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Oxygen Exchange in the Bis(oxalato)platinate(II) Ion and in Free Oxalate[1,2]

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The kinetics of oxygen exchange between $Pt(C_2O_4)_2^{-2}$ and solvent water and between free oxalate and solvent water have been examined in weakly acidic and neutral media at low ionic strength from 25 to 45°. The exchange in free oxalate, which over the pH range 1–7 is described by the rate law $R = 4(k_1[H^+][H_2C_2O_4] + k_2[H^+][HC_2O_4^-])$, may be explained by pre-equilibrium protonation of carbonyl oxygens in undissociated oxalic acid and bioxalate followed by rate-determining bimolecular reaction with water in accord with the A-2 mechanism. In $Pt(C_2O_4)_2^{-2}$ all oxygens appear to exchange at the same rate. Over the pH range 3–8 exchange in the complex is described by the rate law $R = 8(k_a[H^+] + k_b[OH^-])[Pt(C_2O_4)_2^{-2}]$. The acid-catalyzed path, which predominates at pH <5.5, shows an extremely close parallelism to the path corresponding to the term $k_2[H^+][HC_2O_4^-]$ in the free oxalate exchange, as indicated by the similarity of rate constants, activation energies, and activation entropies. The results strongly support the view that the same type of acid-catalyzed exchange mechanism is operative in bioxalate and $Pt(C_2O_4)_2^{-2}$, with exchange in the complex proceeding also through pre-equilibrium protonation of a carbonyl oxygen followed by solvent attack.

As an extension to an earlier study[3] of oxalate exchange between $Pt(C_2O_4)_2^{-2}$ and free oxalate we have examined the kinetics of oxygen exchange between water and both $Pt(C_2O_4)_2^{-2}$ and free oxalate over the weakly acidic to neutral pH range. The results have led us to suggest that the same type of acid-catalyzed oxygen exchange mechanism (A-2) is operative in $Pt(C_2O_4)_2^{-2}$ and $HC_2O_4^-$, and to predict that, as a first approximation, all nonlabile oxalato complexes of the type $M(C_2O_4)_n^{-n}$ will exchange oxygen with water at a similar rate under comparable acidic conditions.[2] These ideas receive support from the recent report by Bunton, *et al.*,[4] who have examined oxygen exchange in $Cr(C_2O_4)_3^{-3}$, $Co(C_2O_4)_3^{-3}$, and oxalic acid for strongly acidic conditions.

Experimental

(A) **Materials.**—Sodium bis(oxalato)platinate(II) solutions were prepared from potassium bis(oxalato)platinate(II) dihydrate as previously described.[3] Water containing approximately 6 atom % of oxygen-18 was purchased from the Research and Development Co. Ltd., Weizmann Institute, Rehovoth, Israel. One sample of "normal" water was triple-distilled and used in all experiments. All other materials employed were of reagent grade.

(B) **Preparation of Exchange Solutions.**—For the study of oxygen exchange in the complex, reactant solutions were prepared by mixing appropriate weights of sodium bis(oxalato)platinate(II) solution and enriched water. Where necessary, sodium phosphate[5] and/or perchlorate solutions were added to adjust hydrogen ion concentrations and ionic strength. The pH values were measured to within ±0.02 unit using a Beckman Zeromatic pH meter which was standardized with National Bureau of Standards recommended buffers. Recorded pH values refer to these measured values. For the numerical evaluation of rate constants $-\log [H^+]$ has been identified with the measured pH. Exchange mixtures were usually ~0.01 *M* in oxalate with an over-all oxygen-18 content of 1–2 atom %. The reaction was studied at five different pH values, namely 3.10, 3.74, 5.55, 6.55, and 8.10. At the two lower pH values unbuffered exchange solutions were employed. Under these conditions the pH of a bis(oxalato)platinate(II) solution increases very slowly.[6] This effect was corrected by periodically removing a small portion of the exchange solution and allowing it to stand over Dowex 50W-X8 ion-exchange resin in the H^+ form. A sufficient volume of this acidified solution was then added to the exchange mixture to increase the hydrogen ion concentration to its initial value. In this way it was possible to maintain the pH within a range of 0.05 unit. Reactant solutions were stored in the dark at a temperature of 25, 35, or 45 ± 0.05°.

A similar procedure was employed for the free oxalate exchange reaction which was studied at three different pH values, namely 3.74, 4.90, and 6.55. In the first two cases the system was self-buffering,[7] and it was only necessary to use a phosphate buffer at the higher pH value.

(C) **Exchange Procedure and Calculations.**—Quenching of the reactions was achieved by adjusting the pH of duplicate samples to ~3.5 and precipitating silver salts through the addition of $AgClO_4$ solution. Under the experimental conditions phosphate was not precipitated. The precipitated salts were washed with water, dried under vacuum for 12 hr., and thermally decomposed to give carbon dioxide.

$$Ag_2[Pt(C_2O_4)_2] \longrightarrow 2Ag + Pt + 4CO_2$$

$$Ag_2C_2O_4 \longrightarrow 2Ag + 2CO_2$$

(The stoichiometry of the complex decomposition was verified by weighing the amount of CO_2 liberated from a known weight of anhydrous complex.) The carbon dioxide was dried and collected by a routine vacuum line technique and analyzed for oxygen-18 content by mass spectrometry. By considering the apparent rate of oxygen exchange to be first-order with respect to the difference between the oxygen-18 concentrations in the solvent and the oxalate,[8,9] the pseudo-first-order rate constants for the reaction could be calculated.[10]

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[1] Supported by the National Science Foundation under Grant GP 1582.

[2] Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

[3] J. E. Teggins and R. M. Milburn, *Inorg. Chem.*, **3**, 364 (1964).

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

[5] Ionic strengths were calculated using the equilibrium data of L. F. Nims, *J. Am. Chem. Soc.*, **55**, 1948 (1933).

[6] The increase is probably caused by the consumption of hydrogen ion by free oxalate released in the aquation reaction. Since the liberation of less than 0.3% of the total oxalate per week would account for the observed decrease in hydrogen ion concentration at 25°, the presence of free oxalate could not have a measurable effect on the calculated rate constants for the exchange in the complex, particularly considering the closeness of the oxygen exchange rates for free and complexed oxalate.

[7] H. S. Harned and L. D. Fallon, *J. Am. Chem. Soc.*, **61**, 3111 (1939).

[8] D. R. Llewellyn and A. L. Odell, Proceedings of the Australian Atomic Energy Symposium, 1958, p. 623.

[9] M. L. Bender, R. R. Stone, and R. S. Dewey, *J. Am. Chem. Soc.*, **78**, 319 (1956).

[10] For similar calculations see J. P. Hunt and H. Taube, *J. Chem. Phys.*, **19**, 603 (1951).

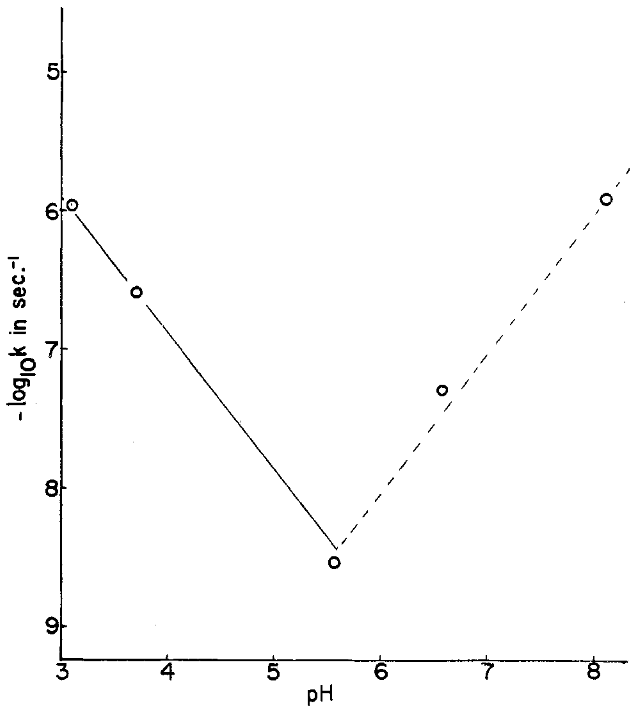


Figure 1.—Dependence of first-order rate constants on hydrogen ion concentration for oxygen exchange between $Pt(C_2O_4)_2^{-2}$ and water. Temperature 45° and ionic strength 0.05. Solid line gives rate constants predicted for acid-catalyzed reaction from results at pH 3.74, assuming a rate law of the form $R = k'[H^+][Pt(C_2O_4)_2^{-2}]$; broken line gives rate constants predicted for base-catalyzed reaction from results at pH 8.10, assuming a rate law of the form $R = k''[OH^-][Pt(C_2O_4)_2^{-2}]$. The total rate constant should be equal to the sum of the two lines. Although the line corresponding to the base-catalyzed reaction is relatively inaccurate, it can be seen that the experimental data are in agreement with the proposed rate law to within a factor of ~2 over a pH range in which the $[H^+]$ varies by a factor of 10^5.

Results

Under the more acidic conditions an appreciable amount of exchange could be observed within a few weeks. For example, Tables I and II indicate typical results for the calculated first-order rate constants (k) at 45° for the complex and free oxalate reactions, respectively. First-order rate constants so obtained are given in Table III (with the exception of series 8–10 which are recorded in Table IV).

Table I

Exchange of Oxygen-18 between $Pt(C_2O_4)_2^{-2}$ and Water[a]

Time, hr.	Excess atom % O-18 in complex	% exchange	k,[b] hr.$^{-1}$ × 10^3
89.3	0.1036	9.2	1.13
191.2	0.2225	19.8	1.05
258.3	0.2700	24.0	1.01

Average first-order rate constant = 2.9 × 10^{-7} sec.$^{-1}$

[a] pH 3.74, 45°, ionic strength = 0.029, excess atom % O-18 initially present in solvent = 1.126. [b] A small correction to the values has been made taking into account the slight pH drift discussed in the text.

Table II

Exchange of Oxygen-18 between Free Oxalate and Water[a]

Time, hr.	Excess atom % O-18 in oxalate	% exchange	k_1, hr. × 10^4
113.7	0.0806	6.7	6.08
253.7	0.1666	13.8	5.88
384.0	0.2462	20.4	5.95
421.5	0.2730	22.4	6.01

Average first-order constant = 1.7 × 10^{-7} sec.$^{-1}$

[a] pH 3.74, 45°, ionic strength = 0.055, excess atom % O-18 initially present in solvent = 1.207.

Table III

First-Order Rate Constants for the Exchange of Oxygen between Free or Complexed Oxalate and Water

Series[a,b]	pH	Ionic strength	Temp., °C.	k, sec.$^{-1}$ [c]
1 (51%)	3.10	0.023	45	1.3 × 10^{-6}
2 (24%)	3.74	0.028	45	2.9 × 10^{-7}
3 (46%)	3.74	0.020	34.9	1.5 × 10^{-7}
4 (14%)	3.74	0.020	25	6.3 × 10^{-8}
5 (0.5%)	5.55	0.053	45	3 × 10^{-9}
6 (10%)	6.55[d]	0.103	45	5.2 × 10^{-8}
7 (52%)	8.10[d]	0.182	45	1.2 × 10^{-6}
A (22%)	3.74	0.054	45	1.7 × 10^{-7}
B (23%)	3.74	0.149	45	1.7 × 10^{-7}
C (5%)	3.74	0.056	25	3.2 × 10^{-8}
D (1%)	4.90	0.059	45	6 × 10^{-9}
E (0.1%)	6.55	0.060	45	$<10^{-9}$

[a] Numerals refer to the exchange in $Pt(C_2O_4)_2^{-2}$, letters to the exchange in free oxalate. [b] Values in parentheses indicate the maximum amount of exchange observed. [c] The calculated standard deviations are of the order of 5% of the rate constants, except for series 5, D, and E where the rate constants and experimental errors are of similar magnitude. [d] The base-catalyzed reaction was accompanied by extensive decomposition of the complex ion and was studied mainly to determine the upper pH limit of the acid-catalyzed reaction.

Because of the limited solubility of sodium bis(oxalato)platinate(II), the ionic strengths of its solution cannot be varied over a wide range. Consequently, variations in rate constants caused by ionic strength effects are of the same order of magnitude as the experimental errors. In order to study the effect as accurately as possible, three reaction solutions were prepared which were similar apart from their sodium perchlorate content. A comparison of the amounts of exchange which took place in these solutions under identical reaction conditions showed that increasing the ionic strength decreases the exchange rate, as illustrated in Table IV.

Table IV

Ionic Strength Dependence of Oxygen Exchange between Bis(oxalato)platinate(II) Ion and Water[a]

Series	Ionic strength	% exchange[b]	k, sec.$^{-1}$
8	0.021	20.4 21.4	1.9^4 × 10^{-7}
9	0.054	18.1 18.5	1.6^7 × 10^{-7}
10	0.182	11.9 12.1	1.0^6 × 10^{-7}

[a] pH 3.74, 34.9°, reaction time 336 hr. [b] Duplicate analyses are shown for each series.

The calculated values of the activation energies and entropies are given in Table VI.

With the reaction conditions described for series 2, varying the bis(oxalato)platinate(II) ion concentration in the concentration range 4 × 10^{-3} to 10^{-2} M

had no significant effect upon the calculated rate constant.

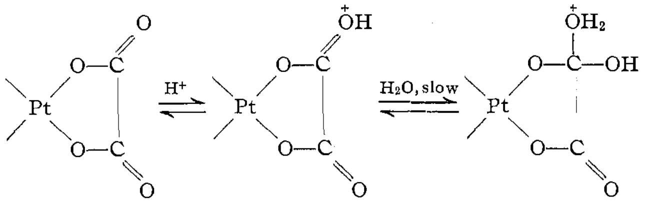
Discussion

The experimental data for oxygen exchange between the bis(oxalato)platinate(II) ion and water are consistent with the rate law given by eq. 1.[11] The agreement between this expression and the experimental data is illustrated in Figure 1. At 45° and ionic

$$\text{oxygen exchange rate} = 8(k_a[H^+] + k_b[OH^-])[Pt(C_2O_4)_2^{-2}] \quad (1)$$

strength 0.05, the values of k_a and k_b are 1.4×10^{-3} and $\sim 1.0\ M^{-1}\ \text{sec.}^{-1}$, respectively. The relative values of these constants are such that the acid-catalyzed exchange predominates at pH values below 5.5.

The kinetic data for the acid-catalyzed complex exchange reaction are consistent with a mechanism involving initial protonation of a carbonyl oxygen followed by the rate-determining reaction of the intermediate with the solvent, *i.e.*



Intermediate I Intermediate II

The two peripheral oxygens bound to the upper carbon in intermediate II should be equivalent because of rapid proton transfer. The view that the C–O bonds to peripheral oxygens are of carbonyl type receives support from X-ray[12] and infrared studies.[13]

Only the outer oxygens could exchange by this mechanism. However, if the ligands undergo one-ended dissociation and reattachment at a rate significantly greater than the slow oxygen exchange, all ligand oxygens could be kinetically equivalent. From Figure 2, it can be seen that the assumption that the exchange rate is first order with respect to all rather than half the ligand oxygen atoms is in better agreement with the experimental data.

The ionic strength dependence of the reaction and the calculated entropy of activation (~ -30 e.u.) are characteristic of mechanisms in which the activated complex contains oppositely charged reactants and a solvent molecule.[14,15]

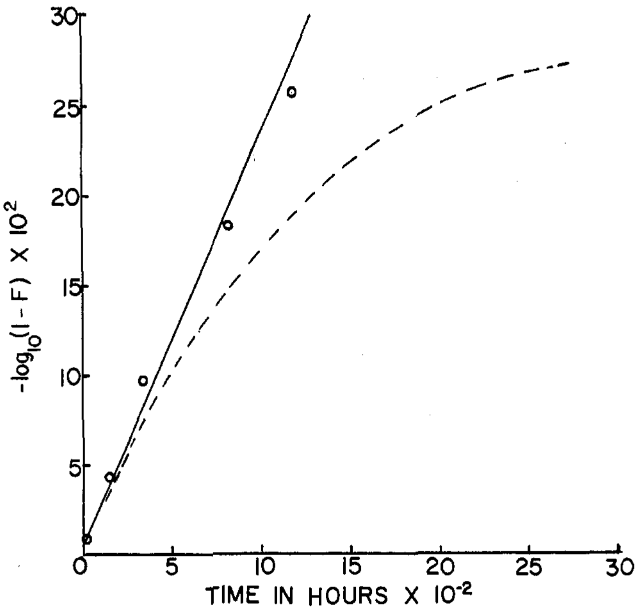


Figure 2.—Exchange of oxygen between $Pt(C_2O_4)_2^{-2}$ and water at pH 3.74, with temperature 34.9° and ionic strength 0.020. F is the fraction of the total ligand oxygen which has exchanged with the solvent. The experimental points would be expected to be on a straight line if all ligand oxygens exchange at a similar rate, and to be on the indicated curve if only half the ligand oxygens exchange at twice that rate.

The postulated mechanism for oxygen exchange in the bis(oxalato)platinate(II) ion is consistent with the A-2 mechanism recognized for many carboxylic esterification, hydrolysis, and oxygen-exchange reactions.[9,16,17] Support is available for the predominant protonation of the –COOH group[18,19] to form kinetically active species.[20] Since the carbonyl protonation mechanism requires the initial protonation of an oxygen atom which is not in the vicinity of the metal center, it might be predicted that all oxalato–metal complexes of the type $M(C_2O_4)_n^{-n}$ would, as a first approximation, exchange oxygen with the solvent at similar rates under comparable acidic conditions. Furthermore, the reactivity of any oxalato group should be strongly dependent upon the number of carbonyl oxygens present and relatively insensitive to the over-all charge on the molecule. Thus, uncomplexed oxalate species might be expected to react at rates proportional to the number of carbonyl groups per formula unit. This hypothesis is confirmed by considering the exchange data for uncomplexed oxalate in Table III and the reported data of Milburn and Taube,[21] which may be expressed in the form of the rate law[22]

$$\text{rate} = 4k_1[H^+][H_2C_2O_4] + 4k_2[H^+][HC_2O_4^-] + 4k_3[H^+][C_2O_4^{-2}] \quad (2)$$

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[11] For exchange between a species Y containing n kinetically equivalent oxygens per formula unit and water in large excess, R (rate of exchange in g.-atoms of oxygen per liter per unit time) $= nk[Y]$, where k is the pseudo-first-order rate constant as obtained herein; see A. C. Wahl and N. A. Bonner, "Radioactivity Applied in Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 8.

[12] J. N. Van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **4**, 35 (1951); **5**, 196, 499 (1952).

[13] J. Fujita, A. E. Martell, and K. Nakamoto, *J. Chem. Phys.*, **36**, 324, 331 (1962).

[14] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, 2nd Ed., New York, N. Y., 1961, p. 150.

[15] R. W. Taft, Jr., *J. Am. Chem. Soc.*, **74**, 5372 (1952).

[16] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., p. 767.

[17] C. A. Bunton, D. H. James, and J. B. Senior, *J. Chem. Soc.*, 3364 (1960).

[18] R. Stewart and K. Yates, *J. Am. Chem. Soc.*, **82**, 4059 (1960).

[19] G. Fraenkel, *J. Chem. Phys.*, **34**, 1466 (1961).

[20] G. Aksnes and J. E. Prue, *J. Chem. Soc.*, 103 (1959).

[21] R. M. Milburn and H. Taube, *J. Am. Chem. Soc.*, **81**, 3515 (1959).

[22] The rate law defined by eq. 2 is kinetically indistinguishable from such other forms as: $R = \{k'[H^+] + k''[H^+]^2\}[HC_2O_4^-]$. However, the proposed rate law offers a simple explanation for the values of the constants as given in Table VI.

At 25° and ionic strength 0.06, $k_1 = 3.2 \times 10^{-4}\ M^{-1}$ sec.$^{-1}$, $k_2 = 2.6 \times 10^{-4}\ M^{-1}$ sec.$^{-1}$, and $k_3 \sim 0$, where R is in g.-atom l.$^{-1}$ sec.$^{-1}$. The values of k_1, k_2, and k_3 are proportional to the relative reactivities of the corresponding free oxalate species. The observation that $H_2C_2O_4$ is only 40% more reactive than $HC_2O_4^-$ (which on the basis of carbonyl oxygens would be predicted to exchange oxygen at half the rate for the acid) can be attributed to the charge on the anion favoring protonation. The small influence of charge is consistent with the very small substitutent effects observed for oxygen exchange in substituted benzoic acids[9] and for acid hydrolysis of corresponding esters.[23]

The agreement between equation 2 and the experimental data is compared in Table V.

TABLE V
RATE CONSTANTS AT 25° FOR ACID-CATALYZED OXYGEN EXCHANGE IN UNCOMPLEXED OXALATE

pH	Ionic strength	Rate constant k, M^{-1} sec.$^{-1}$ ^{a} Obsd.	Calcd.
1.23^b	0.059	3.0×10^{-4}	3.2×10^{-4}
2.61^b	0.107^c	3.4×10^{-4}	2.9×10^{-4}
3.74^d	0.056	1.8×10^{-4}	1.9×10^{-4}
4.90	0.059	$\sim 1 \times 10^{-4}$	6.0×10^{-5}
6.55^e	0.060	?	1.6×10^{-6}

[a] From $R = 4k[H^+]$[total oxalate]; see ref. 11. [b] Experimental values from ref. 21. [c] Small differences in ionic strength should have little effect on rate constant. See series A and B. [d] K_2 for oxalic acid from ref. 7. [e] No significant exchange observed in 1 month.

The mechanistic interpretation further predicts that the acid-catalyzed exchange in $HC_2O_4^-$ should proceed at half the rate of the $Pt(C_2O_4)_2^{-2}$ reaction under comparable conditions, in proportion to the number of carbonyl oxygens per oxalate. This is because the formal charge per oxalate is −1 for both species and because a protonated oxygen in the complex ion will not be in immediate proximity to the metal atom. In addition, the two reactions would be expected to proceed with similar activation energies and entropies. These predictions are in very good agreement with the experimental data, as indicated by Table VI.

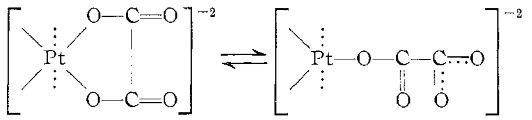
TABLE VI
KINETIC DATA FOR ACID-CATALYZED OXALATE–WATER EXCHANGE REACTIONS

Oxalato species	Carbonyl type oxygens (fraction)	k at 25°,^{a} M^{-1} sec^{-1} × 10^4	Activation energy, kcal. mole^{-1}	Activation entropy, e.u.
$H_2C_2O_4$	$^1/_2$	3.2	...	...
$HC_2O_4^-$	$^1/_4$	2.6	15.0 (±1.5)^b	−28 (±4)^b
$C_2O_4^{-2}$	0	c		
$Pt(C_2O_4)_2^{-2}$	$^1/_2$	3.5	14.7 (±1.0)^d	−27 (±3)^d

[a] From R (g.-atom l.$^{-1}$ sec.$^{-1}$) = $4[H^+]$[total oxalate]; see ref. 11. [b] Values apply to ionic strength 0.055 and pH 3.74. Under these conditions the only significant reaction path is the acid-catalyzed exchange in the bioxalate ion (see text). [c] No measurable exchange rate. [d] Values were obtained at pH 3.74 and apply to ionic strength 0.020 with correction of the rate constant at 45° (series 2) to this condition (see Table III).

It might be argued that the similar kinetic data for the $Pt(C_2O_4)_2^{-2}$ and $HC_2O_4^-$ reactions can be interpreted on the basis of the complex exchange proceeding through prior dissociation of an oxalato ligand followed by oxygen exchange between solvent and free oxalate. However, this mechanism would require that $Pt(C_2O_4)_2^{-2}$ be almost completely dissociated under the experimental conditions in order to explain the similar exchange rates for free and complexed oxalate. Such a condition is inconsistent with the extreme nonlability of the platinum complex with respect to oxalate exchange.[3] Data on hydrogen ion concentration changes in solutions of bis(oxalato)platinate(II) ion[6] are also inconsistent with the rapid dissociation of a large proportion of the oxalato ligands.

An alternative mechanism could involve oxygen exchange at the free end of an oxalato ligand formed in a pre-equilibrium reaction involving breakage of one metal–oxygen bond per ligand, for example



In order for the free and complexed oxalate exchange reactions to proceed at similar rates, the postulated intermediate would have to be present in high concentrations or else be much more reactive than bioxalate ion under comparable conditions. The suggestion that in the relevant pH range a small fraction of the bis(oxalato)platinate(II) ion (~0.01%) will be in the form of such a species, in rapid equilibrium with the parent ion, was put forward to explain the kinetics of the oxalate exchange reaction.[3] However, there is no experimental evidence to suggest that a monodentate ligand would exchange oxygen with the solvent 10^4 times faster than free oxalate under comparable conditions.

The one-ended dissociation mechanism was earlier adopted by Llewellyn and Odell[8] to explain the observation that all oxygen atoms in the tris(oxalato)-chromate(III) ion exchange with water at a similar rate to oxygens in oxalic acid in comparable acidic media. Support for the mechanism is provided by the fact that the acid-catalyzed hydrolysis of the chromium(III) complex probably proceeds *via* such an intermediate.[24] Although racemization, which probably involves the breakage of one metal–oxygen bond per ligand,[24b] is known to proceed more rapidly than oxygen exchange in tris(oxalato)chromate(III) ion, there is no reason to indicate that any intermediate involved in the racemization reaction is unusually reactive with respect to oxygen exchange. Nevertheless, a mechanism similar to that indicated for racemization of $Cr(C_2O_4)_3^{-3}$ could account for the kinetic equivalence of all oxygens in $Pt(C_2O_4)_2^{-2}$, regardless of the actual oxygen exchange mechanism, providing that the latter reaction is the slower.

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(23) E. W. Timm and C. N. Hinshelwood, *J. Chem. Soc.*, 862 (1938).

(24) K. Khrishnamurty and G. M. Harris, *J. Phys. Chem.*, **64**, 346 (1960); (b) *Chem. Rev.*, **61**, 213 (1961).

Additional support for the carbonyl protonation mechanism is provided by the recent report by Bunton, *et al.*,[4] on the oxygen exchange reactions of $H_2C_2O_4$, $Co(C_2O_4)_3^{-3}$, and $Cr(C_2O_4)_3^{-3}$ in strongly acidic media. Under comparable conditions the calculated rate constants, activation energies, and frequency factors are essentially identical, from which the authors conclude that oxygen exchange proceeds in all three cases *via* prior protonation of a carbonyl oxygen. Although these reported values are quite similar to the reaction parameters for $Pt(C_2O_4)_2^{-2}$, an exact comparison is inappropriate because experiments on the latter complex were carried out under conditions involving much lower ionic strength and acidities.

The carbonyl protonation mechanism is also consistent with the report[25] that the carbonyl oxygen in $Co(NH_3)_5C_2O_4^+$ is the most labile. In the corresponding bidentate complex, $Co(NH_3)_4C_2O_4^+$, only half the oxygens, presumably the outer oxygens, exchange rapidly. This result might be predicted because the bond breakage necessary for the equilibration of ligand oxygens should be inhibited in a cationic species.

The carbonyl protonation mechanism is thus consistent with all reported data for oxygen exchange in oxalate species. Also, since protonation of a carbonyl oxygen would weaken the corresponding metal–oxygen bond in a bidentate oxalato ligand, it is likely that acid-catalyzed hydrolysis and racemization reactions proceed through initial protonation of a carbonyl oxygen.

The mechanism predicts that under comparable acidic conditions all nonlabile oxalato complexes of the type $M(C_2O_4)_n^{-n}$ will exchange oxygen at a similar rate. A convenient test of the mechanism would be provided by a study of the oxygen and oxalate exchange reactions of the bis(oxalato)palladate(II) ion. Since palladium–ligand bonds are usually more labile than corresponding platinum bonds, the oxalate exchange reaction in the palladium complex (which involves Pd–O bond breakage) should be much faster than exchange in the platinum complex under comparable conditions, whereas the oxygen exchange reactions should proceed at rates independent of the metal.

[25] C. Andrade, R. B. Jordan, and H. Taube, Abstracts of Papers, 141st National Meeting of the American Chemical Society, March 1962, p. 13M.

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The Preparation and Properties of [Re(amine)$_4$O$_2$]$^+$ Type Ions

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Methods of preparation are given for $[Re(amine)_4O_2]^+$ type ions and related oxohydroxy and dihydroxy complexes, where amine = py, CH_3NH_2, $C_2H_5NH_2$, $C_3H_7NH_2$, $^1/_2$en. The en and py complexes react with dilute and concentrated HCl to produce $[Re(amine)_2Cl_2O(OH)]$ and $[Re(amine)_2Cl_2(OH)_2]Cl$, respectively. $[Re(en)Cl_2(OH)_2]^+$ reacts further with concentrated HCl to produce $[ReCl_4(OH)_2]^-$, and the rates of formation of both these complexes have been followed spectrophotometrically in 12.4 *M* HCl solution. These complexes of Re^{+5} are diamagnetic but, after making the diamagnetic corrections for the ligands, a small residual, temperature-dependent paramagnetism exists for the rhenium ion.

Introduction

In recent years, there has been an interest in the coordination chemistry of rhenium. Much of this activity has centered around the +3, +4, and +5 oxidation states. With simple amine ligands, only a few complexes have been prepared and little is known about their reactivities or the products of their reactions. It was our intention to study the rates of isotopic and ligand-exchange reactions of the amine complexes of Re^{+5} having the general formula $[Re(amine)_4O_2]^+$. This paper reports the preparation of these complexes and some of their physical and chemical properties. The kinetics and products of the interactions with HCl were especially interesting.

Lebedinskii and Ivanov-Emin[1] prepared and characterized the first compound of this group, $[Re(en)_2O_2]Cl$, and found that it was basic toward HCl, giving $[Re(en)_2O(OH)]Cl_2$ and $[Re(en)_2(OH)_2]Cl_3$ reversibly. Improved methods of preparation have been given.[2,3] Burovaya[4] prepared $[Re(py)_4O_2]Cl$ and determined its crystal structure. Various methods have been used for preparing this complex,[5-8] but there is at present no complete description of a method producing a reasonable yield of pure material. Lebedinskii and Ivanov-Emin[6] started with K_2ReOCl_5 because, they claimed, K_2ReCl_6 or K_3ReCl_6 reacted with 50% H_2O–pyridine to give only hydrated ReO_2. However, Sur and Sen[7] obtained $[Re(py)_4O_2]Cl$, together with other products, by

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