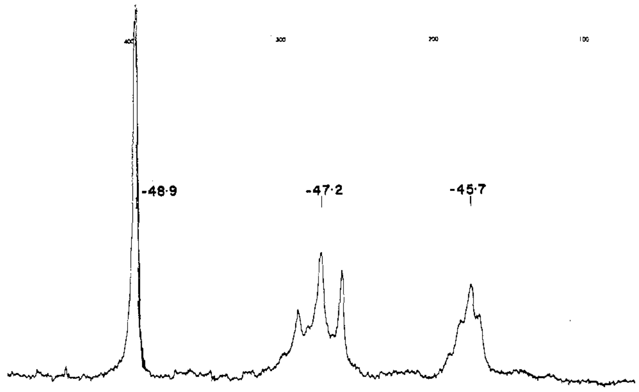

Figure 1.—Part of the ^{19}F nmr spectrum of a liquid made by mixing $BrSO_3F$ with $Au(SO_3F)_3$ in an 8:1 molar ratio. Chemical shifts are in ppm with respect to $CFCl_3$ as an external standard.

8:1 molar ratio liquid mixture of bromine(I) fluorosulfate with gold(III) fluorosulfate at room temperature. Fluorotrichloromethane was used as an external reference. Part of the spectrum is shown in Figure 1.

Discussion

While compounds of stoichiometry $Au(SO_3F)_3$ and $Pt(SO_3F)_4$ are in harmony with the other chemistry of the two noble metals, it is somewhat surprising that $BrSO_3F$ reacts so readily. The adducts of $BrSO_3F$ with $Au(SO_3F)_3$ and $Pt(SO_3F)_4$ are of sufficient interest to merit further study.

The nmr spectrum of the 1:8 liquid mixture of $Au(SO_3F)_3$ with $BrSO_3F$ contains a sharp single peak at a chemical shift of −37.9 ppm. Other peaks are shown in Figure 1. Relative areas of the bands centered at −37.9, −45.7, −47.2, and −48.9 ppm are approximately 5:2.2:4:3. It is apparent that fluorosulfate groups are present in several environments and that exchange among at least some of these is slow enough to allow several bands to appear in the spectrum. Since the quadrupole moments of both gold and bromine are high, it is unlikely that the ^{19}F nmr spectrum shows evidence of coupling with the spins of Br or Au.[7,8] The spectrum is not interpreted in terms of possible molecular structures.

The Raman spectrum of solid $Au(SO_3F)_3$ reported in Table I has some of the characteristics of spectra of substances containing the SO_3F^- ion. There are marked differences, however, which make it appear that gold(III) fluorosulfate is covalent and probably polymeric. This state of affairs is in agreement with the structure of other gold(III) compounds. Complex vibrational spectra of several fluorosulfates have been interpreted to indicate the existence of polymers.[9,10] Fluorosulfate groups may serve as bridges.

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Acid-Catalyzed Exchange of Oxalate Oxygen between Oxalatotetraaquochromium(III) Ion and Solvent Water

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In a continuation of our interest in metal–oxalato complexes[1] we have undertaken an examination of acid-catalyzed exchange of oxygen between oxalate in $Cr(H_2O)_4C_2O_4^+$ and solvent water. The results add to those obtained by others[2-4] on some closely related chromium(III) complexes. All oxalate oxygens in $Cr(H_2O)_4C_2O_4^+$ exhibit kinetic equivalence in their exchange with solvent, as has been found for all chromium(III) oxalato complexes thus far examined. The present experimental results on $Cr(H_2O)_4C_2O_4^+$, together with predictions which can be made about the kinetics of oxygen exchange between coordinated water and solvent, enable one to limit considerably the mechanistic possibilities for the exchange processes. As a by-product of the study we conclude that cerium(IV) perchlorate oxidation of $Cr(H_2O)_4C_2O_4^+$ in acidic solution to produce carbon dioxide involves Cr–O bond cleavage without accompanying C–O bond cleavage.

Experimental Section

Reagents.—Materials were reagent grade in quality except where otherwise specified. Water enriched in ^{18}O was obtained from Yeda Research and Development Co., Inc. Solutions of perchloric acid and sodium perchlorate, prepared by standard procedures,[1] were used to control acidity and ionic strength.

An aqueous solution of $[Cr(H_2O)_4C_2O_4]ClO_4$ was prepared by allowing $[Cr(H_2O)_6](ClO_4)_3$ (G. F. Smith) to react with sodium oxalate.[5] Equal volumes of 0.10 *M* solutions were mixed, the pH was adjusted into the range 3–4, and the solution was heated to incipient boiling for 0.5 hr. The cooled solution was diluted approximately 20-fold with 0.01 *M* $HClO_4$ and passed onto a Dowex-50W-X8 column in the hydrogen ion form. The column was washed with 0.01 *M* $HClO_4$ and then eluted with 0.1 *M* $HClO_4$ until the violet band due to the complex passed off the column. A middle fraction of this effluent solution was carefully concentrated by rotary evaporation at room temperature. During this process the pH was periodically adjusted to 3–4 with $KHCO_3$. After the preparation had been cooled overnight in a refrigerator, the $KClO_4$ produced was filtered from the final solution.

Chromium was analyzed[6] by converting the complex to CrO_4^{2-} and, for solutions which were 0.1 *M* in NaOH, comparing the absorbance at 372 nm with values given by standard solutions also in 0.1 *M* NaOH. The oxalate concentration was determined by the method of Hamm.[7] The oxalate to chromium ratio was found to be 1.006 to 1.000.

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Except for exchange of oxygen with solvent (see below) the $Cr(H_2O)_4C_2O_4^+$ ion maintains its identity in solution for the acidic conditions and times involved in the present study. Thus, the absorption spectrum of solutions of $Cr(H_2O)_4C_2O_4^+$ in 0.10 *M* $HClO_4$ remains unchanged for at least 5 days at 25°. On the other hand, in acidic media (0.2–2 *M* $HClO_4$) the absorbance of a solution of *cis*-$Cr(H_2O)_2(C_2O_4)_2^-$ decreases continuously with time until it reaches a steady state where the spectrum almost overlaps that of the pure $Cr(H_2O)_4C_2O_4^+$ ion at the same concentration.[8]

Measurement of Rates.—Reaction solutions for kinetic runs were prepared from measured volumes and weights of perchloric acid, sodium perchlorate and $[Cr(H_2O)_4C_2O_4]ClO_4$ solutions (all in normal water), normal water, and water enriched in ^{18}O. The complex was the last component to be added. The final concentration of the complex was 0.022 *M*, while the ionic strength was in all cases maintained at 1.00 *M*. The progress of the exchange was followed by the procedure used earlier to examine oxygen exchange between oxalic acid and solvent water.[9] A similar method was used more recently by Aggett, *et al.*,[3a] in their examination of *cis*-$Cr(H_2O)_2(C_2O_4)_2^-$. In the present case, the detailed procedure consisted of withdrawing samples at intervals, cooling these rapidly by adding to an ice-cooled quenching vessel which was being flushed with CO_2-free nitrogen, adding cerium(IV) perchlorate in $HClO_4$ to oxidize the complex, and passing the carrier nitrogen gas (now containing water and CO_2) successively through a Dry Ice–acetone trap (to catch most of the water) and a liquid nitrogen trap (to catch most of the CO_2). The CO_2 was subsequently dried by replacing the liquid nitrogen trap with a Dry Ice–acetone trap and transferring the CO_2 to another liquid nitrogen trap. Analysis for the 46/(44 + 45) mass ratio was accomplished using a Nuclide 6-60-RMS 2 mass spectrometer.

The reaction of the cerium(IV) perchlorate solution with the chilled samples of reaction solution to produce CO_2 was shown to be sufficiently rapid for our purposes. Thus, in one experiment the addition of a measured amount of cerium(IV) perchlorate solution to a chilled sample of reaction solution was quickly followed by addition of a known excess of Fe(II) solution, and the remaining Fe(II) was then titrated potentiometrically with standard $Cr_2O_7^{2-}$ solution. In this way it was found that approximately 65% of the $Cr(H_2O)_4C_2O_4^+$ had reacted with the added Ce(IV) in less than 30 sec. The experimental conditions were therefore at least as favorable as those used in the earlier exchange studies on oxalic acid.[7] In agreement with this conclusion, it was found that no significant amount of isotopic exchange occurred in the period of time between the withdrawal of the sample of exchanging solution and the trapping of the solid CO_2 samples (see below).

First-order rate constants were obtained by plotting the left-side of eq 1 against time

$$\ln [(N_\infty - N_0)/(N_\infty - N_t)] = kt \qquad (1)$$

Here *N* is the atom fraction of the oxygen-18, obtained from the isotope ratio for carbon dioxide by standard procedures, as described elsewhere.[1a,10] When N_∞ values were calculated on the assumption that only two of the oxalate oxygens exchange, the rate plots exhibited marked curvature which clearly indicated the inappropriateness of the assumption.[11] However, when the N_∞ values were calculated on the assumption that all four oxalate oxygens exchange, linear plots for eq 1 were obtained. That these lines pass close to the point 0,0 confirms the satisfactory nature of the experimental procedure for quenching the exchange reaction. As an example, in Figure 1 we have plotted the data for a typical kinetic run for each of the two ways described above for calculating N_∞. Table I lists the rate constants for the various conditions examined, calculated from the slopes of the least-squares lines for eq 1 on the basis that all oxalate oxygens are kinetically equivalent.

TABLE I

PSEUDO-FIRST-ORDER RATE CONSTANTS FOR EXCHANGE OF OXALATE OXYGEN[a]

Expt no.	$[H^+]$, *M*	*T*, °C	$k \times 10^5$, sec^{-1} [b]
1	0.100	25.0	0.278 (5)
2	0.200	25.2	0.527 (7)
3	0.400	25.2	1.09 (6)
4	0.800	25.2	1.97 (6)
5	0.400	34.9	2.95 (6)
6	0.400	44.9	6.62 (6)

[a] Ionic strength = 1.00 *M*. [b] Rate constants calculated from least-squares plot of eq 1, on the basis that all four oxalate oxygens exchange at the same rate. Numbers in parentheses give number of points used to compute the least-squares slope.

Discussion

As with other chromium(III)–oxalato complexes which have been examined,[2-4] the inner and outer oxalate oxygens in $Cr(H_2O)_4C_2O_4^+$ undergo acid-catalyzed exchange with solvent water at kinetically indistinguishable rates. In this regard, chromium(III)–oxalato complexes exhibit distinctly different behavior from analogous oxalato complexes of cobalt(III)[12] and rhodium(III),[1a,13] although the result is similar to that observed for the $Pt(C_2O_4)_2^{2-}$ ion.[10]

The exchange of oxygen between oxalate in $Cr(H_2O)_4C_2O_4^+$ and solvent water appears to be first order in $[H^+]$ and exhibits an activation energy of 17.1 (±1.5) kcal mol^{-1}. The kinetic pattern is in all regards very similar to that found for other chromium(III) complexes. A comparison of results obtained for various chromium(III) complexes is shown in Table II.[14]

The constants in column C of Table II are a measure of the rates (for the acidity, ionic strength, and temperature specified) at which the complexes at 1 *M* concentration exchange oxygen with solvent (in gram-atoms of oxygen per liter per second). Other things being equal, complexes containing more oxalate oxygen per formula unit would be expected to have larger values for these constants. On the other hand, the constants in column E give the rates at which the complexes, at a concentration 1 g-atom of oxalate oxygen/l., exchange oxygen (in gram-atoms per liter per second).[14] The relative values of these constants give a direct measure of the influence of the environment on the rate at which a coordinated oxalate exchanges its oxygen with solvent. The remarkable feature is that these values vary by a factor of only ~4 for complexes which vary in charge from −3 to +1. The very small influence of charge was noted elsewhere in relation to $Rh(C_2O_4)_3^{3-}$, $Pt(C_2O_4)_2^{2-}$, $HC_2O_4^-$, and $H_2C_2O_4$,[10,13] and it has been further discussed in relation

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[8] D. Banerjea and M. S. Mohan, *J. Inorg. Nucl. Chem.*, **26**, 613 (1964).

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

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

[11] Because the concentration of $Cr(H_2O)_4C_2O_4^+$ was low compared to solvent water, it makes essentially no difference whether or not onei ncludes the four coordinated waters in computing the values of N_∞ for the CO_2. Perchlorate oxygen is not considered to exchange under the reaction conditions used.

[12] (a) C. Andrade, R. B. Jordan, and H. Taube, *Inorg. Chem.*, **9**, 711 (1970); (b) R. B. Jordan, C. Andrade, and H. Taube, *Proc. Symp. Coord. Chem., Tihany, Hungary, 1964*, 381 (1965).

[13] L. Damrauer and R. M. Milburn, *J. Amer. Chem. Soc.*, **90**, 3884 (1968).

[14] The rate expression plotted in the present study was eq 1. Equivalent expressions are $-\ln (1 - F) = kt$, where *F* is the fraction of the exchange and $-\ln (a_\infty - a_t) = kt +$ constant, where *a* refers to the atom fraction of ^{18}O. In evaluating their data, Odell, *et al.*,[3] Broomhead, *et al.*,[4] and Stieger, *et al.*,[2] used one or other of the above expressions and then multiplied the resulting *k* values by the number of kinetically equivalent oxygens to obtain the rate constants which they report. In Table II we give these reported rate constants (column C); we list also adjusted constants obtained by dividing these values by the number of kinetically equivalent oxygens (column E). The pseudo-first-order rate constants in column E have the units of sec^{-1} and are appropriate to both the rate-law expressions $d[Cr(C_2O_4)_n{}^{3-2n}]/dt = k[Cr(C_2O_4)_n{}^{3-2n}]$ and $d[O]/dt = k[O]$, where [O] represents the concentration of oxalate oxygen in g-atoms $l.^{-1}$. This feature is easily appreciated if one notes that, for a given concentration of complex, [O] will be 4*n* times $[Cr(C_2O_4)_n{}^{3-2n}]$, and the rate expressed in gram-atoms of oxygen per liter per second will also be 4*n* times the rate expressed in moles of complex per liter per second.

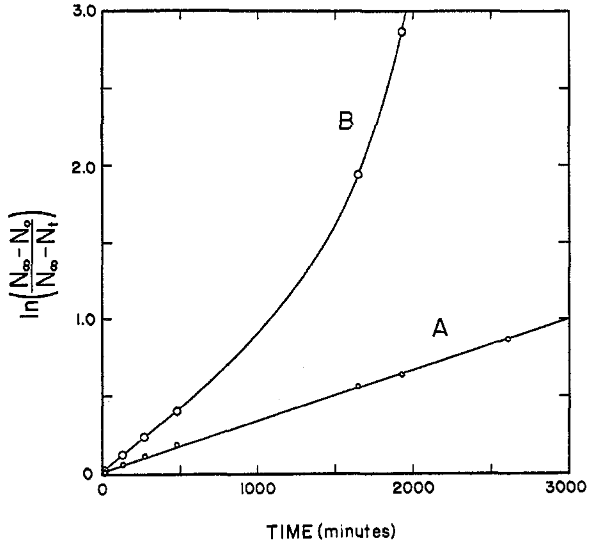


Figure 1.—Rate plots for experiment 2 ($[Cr(H_2O)_4C_2O_4^+]$ = 0.022 M, $[H^+]$ = 0.200 M, ionic strength = 1.00, T = 25.2°): (A) N_∞ calculated assuming all four oxalate oxygens exchange; (B) N_∞ calculated assuming only two oxalate oxygens exchange.

TABLE II

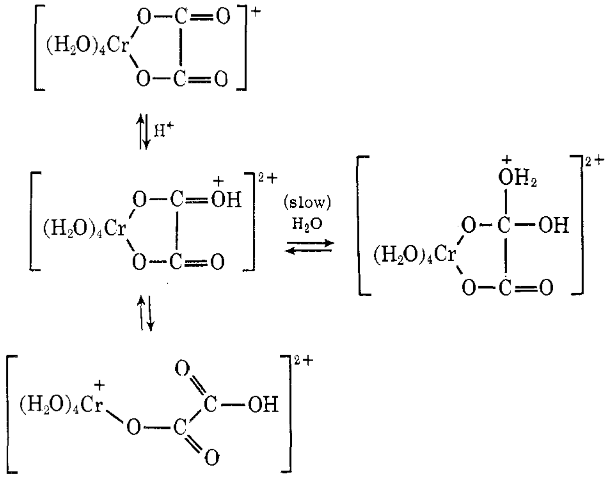
RATE CONSTANTS FOR ACID-CATALYZED EXCHANGE OF OXALATE OXYGEN[a]

A Complex	B Ionic strength	C Reported $k \times 10^4$, g-atoms mol^{-1} sec^{-1}	D No. of ex-changing oxygens	E Adjusted $k \times 10^4$, sec^{-1} [b]
$Cr(C_2O_4)_3^{3-}$ [c]	1.1	12.8	12	1.05
$Cr(H_2O)_2(C_2O_4)_2^-$ [d]	1.1	3.84	8	0.48
$Cr(H_2O)_2(C_2O_4)_2^-$ [e]	[i]	3.92	8	0.49
$Cr(phen)(C_2O_4)_2^-$ [f]	1.0	8.20	8	1.03
$Cr(bipyr)(C_2O_4)_2^-$ [f]	1.0	9.32	8	1.17
$Cr(H_2O)_4C_2O_4^+$ [g]	1.0	(1.00)[j]	4	0.25
$Cr(phen)_2C_2O_4^+$ [h]	1.0	2.71	4	0.68
$Cr(bipyr)_2C_2O_4^+$ [h]	1.0	2.75	4	0.69
$Cr(en)_2C_2O_4^+$ [h]	1.0	2.76	4	0.69

[a] $[H^+]$ = 1.00 M; T = 25.0°. [b] Obtained by dividing the value of k reported in ref 2, 3, or 4 by the number of kinetically equivalent oxygens per formula unit (refer to footnote 14). [c] Reference 3b. [d] Reference 3a. [e] Reference 2. [f] Reference 4b. [g] Present study. [h] Reference 4a. [i] Not specified. [j] Obtained by multiplying our measured value by 4.

to cobalt(III) and chromium(III) complexes by Broomhead, *et al.*[4] As has been discussed in more detail elsewhere,[1a] the similarity in rates is most probably due to a cancellation of electronic effects.

Consideration of the mechanistic details of the exchange of oxalate oxygen require one to consider the complex as a whole, including the mode by which coordinated water exchanges with solvent. In the case of the related *cis*-$Cr(H_2O)_2(C_2O_4)_2^-$, this matter has been considered in detail by Stieger, Harris, and Kelm.[2] Using ^{17}O nmr, these workers were able to follow the exchange with solvent of both coordinated water oxygen and oxalate oxygen. A slow, relatively pH-independent exchange of the coordinated water oxygen was observed ($t_{1/2}$ = 49 hr at 25° and pH 2.4)[15] which is remarkably similar to the situation found earlier[16] for $Cr(H_2O)_6^{3+}$ ($t_{1/2} \sim$ 50 hr at 25° for pH 1.5–2.5). On this basis, these authors have made the very reasonable prediction that the half-life for water oxygen in $Cr(H_2O)_4C_2O_4^+$ at comparable temperatures will also be in the range 40–50 hr and will be relatively independent of acidity. On this basis we can conclude that for the more acidic solutions used in the present study, $Cr(H_2O)_4(C_2O_4)^+$ exchanges oxalate oxygen with solvent significantly more rapidly than it exchanges coordinated water oxygen. Moreover, the two exchange processes almost certainly exhibit different dependencies on the hydrogen ion concentration. These conditions require an interchange of outer and inner oxygen which proceeds independently of any exchange of coordinated water oxygen. We therefore conclude that oxalate oxygen exchanges in $Cr(H_2O)_4C_3O_2^+$ by a mechanism similar to that suggested before for $Rh(C_2O_4)_3^{3-}$, with the difference that an interchange of inner and outer oxalate oxygen in the case of the chromium(III) complex exceeds the rate of exchange of the outer oxygens.



The general features of this mechanism are similar to those proposed for the exchange of oxalate oxygen with solvent in the case of *cis*-$Cr(H_2O)_2(C_2O_4)_2^-$ ion.[2,3a] In agreement with Stieger, *et al.*,[2] we do not require the five-coordinate intermediate to be directly involved in the step in which oxygen is exchanged with solvent.

Considerably earlier it had been shown that when oxalic acid is oxidized by cerium(IV) in acidic media, none of the oxygen in the CO_2 is derived from the solvent.[9] The fact that plots of the type shown in Figure 1 pass very close to the point 0,0 now demonstrates the result that when $Cr(H_2O)_4C_2O_4^+$ is oxidized by cerium(IV), the CO_2 produced still derives essentially all of its oxygen from the coordinated oxalate. This result eliminates the possibility of a carbon–oxygen scisson. The essential features of the oxidation mechanism are then likely to be as follows.

$$(H_2O)_4Cr^{III}C_2O_4^+ \xrightarrow[\substack{H_2O^* \\ \text{(rate} \\ \text{determining)}}]{Ce^{IV}} (H_2O)_4CrC_2O_4^{2+} \xrightarrow[\substack{H_2O^* \\ \text{(fast)}}]{Ce^{IV}} (H_2O)_4Cr(H_2O^*)_2^{3+} + 2CO_2$$

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[15] In a somewhat earlier study on *cis*-$Cr(H_2O)_2(C_2O_4)_2^-$, Aggett *et al.*,[3a] observed no significant exchange between coordinated water oxygen, and solvent water over a period of 8 days for both neutral and acidic media at room temperature. This finding and that of Stieger, *et al.*, on the exchange of coordinated water oxygen are in clear contradiction, and it would appear that one or other of the experimental results must be in error. Stieger, *et al.*, do not comment on the findings of Aggett, *et al.* However, in our view the results of Stieger, *et al.*, make better chemical sense in view of the known exchange behavior for $Cr(H_2O)_6^{3+}$. Some further work on this system will, however, probably be necessary.

[16] J. P. Hunt and H. Taube, *J. Chem. Phys.*, **19**, 602 (1951).