34
R6	0.397	0.54	50.0	2.55	0.15
R7	0.104	0.54	53.2	0.485	0.33
R8	0.208	0.54	53.2	1.38	0.50
R9	0.397	0.53	53.2	3.90	1.2
R10	0.0519	0.54	56.4	0.272	0.62
R11	0.104	0.54	56.4	0.698	0.60
R12	0.208	0.53	56.4	1.97	0.35
R13	0.415	0.54	56.4	5.97	0.23
R14	0.502	0.53	56.4	8.17	0.23
R15	0.207	0.53	63.9	5.22	0.61
R16	0.208	0.24	56.4	3.27	0.30
R17	0.209	0.71	42.9	0.343	0.63
R18	0.208	0.71	48.1	0.625	0.63
R19	0.208	0.71	56.4	1.63	0.37
R20	0.207	0.70	63.9	4.38	0.25
R21	0.589	1.81	56.4	7.35	0.29
R22	0.592	2.98	45.0	2.20	0.30
R23	0.591	2.97	50.0	4.25	0.57
R24	0.589	2.96	56.4	9.53	0.25
R25	0.587	2.95	63.9	23.7	0.38

[a] Complex concentration equal to $\sim 5.2 \times 10^{-3}$ *M* for all experiments. [b] Rate constant calculated from least-squares slope for plot of log (degrees) against time. [c] Equal to the standard deviation for the least-squares slope × 100, divided by the least-squares slope.

There is no apparent trend in the k_{obsd} values for outer-oxygen exchange as the concentration of $Rh(C_2O_4)_3^{3-}$ is varied from 5.00×10^{-3} to 20.0×10^{-3} *M*, with $[H^+] = 0.0978$ *M*, temperature = 25.1°, and $\mu \sim 0.5$ *M* (experiments 8; 3, 4, 5; 7), and the reaction is consequently considered to be first order with respect to complex concentration.

Values of k_{obsd} for both inner- and outer-oxygen exchange are very nearly proportional to [H$^+$] for constant conditions of temperature and ionic strength, and as a fairly good approximation the exchange reactions may be considered to be first order in [H$^+$]. For both exchanges there is a suggestion of additionally enhanced rates at higher [H$^+$], possibly due to rate law terms proportional to $[H^+]^2$, although further work would have to be undertaken to test this possibility.

Activation parameters for the two processes, obtained from plots of log k_{obsd} against $1/T$ (°K) for constant [H$^+$] and ionic strength, are included in Table III.

Racemization Studies. The racemization of $Rh(C_2O_4)_3^{3-}$ was followed at 365 nm with the Perkin-Elmer 141 spectropolarimeter. Reaction solutions were prepared at room temperature, the last reagent to be added being a solution of the complex, and volume and concentration corrections were made for the appropriate temperature for each kinetic run. For each run a blank solution containing all components except the complex was prepared, allowed to reach reaction temperature, and used to zero the instrument. After rinsing with reaction solution several times, the cell was filled and the solution was brought to temperature. Zero time was considered to be whenever the first optical rotation measurement was taken. The polarimeter cell was always removed from the cell compartment between readings to avoid possible catalysis by the 365-nm mercury line. The temperature of the thermostating water was measured just prior to its entering and immediately after its leaving the cell, and it was possible to know the cell temperature to within ±0.05°.

A first-order rate equation for a racemization reaction can be expressed in the form of eq 2, where *A* is the optical rotation.

$$\log (A_0/A) = (k/2.303)t \tag{2}$$

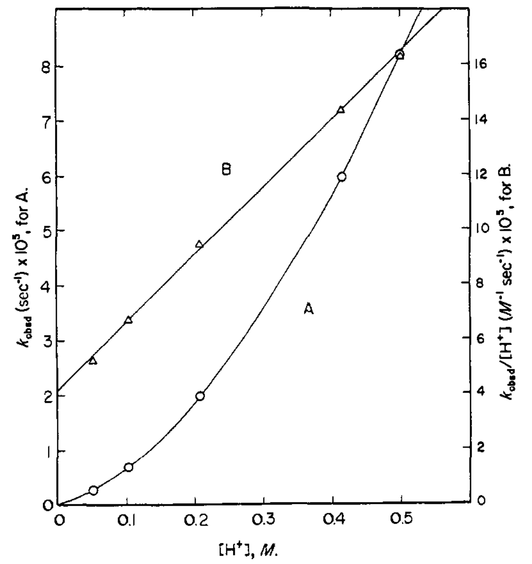

Figure 1. Plots of k_{obsd} and $k_{\text{obsd}}/[H^+]$ against [H$^+$] for racemization; temperature 56.4°, ionic strength 0.54.

Pseudo-first-order rate constants could be obtained from the linear plots which result when log *A* is plotted against time. The observed rate constants are given in Table IV. In Figure 1 we show a plot of k_{obsd} and of $k_{\text{obsd}}/[H^+]$ against [H$^+$], for conditions of constant temperature and ionic strength. The linearity of plots of $k_{\text{obsd}}/[H^+]$ against [H$^+$] demonstrates that k_{obsd} can be expressed in the form[16]

$$k_{\text{obsd}} = k_{r2}[H^+] + k_{r3}[H^+]^2 \tag{3}$$

Values of k_{r2} and k_{r3} obtained from least-squares plots of $k_{\text{obsd}}/[H^+]$ against [H$^+$] are given in Table V. Activation parameters obtained from plots of log k_{r2} and log k_{r3} against $1/T$ (°K) are included in Table III.

Table V. Values of k_{r2} and k_{r3} at Ionic Strength 0.54

Temp, °C	$k_{r2} \times 10^5$, M^{-1} sec^{-1}	$k_{r3} \times 10^5$, M^{-2} sec^{-1}
45.1	1.15	5.45
50.1	1.87	11.5
53.2	2.97	17.0
56.4	4.18	24.2

Aquation Studies. The aquation reaction was followed by observing changes in the absorbances of solutions at 400 nm with a Cary-16 spectrophotometer. Reaction solutions were prepared from appropriate stock solutions at room temperature, or at reaction temperature. Volume and concentration corrections for expansion of solutions were made. Reaction solutions were held at temperature in a thermostat, and at appropriate times aliquots were withdrawn, rapidly cooled to room temperature, and examined in 1-cm cells. The absorbance of the sample cell when filled with water, compared to the blank cell similarly filled, was determined at least once a day to allow for possible instrumental drift.

Pseudo-first-order rate constants were obtained by plotting $-\log (A_\infty - A_t)$ against time, the slope being $(k/2.303)$. Except for the very early stages of reaction, where a very slight and relatively rapid initial drop in absorbance occurs, the absorbance continues to decrease steadily and the system exhibits good first-order kinetics. In determining the least-squares slopes to establish the pseudo-first-order rate constants, these points at very early times were not included. The primary reaction observed is the release of one oxalate ligand for each tris(oxalato)rhodate(III) ion[7]

$$Rh(C_2O_4)_3^{3-} + 2H_3O^+ \rightleftharpoons Rh(C_2O_4)_2(H_2O)_2^- + H_2C_2O_4 \tag{4}$$

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(15) A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," Wiley, New York, N. Y., 1951, p 13.

(16) It should be noted that the [H$^+$] range used was 0–0.5 *M*, and for this range the Hammett acidity function is very nearly equal to $-\log [H^+]$.

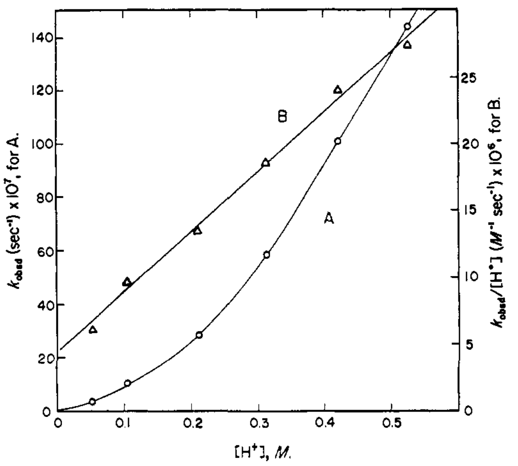

Figure 2. Plot of k_{obsd} and $k_{obsd}/[H^+]$ against $[H^+]$ for the aquation reaction; temperature 67.0°, ionic strength 0.54.

and thus the absorbance of a solution which contains 1 mol of released oxalate per mole of initial complex was considered to be the infinite absorbance value. As a check on this feature, a kinetic run was set up (temperature = 53.3°, $[H^+] = 0.526\ M$, $\mu = 0.54$) and the absorbance changes were followed in the normal way. After about 2.5 weeks (calculated to be about nine half-lives, >99.8% reaction) the absorbance had leveled off to a constant value (initial value, 0.750; 11 days, 0.411; 15 days, 0.408; 17 days, 0.407). The free oxalic acid in the aquated solution was then determined quantitatively by precipitation and separation as CaC_2O_4 and titration with potassium permanganate.[17] In comparison to the theoretical amount calculated using reaction 4, 1.5% excess free oxalic acid was found. This difference is similar to errors experienced in blank experiments with known amounts of sodium oxalate at the same concentration levels.

It is therefore concluded that, for the conditions of our experiments, the equilibrium position for reaction 4 lies far to the right and very little further aquation takes place. No assumption is made as to the proportion of cis and trans isomers in the product. The resulting extinction coefficient for $Rh(C_2O_4)_2(H_2O)_2^-$ (ϵ 163) was used to calculate A_∞ values for other kinetic runs.

Data for the aquation studies are given in Table VI. In Figure 2 we show a plot of k_{obsd} and $k_{obsd}/[H^+]$ against $[H^+]$. The linearity of the latter plot demonstrates that k_{obsd} can be expressed in the form[16,18,19]

$$k_{obsd} = k_{a2}[H^+] + k_{a3}[H^+]^2 \qquad (5)$$

Activation parameters, obtained from plots of log k_{a2} and log k_{a3} against $1/T$(°K) are included in Table III.

Table VI. Pseudo-First-Order Rate Constants for the Aquation (Reaction 4) at Ionic Strength 0.54[a]

Expt no.	$[H^+]$, M	Temp, °C	$k \times 10^7$, sec^{-1}	% deviation[b]
A1	0.105	45.2	0.65	2.3
A2	0.210	45.2	2.05	0.6
A3a,b	0.315	45.2	4.52, 3.88	4.1, 1.4
A4	0.420	45.2	6.62	1.5
A5a,b	0.526	45.2	10.3, 9.87	1.5, 3.2
A6	0.526	45.2	11.2	2.3
A7	0.104	56.3	2.72	3.8
A8	0.208	56.3	9.0	1.3
A9	0.309	56.3	17.5	0.8
A10	0.421	56.3	25.3	2.2
A11	0.421	56.3	27.3	0.7
A12	0.519	56.3	40.5	1.0
A13	0.526	56.3	40.8	2.3
A14	0.0526	67.0	3.22	5.0
A15	0.105	67.0	10.1	0.7
A16	0.210	67.0	28.3	0.9
A17	0.313	67.0	58.3	0.7
A18	0.421	67.0	101	0.4
A19	0.526	67.0	144	0.4
A20	0.0525	75.0	9.40	0.9
A21	0.105	75.0	22.3	1.8
A22	0.210	75.0	71.5	1.6
A23	0.315	75.0	144	1.4
A24	0.421	75.0	255	0.7
A25	0.525	75.0	375	0.6

[a] Complex concentration equal to $\sim 2.5 \times 10^{-3}\ M$ for all experiments. [b] Equal to standard deviation for the least-squares slope × 100, divided by the least-squares slope.

Discussion

For the reactions and conditions studied it is clear that outer-oxygen exchange occurs most rapidly; followed by inner-oxygen exchange and racemization, which proceed at similar rates; and by aquation, which is the slowest of the processes examined (refer to Table III). Thus at 56.3° outer-oxygen exchange proceeds nearly 20 times more rapidly than inner-oxygen exchange; at lower temperatures the difference is greater.[13] Also at 56.3°, and with $[H^+] = 0.20\ M$, when 50% of the inner oxygens have exchanged only ~4% of the complex has aquated, and when 50% of the optically active complex has racemized only ~3% of the complex has aquated.

In considering possible relations among the several reactions, knowledge of the structure of $Rh(C_2O_4)_3^{3-}$ in solution is of importance. Because substitution at the rhodium(III) center is very slow, the coordination environment which exists for the rhodium in the solid phase will also be maintained for some time after dissolution of the solid in water. Recently a complete X-ray structural analysis of $K_3Rh(C_2O_4)_3 \cdot 4.5H_2O$ has been completed by Dalzell and Eriks in our laboratories which shows conclusively that all oxalates in this complex are fully chelated.[20] In the present studies, solutions were usually prepared from $K_3Rh(C_2O_4)_3 \cdot 1.5H_2O$. However, because of the ease of interconverting the 4.5- and 1.5-water compounds, we believe we can confidently assume that when $K_3Rh(C_2O_4)_3 \cdot 1.5H_2O$ is dissolved in water each rhodium will be coordinated to three fully chelated oxalates. The results of the X-ray structural analysis of $K_3Rh(C_2O_4)_3 \cdot 4.5H_2O$ would appear to supersede the views of Porte, *et al.*,[21] who suggested, largely on the basis of proton nmr evidence, that half of the rhodiums in solid $K_3Rh(C_2O_4)_3 \cdot H_2O$ are coordinated to two bidentate and one monodentate oxalates.[22,23]

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

(18) Curvature of the type shown in our plot of k_{obsd} *vs.* $[H^+]$ (Figure 2) was observed also by Barton and Harris (ref 7a). In their case solutions which were up to 2.5 M in $[H^+]$ were studied (the region $[H^+]$ = 0–0.5 M was not examined in detail) and the authors chose to interpret the results in terms of a path first order in $[H^+]$ and an activity effect (log k_{obsd} *vs.* $\mathcal{H}_0$ being linear). The results presented by Barton and Harris in their Figure 1 can also be fitted by a two-term rate law of the type given by our eq 5, although for their results it is not an easy matter to judge the merits of this view in comparison to the activity effect explanation. In the case of our studies we feel compelled to use the two-term rate law because of the feature cited in ref 16.

(19) A similar pattern of acid-dependent behavior in the aquation of $Cr(C_2O_4)_3^{3-}$ was observed by K. V. Krishnamurty and G. M. Harris, *J. Phys. Chem.*, 64, 346 (1960). The authors here interpret the results with use of a two-term rate law, while C. A. Bunton, *et al.*, *J. Chem. Soc.*, 4622 (1964), favor an acidity-function explanation.

(20) B. Dalzell and K. Eriks, *J. Amer. Chem. Soc.*, **93**, 4298 (1971).

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

The rates and activation parameters for acid-catalyzed exchange of the outer oxygens of $Rh(C_2O_4)_3^{3-}$ with water conform closely to earlier expressed expectations[11] for an ion of type $M(C_2O_4)_3^{3-}$. In accord with our earlier views, outer-oxygen exchange is considered to proceed by an A2 mechanism as represented by steps 1 and 2 of Figure 3. This mechanism differs from that proposed by Bunton, *et al.*,[14] for exchange in $Cr(C_2O_4)_3^{3-}$ and $Co(C_2O_4)_3^{2-}$ in that their mechanism requires a ring opening before *any* oxygens can exchange. The scheme of Bunton, *et al.*, is clearly unable to accommodate either exchange in $Rh(C_2O_4)_3^{3-}$ or the more recent results of Broomhead, *et al.*,[24] on $Co(C_2O_4)_3^{3-}$, which indicate that here also only one-half of the oxygens exchange rapidly with solvent. Even in the case of $Cr(C_2O_4)_3^{3-}$, as with $Pt(C_2O_4)_2^{2-}$, where all oxygens appear to be kinetically equivalent, the exchange with solvent may well proceed in the way represented by steps 1 and 2 of Figure 3. In these cases the requirement is that interchange of inner and outer oxygens must occur more rapidly than the exchange with solvent. Support for this interpretation was given earlier[11] in the case of $Pt(C_2O_4)_2^{2-}$, and the view has been discussed more recently for chromium(III) complexes by Broomhead, *et al.*[25]

The outer-oxygen rate, in terms of the mechanism represented by reactions 1 and 2 of Figure 3, will be proportional to the product of the equilibrium constant for reaction 1 (K_1) and the forward rate constant for reaction 2 (k_2). The similar rates observed for such differently charged species as $Rh(C_2O_4)_3^{3-}$, $Pt(C_2O_4)_2^{2-}$, and $HC_2O_4^-$ do not necessarily imply that the individual K_1 and k_2 values are also close to coincident in these cases, but merely that the K_1k_2 products are very similar. In this respect Menon[26] has attributed the very small substituent effects observed for oxygen exchange in various para-substituted benzophenones to opposing substituent effects on the equilibrium constants for protonation and rate constants for formation of the tetracovalent intermediates.

Of the chelated oxalato complexes which have been examined with respect to acid-catalyzed oxygen exchange, only $Rh(C_2O_4)_3^{3-}$ and $Ir(C_2O_4)_3^{3-}$ ions[27] and various complexes of cobalt(III)[24,25,28] have been found to exhibit kinetically distinct outer and inner oxygens. The discrimination in these cases is clearly a function of the relative inertness of the metal–oxygen bonds for these d^6 spin-paired complexes in comparison to the outer-oxygen rates. Such kinetically distinct oxygens were not found for the $Pt(C_2O_4)_2^{2-}$ ion[11] and have not been observed for any chromium(III) complexes thus far examined.[14,25,29]

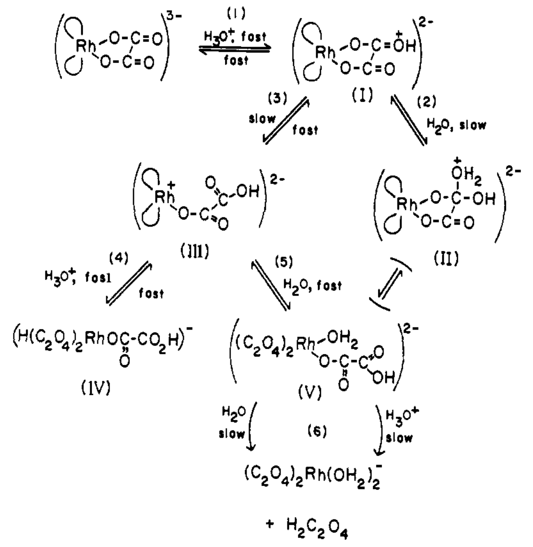

Figure 3.

Under comparable conditions, in the temperature range examined, inner-oxygen exchange proceeds at very similar rates to the racemization process. It was an initial comparison between our measured inner-oxygen exchange rates and the data of Odell, *et al.*,[6] on the racemization which in fact led us to look at the latter process in further detail.

Our racemization data for the specific conditions of 56.4°, $\mu = 0.24$, and $[H^+] = 0.208$ *M* ($k_{obsd} = 1.96 \times 10^{-3}$ min^{-1}) gave a rate constant which was found to be in fair agreement with the pseudo-first-order rate constant which we calculated[30] from the data of Odell, *et al.*,[6] for essentially identical conditions (56.3°, $\mu = 0.23$, $[H^+] = 0.21$ *M*, $k_{obsd} = 1.80 \times 10^{-3}$ min^{-1}). Like these workers, we found that the rate increased more rapidly than the stoichiometric acidity. Odell, *et al.*, did not discuss the rate law for the process, but our results are clearly in accord with the relationship given by eq 3. Corresponding to the terms in the rate law which are first order and second order in hydrogen ion concentration, we obtain the activation energies (for ionic strength 0.54) of 23.9 ± 1.5 and 27.4 ± 1.5 kcal mol^{-1} ($\Delta H^{\ddagger}$ values 0.6 kcal lower). These values are significantly higher than the earlier reported[6] apparent activation energy of $E_a = 20 \pm 1$ kcal mol^{-1}. The activation parameters we find for the term first order in $[H^+]$ compare very closely to values obtained for inner-oxygen exchange (Table III), and this feature is highly suggestive of a parallelism in the mechanisms.

We interpret our data for oxygen exchange, racemization, and aquation in terms of the mechanistic outline shown in Figure 3. The conversion of $Rh(C_2O_4)_3^{3-}$ to II, by the path shown or in a single step, provides for the exchange of outer oxygens. The slower formation of a pentacoordinated intermediate III permits interchange of inner and outer oxygens, hence accommodating inner-oxygen exchange as well as allowing for the possibility of inversion, which we assume can receive assistance through additional protonation.[31]

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(22) Alternative explanations for the nmr data are possible.

(23) R. D. Gillard, *et al.*, *J. Chem. Soc. A*, 3006 (1969), have offered extensive comments on the nature of crystalline complexes of type $K_3[M(C_2O_4)_3]\cdot xH_2O$ and on solutions of these complexes, including the rhodium(III) complex, although no definitive conclusions on structural features for the rhodium complex could be drawn.

(24) J. A. Broomhead, I. Lauder, and P. Nimmo, *Chem. Commun.*, 652 (1969); *Proc. Int. Conf. Coord. Chem.*, *1969*, 12, Supplement to Program Handbook (1969).

(25) (a) J. A. Broomhead, N. Kane-Maguire, I. Lauder, and P. Nimmo, *Chem. Commun.*, 747 (1968); (b) J. A. Broomhead, N. Kane-Maguire, and I. Lauder, *Inorg. Chem.*, **9**, 1243 (1970).

(26) B. C. Menon, Ph.D. Thesis, University of Arkansas, 1964.

(27 Results for the iridium complex by Wodetski and Milburn, presented under ref 2.

(28) (a) R. B. Jordan, C. Andrade, and H. Taube, *Proc. Symp. Coord. Chem. 1964*, 38 (1965); (b) C. Andrade, R. B. Jordan, and H. Taube, *Inorg. Chem.*, **9**, 711 (1970).

(29) (a) D. R. Llewellyn and A. L. Odell, Proceedings of the Australian Atomic Energy Symposium, 1958, p 623; (b) J. Agget, I. Mawston, A. L. Odell, and B. C. Smith, *J. Chem. Soc. A*, 1413 (1968).

(30) A corrected value which is $(2.303)^2$ times the value reported.

(31) It is of interest to note that a rate-law term proportional to $[H^+]^2$ is also observed for the racemization of $Cr(C_2O_4)_2bipy^-$ and $Cr(C_2O_4)_2phen^-$ ions (ref 25). Rate-law terms independent of $[H^+]$ are also observed for the racemization of these complexes. That there is

Inversion could occur in the interconversion of I and III, or in separate relatively rapid reactions of III or IV (by twist mechanisms, or oxygen–oxygen displacements). It is also reasonable that water addition to III would be rapid, and to some extent competitive with ring closure. Such water addition would result in a stabilized monodentate oxalate ligand and would provide the obvious path toward complete aquation.

Any suggestion that racemization could occur through a twist mechanism in I does not explain the kinetically similar inner-oxygen exchange, nor does it accommodate the beginning of aquation. It has also been suggested that inner–outer oxygen equilibration, for some oxalato complexes, may occur through occasional rotation of oxalate about its carbon–carbon bond. This mechanism is unlikely to be important here, because it does not explain the kinetically similar racemization, or again the beginning of aquation.

The possibility that V forms directly from II should be considered (see Figure 3, arrows in parentheses). Such a process could involve Rh–O or O–C bond cleavage, and in either case we would have an alternate route toward complete aquation. Rhodium–oxygen bond cleavage with entry of solvent water would allow for exchange of the inner oxygen, although in comparison to the mechanism involving III it is much less obvious that inner-oxygen exchange and racemization should be kinetically so similar. Oxygen–carbon bond cleavage does not allow for exchange of inner oxygen, nor is it apparent that racemization would result. In summary, it appears to us that the close coincidence of inner-oxygen exchange and racemization kinetics is much more readily accommodated by the proposed mechanism involving intermediate III.

Acknowledgment. We wish to express our thanks to Professor Richard H. Holm of the Massachusetts Institute of Technology for allowing us to make use of his Perkin-Elmer 141 spectropolarimeter.

no comparable [H^+]-independent term for the racemization of $Rh(C_2O_4)_3^{3-}$ is probably attributable to the greater inertness of the metal–oxygen bonds in this case.

Mechanism of Oxidative Cycloaddition of Olefins to Metal Dithiolenes

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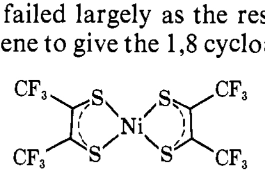
Contribution from the Department of Chemistry, University of California, Riverside, California 92502. Received February 24, 1971

Abstract: The strong inorganic oxidant bis[*cis*-(1,2-perfluoromethylethene-1,2-dithiolato)]nickel reacts readily with olefins to form 1:1 adducts in which two new sulfur–carbon bonds have been formed and the olefin becomes the backbone of a new chelate ring. Two classes of behavior have been distinguished by the present studies. First, when a nonconjugated olefin is used, adduct formation (which always obeys a second-order rate law) is slow (~1 l. mol^{-1} sec^{-1} at 25°) and the reaction product dissociates in light to a photostationary state. Second, when a conjugated olefin is used the reaction is very fast (>10^5 l. mol^{-1} sec^{-1} at 25°) and is thermally reversible. These observations are readily explained by a simple orbital correlation model.

A recent attempt to catalyze the valence isomerization, quadricyclene–norbornadiene, with bis[*cis*(1,2-perfluoromethylethene-1,2-dithiolato)]nickel (**1**) (nickel dithiete) failed largely as the result of **1** reacting with norbornadiene to give the 1,8 cycloaddition product 2.[1] On the basis of structural and spectroscopic results, this reaction has been described as an oxidative cycloaddition.



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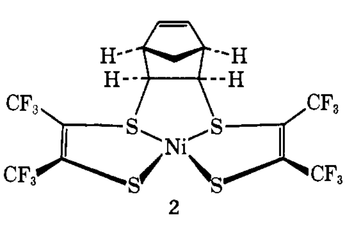

2

Based on recent kinetic, photochemical, and thermodynamic results, we are now able to present a more detailed interpretation of this interesting reaction.

A simple orbital correlation model is presented which concisely explains the nickel dithiete–olefin reactions.

Experimental Section

Preparation of Compounds. $NiS_4C_4(CF_3)_4$ was prepared according to the method of Davison *et al.*,[2] and the norbornadiene adduct according to ref 1. Reagent grade solvents were dried over Linde Type 4A molecular sieves. The microanalysis was carried out by C. F. Geiger, Ontario, California.

The 2,3-Dimethylbutadiene–Bis[*cis*-(1,2-perfluoromethylethene-1,2-dithiolato)]nickel Adduct. Slow diffusion at 5° of a $NiS_4C_4(CF_3)_4$ *n*-hexane solution (100 mg, 0.196 mmol in *ca.* 50 ml) into a CCl_4 solution of the olefin (1 g, 12.2 mmol in 5 ml) gave yellow-green prismatic crystals (82 mg, 71%), mp 153–154° dec. *Anal.* Calcd

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[1] R. M. Wing, G. C. Tustin, and W. H. Okamura, *J. Amer. Chem. Soc.*, 92, 1935 (1970).

[2] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, 2, 1227 (1963).