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The Cerium(IV) Oxidations of Tris(oxalato)chromate(III) and Tris(oxalato)rhodate(III) Ions in Aqueous Sulfuric Acid[1,2]

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$Cr(C_2O_4)_3^{3-}$ and $Rh(C_2O_4)_3^{3-}$ react with Ce(IV) in aqueous sulfuric acid with the stepwise oxidation of coordinated oxalate, the initial reactions proceeding to produce bis-oxalato complexes. For the $Cr(C_2O_4)_3^{3-}$–Ce(IV) system evaluation of rate constants for the initial direct redox reaction requires consideration of the competing aquation of $Cr(C_2O_4)_3^{3-}$. In 1 *M* sulfuric acid at 25° the second-order rate constant for the direct *one-electron* oxidation of $Cr(C_2O_4)_3^{3-}$ is 4.0 (± 0.5) $\times 10^{-2}$ M^{-1} sec^{-1}, while for the corresponding direct *one-electron* oxidation of $Rh(C_2O_4)_3^{3-}$ the rate constant is 6.1 (± 1.0) $\times 10^{-4}$ M^{-1} sec^{-1}. Rate behavior for several aqueous–acidic sulfate solvents, differing in concentrations of hydrogen ion and sulfate ion, suggests that activated complexes for the initial direct redox reactions of $Cr(C_2O_4)_3^{3-}$ and $Rh(C_2O_4)_3^{3-}$ are of generally similar but not identical compositions. The measured $\Delta H^{\ddagger}$ values for both systems exhibit slight temperature dependences which are probably caused by small changes with temperature in the average compositions of activated complexes. At corresponding temperatures the $\Delta H^{\ddagger}$ value for the rhodium system is significantly higher than that for the chromium system. The initial direct redox step for each complex is interpreted as involving oxidation of a coordinated oxalate to an oxalate radical anion. Factors which are likely to contribute to differences in the redox reactivities of $Rh(C_2O_4)_3^{3-}$ and $Cr(C_2O_4)_3^{3-}$ are discussed.

The area concerned with reactions of coordinated ligands in metal complexes has received increased attention over the past several years.[3] A matter of interest to us has been the reactions of inert metal complexes containing oxidizable ligands toward external oxidizing agents,[4] and in this connection particular attention has been centered on the oxidation of metal–oxalato complexes by cerium(IV). An earlier study reported on the oxidation of oxalato complexes of chromium(III), and while major emphasis of this work was on the *cis*-$Cr(H_2O)_2(C_2O_4)_2^-$–Ce(IV) reaction, a preliminary account of the $Cr(C_2O_4)_3^{3-}$–Ce(IV) reaction was also given.[5] Aqueous acidic–sulfate media were used to avoid polynuclear species of cerium(IV)[6] and to keep reaction rates in a conveniently measurable range. As part of an inquiry into the role of the central metal of the complex in reactions of this type, the $Cr(C_2O_4)_3^{3-}$–Ce(IV) reaction has now been examined in further detail, and the $Rh(C_2O_4)_3^{3-}$–Ce(IV) reaction has been studied under similar conditions. The two reactions have much in common and are conveniently described together. Some different features appear for the reactions of Ce(IV) with $Co(C_2O_4)_3^{3-}$ and with $Ir(C_2O_4)_3^{3-}$, and these systems will be described separately.[7]

Experimental Section

Materials.—Preparative methods for potassium tris(oxalato)chromate(III) and for solutions containing *cis*-bis(oxalato)diaquochromate(III) ion have been described.[5] Solutions of these complexes used for kinetic studies were standardized by analysis for chromium as before.[5] Potassium tris(oxalato)rhodate(III) was prepared by Barton's modification of Werner's method.[8] The salt was dried under vacuum, allowed to equilibrate with the atmosphere, and finally stored in a calcium chloride desiccator. After the salt had reached constant weight, it was analyzed.[9] *Anal.* Calcd for $K_3Rh(C_2O_4)_3 \cdot 1.5H_2O$: C, 14.10; H, 0.59; K, 23.15. Found: C, 14.1; H, 0.48; K, 23.2. For kinetic experiments solutions of potassium tris(oxalato)rhodate(III) were prepared from the weighed salt. The method of Ayres and Forrester[10] was used to prepare a sample of $[Rh(H_2O)_6](ClO_4)_3$.

The preparation of standard solutions of cerium(IV) and cerium(III) and analytical methods for cerium(IV) and cerium(III) were as before.[5] The solvent used for the majority of experiments was aqueous 1.00 *M* sulfuric acid, but to investigate the role of hydrogen ion and sulfate ion some additional aqueous acidic–sulfate solvents consisting of mixtures of sulfuric acid and sodium sulfate were used.

Stoichiometries.—Our earlier report[5] gave support for the view that $Cr(C_2O_4)_3^{3-}$ is oxidized by Ce(IV) in a stepwise manner, with initial reactions proceeding according to the stoichiometries

$$Cr(C_2O_4)_3^{3-} + 2Ce(IV) + 2H_2O \longrightarrow cis\text{-}Cr(H_2O)_2(C_2O_4)_2^- + 2Ce(III) + 2CO_2 \quad (1)$$

$$cis\text{-}Cr(H_2O)_2(C_2O_4)_2^- + 2Ce(IV) + 2H_2O \longrightarrow Cr(H_2O)_4C_2O_4^+ + 2Ce(III) + 2CO_2 \quad (2)$$

The subsequent reaction of $Cr(H_2O)_4C_2O_4^+$ with Ce(IV) proceeds significantly more slowly than the *cis*-$Cr(H_2O)_2(C_2O_4)_2^-$–Ce(IV) reaction, and the process following Ce(IV) addition to *cis*-$Cr(H_2O)_2(C_2O_4)_2^-$ therefore adheres closely to the stoichiometry

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[2] Presented at the Tenth International Conference on Coordination Chemistry, Tokyo and Nikko, Japan, Sept 1967; see Proceedings, p 302.

[3] See, for example: (a) "Reactions of Coordinated Ligands and Homogeneous Catalysis," Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963; (b) M. Anbar in "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965; (c) J. P. Collman, *et al.*, *J. Am. Chem. Soc.*, **89**, 1082 (1967), and earlier papers; (d) M. A. Bennett, *et al.*, *J. Chem. Soc.*, *A*, 2301 (1967); (e) M. T. Beck and L. Dozsa, *Inorg. Chim. Acta*, **1**, 134 (1967); (f) A. D. Allen, *et al.*, *J. Am. Chem. Soc.*, **89**, 5595 (1967); (g) H. A. Scheidegger, J. N. Amor, and H. Taube, *ibid.*, **90**, 3264 (1968); (h) S. M. Caldwell and A. R. Norris, *Inorg. Chem.*, **7**, 1667 (1968); (i) K. Schug, *et al.*, *ibid*, **7**, 1669 (1968); (j) E. Blinn and D. H. Busch, *J. Am. Chem. Soc.*, **90**, 4280 (1968), and earlier papers; (k) J. E. Hix, Jr., and M. M. Jones, *ibid.*, **90**, 1723 (1968), and earlier papers; (l) J. P. Candlin, K. A. Taylor, and D. T. Thompson, "Reactions of Transition Metal Complexes," Elsevier Publishing Co., Amsterdam, 1968, Chapter 3.

[4] In certain cases it may not be clear whether a reaction of a complex with an external redox reagent is best described as a reaction of a ligand or ligands, a reaction of the central metal, or a reaction of the complex as a whole. In the cases of present interest the ligand has, at least by the end of the reaction sequence, undergone an obvious chemical change.

[5] J. E. Teggins, M. T. Wang, and R. M. Milburn, ref 3a, pp 226–242.

[6] See P. R. Danesi, *Acta Chem. Scand.*, **21**, 143 (1967), and references therein.

[7] To be submitted for publication.

[8] D. Barton and G. M. Harris, *Inorg. Chem.*, **1**, 251 (1962).

[9] Analysis by Schwarzkopf Microanalytical Laboratory.

[10] G. H. Ayres and J. S. Forrester, *J. Inorg. Nucl. Chem.*, **3**, 365 (1957).

represented by reaction 2. On the other hand, reactions 1 and 2 proceed at comparable specific rates, and a stoichiometry approximating reaction 1 can be expected only for the early stages of reaction between $Cr(C_2O_4)_3^{3-}$ and Ce(IV).

The $Rh(C_2O_4)_3^{3-}$–Ce(IV) system presents a similar situation, with redox processes continuing while both Ce(IV) and oxalate remain. Kinetic observations on Ce(IV) consumption, monitored as described below, are consistent with the initial stoichiometries

$$Rh(C_2O_4)_3^{3-} + 2Ce(IV) \longrightarrow Rh(C_2O_4)_2^{-} + 2Ce(III) + 2CO_2 \quad (3)$$

$$Rh(C_2O_4)_2^{-} + 2Ce(IV) \longrightarrow RhC_2O_4^{+} + 2Ce(III) + 2CO_2 \quad (4)$$

with reactions 3 and 4 proceeding at quite similar specific rates.[11-13] Thus, when the initial molar ratio of Ce(IV) to $Rh(C_2O_4)_3^{3-}$ is in excess of 2:1, redox reaction continues at a steady rate even after 2 mol of Ce(IV) has been consumed per mole of $Rh(C_2O_4)_3^{3-}$. Also, one can aquate $Rh(C_2O_4)_3^{3-}$ in aqueous acid to the bis-oxalato complex and free oxalate.[8,12,13] When Ce(IV) in 1 *M* sulfuric acid is added to solutions containing the bis-oxalato complex and free oxalate, prepared by aquation in either 1 *M* sulfuric acid or 2 *M* perchloric acid, and where the Ce(IV) to rhodium ratio is in excess of 2:1, the initial rapid consumption of Ce(IV) by the free oxalate is followed by a continued steady Ce(IV) consumption by the bis(oxalato)rhodate(III). It is apparent here also that a stoichiometry approximating reaction 3 can be expected only for the early stages of the $Rh(C_2O_4)_3^{3-}$–Ce(IV) reaction.

Measurements of Rates of Ce(IV) Consumption.—Reactions were initiated by mixing, at zero time, thermostated solutions of $K_3Cr(C_2O_4)_3$ or $K_3Rh(C_2O_4)_3$ with Ce(IV) solutions. The sulfuric acid was either included in the Ce(IV) solution, or added to the solution of complex immediately before initiating reaction. Where appropriate, sodium sulfate was also included in the reaction mixtures. The rates of the reactions were followed by measuring the Ce(IV) concentration as a function of time.

For the $Rh(C_2O_4)_3^{3-}$ system the time dependence of the Ce(IV) concentration was measured by two independent methods. In the first of these aliquots of the reaction solution were quenched at recorded times by addition of appropriate amounts of standard Fe(II) solution, and the excess Fe(II) was titrated potentiometrically with standard dichromate solution. In the second method, aliquots of the reaction solution were at recorded times diluted (100-fold to 1000-fold) by addition to sufficient 1 *M* sulfuric acid to bring the Ce(IV) concentration into the range $(2–10) \times 10^{-5}$ *M*, and the absorbance of each solution was measured immediately in a 1-cm cell at 320 mμ. The dilution had the effect of markedly slowing down the reaction (initial reaction being second order), and no significant Ce(IV) consumption took place between the time of dilution and the time of absorbance measurements. In 1 *M* sulfuric acid Ce(IV) obeys Beer's law at 320 mμ, and at this wavelength it is the dominant absorbing species with ϵ 5520. For the other reactant, $Rh(C_2O_4)_3^{3-}$, ϵ is 605, and for the presumed initial rhodium product, $Rh(C_2O_4)_2(H_2O)_2^{-}$, ϵ is ~250,[14] while for Ce(III), ϵ is <50. The Ce(IV) concentrations were computed for the initial stages of reaction on the basis that the decreases in absorbances at 320 mμ could be attributed to the Ce(IV) consumption together with the conversion of $Rh(C_2O_4)_3^{3-}$ to $Rh(C_2O_4)_2(H_2O)_2^{-}$. The rates of Ce(IV) consumption as measured by the two experimental methods were in good agreement.

For the $Cr(C_2O_4)_3^{3-}$ system, the Ce(IV) concentration in reaction solutions was measured as a function of time by three separate methods. The first of these involved quenching aliquots of the reaction mixture at various times by addition to excess iron(II) sulfate solution. The resulting Fe(III) concentrations, which were a measure of the Ce(IV) concentrations immediately before quenching, were determined from the absorbance of the thiocyanate complex at 478 mμ, using solutions which were 0.20 *M* in potassium thiocyanate, 10^{-2} *M* in sulfuric acid, and about 6×10^{-5} *M* in Fe(III). Because the iron(III) is slowly reduced by the thiocyanate, the absorbances were measured as a function of time and extrapolated back to the time of quenching. The extrapolated values were used to calculate [Fe(III)] by comparison with a calibration curve obtained under similar conditions. In the second method, which we shall term direct spectrophotometry, absorbances of reacting solutions were measured as a function of time at each of two wavelengths, namely, 480 and 560 mμ. At 560 mμ there is no significant absorption by the Ce(IV), while at 480 mμ the Ce(IV) and the various chromium(III) species both contribute to the absorbance. From the stoichiometries of reactions 1 and 2 and the absorbancy coefficients of $Cr(C_2O_4)_3^{3-}$, *cis*-$Cr(H_2O)_2(C_2O_4)_2^{-}$, $Cr(H_2O)_4C_2O_4^{+}$, and Ce(IV) at each of the two wavelengths, it is possible to calculate values of [Ce(IV)]. A complication is experienced here in that measured absorbances at 480 mμ, extrapolated to zero time, exceed values calculated from the measured absorbances of the individual components by up to about 8%. On the other hand, measured absorbances at 560 mμ, extrapolated to zero time, are in very close agreement with values calculated from the absorbances of the components. The deviations at 480 mμ are attributed to rapid complex formation between Ce(IV) and $Cr(C_2O_4)_3^{3-}$ prior to the initial redox step. It may be noted here that similar small deviations between calculated and observed absorbances in the vicinity of 480 mμ were observed also for the $Rh(C_2O_4)_3^{3-}$–Ce(IV) reaction. For the purpose of calculating Ce(IV) concentrations at various times for the $Cr(C_2O_4)_3^{3-}$ system, an effective absorbancy coefficient for Ce(IV) at 480 mμ was obtained for each experimental run from the absorbance extrapolated to zero time. Any uncertainties which could be introduced by this procedure were reduced below the level of experimental significance by concentrating attention on the initial stages of reaction 1, and this was necessary anyway because reaction 2 and additional reactions become inconveniently important at larger reaction times. Confidence in the procedure is provided by the observation that Ce(IV) concentrations calculated by this direct spectrophotometric approach checked satisfactorily with values obtained by the quenching method described above. The direct spectrophotometric method was more convenient than the quenching method and was therefore used for the majority of kinetic runs. At a later time, after the kinetics of the $Rh(C_2O_4)_3^{3-}$–Ce(IV) system had been examined by the dilution technique in which the absorbance of Ce(IV) was examined directly at 320 mμ, this procedure was also applied to the $Cr(C_2O_4)_3^{3-}$–Ce(IV) reaction. Results for this third and more direct procedure also agreed satisfactorily with the two other methods.

Evaluation of Rate Constants.—Kinetic studies of the $Rh(C_2O_4)_3^{3-}$–Ce(IV) reaction were carried out in 1 *M* sulfuric acid at 25.0° with initial $Rh(C_2O_4)_3^{3-}$ concentrations varied through the range 0.01–0.05 *M* while the initial Ce(IV) concentrations were varied from 0.01–0.07 *M*. The initial redox reaction is first order in each of the two reactants, as shown by satisfactory constancy of second-order rate constants obtained from the initial slopes for plots of the integrated second-order rate expression for the varying initial reactant concentrations (Table IA). At intermediate reaction times deviations from linearity of the second-order plots become apparent, with Ce(IV) consumption now proceeding more rapidly than would be anticipated from the initial second-order rates (see Figure 1). The apparent acceleration is attributed to the consecutive reaction of Ce(IV) with the bis(oxalato)rhodate(III) product of reaction 3 (see above). On

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[11] The $Rh(C_2O_4)_2^{-}$ ion formed by reaction 3 is probably predominantly of the *cis* form, as it is for the bis-oxalato complex formed by acid-catalyzed aquation of $Rh(C_2O_4)_3^{3-}$ ion,[8,12,13] with residual coordination positions about the rhodium occupied by water and/or sulfate.

[12] K. V. Krishnamurty, *Inorg. Chem.*, **1**, 422 (1962).

[13] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 2092 (1963).

[14] The value 250 was obtained when $Rh(C_2O_4)_3^{3-}$ was aquated in 2 *M* perchloric acid for 15 days at 45°; when the aquation was carried out in 1 *M* sulfuric acid, the observed absorbancy coefficient was 270. Use of the second absorbancy coefficient would influence the calculated changes in the Ce(IV) concentration by only ~0.2%.

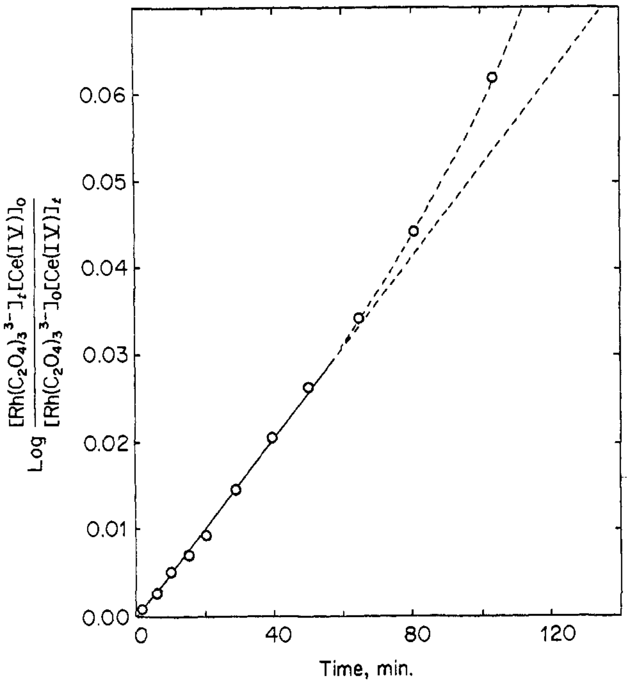

Figure 1.—Second-order rate plot for the $Rh(C_2O_4)_3{}^{3-}$–Ce(IV) reaction in 1 *M* sulfuric acid at 25.0° where $[Ce(IV)]_0 = 0.0434$ *N* and $[Rh(C_2O_4)_3{}^{3-}]_0 = 0.0827$ *N*. Note that concentrations are here expressed in normalities, computed on the basis of reaction 3. Deviation from linearity is attributed to increasing importance of reaction 4.

the other hand, the $Rh(C_2O_4)_3{}^{3-}$–Ce(IV) reaction shows evidence of being slightly inhibited by Ce(III), as indicated by separate experiments in which varying amounts of Ce(III) were added to the initial reaction mixtures (Table ID). Because of the consecutive reaction of the bis-oxalato complex and the apparent Ce(III) inhibition and in order to avoid difficulties associated with possible involvement of sulfate in the coordination sphere of the rhodium, rate constants for the initial redox reaction between $Rh(C_2O_4)_3{}^{3-}$ and Ce(IV) were evaluated from the integrated second-order rate law plots considering the first ~10% of reaction. The rate constants obtained in this way are estimated to be reliable to within about 15%. The data in Table I were obtained on this basis. Note that the rate constants in Table I are expressed in terms of consumption of Ce(IV) and refer to the over-all initial *two-electron* redox reaction 3. (The rate constants for *one-electron* oxidations of the rhodium and chromium complexes given in the Discussion are equal to *half* of the rate constants for the over-all *two-electron* oxidations.) In addition to the data for 25.0°, results are given for 35.0 and 45.0° (Table IB and C).

From preliminary kinetic analysis of the $Cr(C_2O_4)_3{}^{3-}$–Ce(IV) reaction it became apparent that the direct redox reaction could be satisfactorily described by a second-order process, with the reaction rate being proportional to the concentration of each of the two reactants. However, the acid-catalyzed aquation of $Cr(C_2O_4)_3{}^{3-}$ to *cis*-$Cr(H_2O)_2(C_2O_4)_2{}^-$ proceeds for the chosen conditions sufficiently rapidly that it needs to be taken into account in calculating the rate of the direct redox reaction. Also, as previously described,[5] the bis-oxalato complex reacts with Ce(IV) at similar rates to the tris-oxalato complex. Evaluation of rate constants for the direct reaction of Ce(IV) with $Cr(C_2O_4)_3{}^{3-}$ therefore requires consideration of the competing and consecutive processes

$$Cr(C_2O_4)_3{}^{3-} + 2Ce(IV) + 2H_2O \longrightarrow cis\text{-}Cr(H_2O)_2(C_2O_4)_2{}^- + 2Ce(III) + 2CO_2 \quad (5)$$

$$Cr(C_2O_4)_3{}^{3-} + 2H_2O \longrightarrow cis\text{-}Cr(H_2O)_2(C_2O_4)_2{}^- + C_2O_4{}^{2-} \quad (6)$$

$$cis\text{-}Cr(H_2O)_2(C_2O_4)_2{}^- + 2Ce(IV) + 2H_2O \longrightarrow Cr(H_2O)_4C_2O_4{}^+ + 2Ce(III) + 2CO_2 \quad (7)$$

$$C_2O_4{}^{2-} + 2Ce(IV) \longrightarrow 2CO_2 + 2Ce(III) \quad (8)$$

Whereas reactions 1 and 2 were written to imply stoichiometry alone, reactions 5–8 are written to imply kinetically distinct reaction paths—although they do *not* represent elementary steps in a mechanism.[15] The kinetics of reactions 6 and 7 have been previously examined in other media.[5,16,17] For the purposes of the present study the rates of these two processes were reexamined in 1 *M* sulfuric acid and in some additional aqueous acidic sulfate solvents as described below. For reaction 6 in 1 *M* sulfuric acid studies of the absorbance changes at 410 mμ gave the following first-order rate constants: 15.0°, $k = 1.1 \times 10^{-5}$ sec^{-1}; 25.0°, $k = 4.6 \times 10^{-5}$ sec^{-1}; 35.0°, $k = 1.51 \times 10^{-4}$ sec^{-1}. For reaction 7, studies according to the procedures previously described gave the following second-order rate constants for 1 *M* sulfuric acid, expressed in terms of Ce(IV) consumption: 25.0°,

TABLE I

SECOND-ORDER RATE CONSTANTS FOR REACTION 3 IN 1 *M* SULFURIC ACID[a]

A. At 25.0°

No. of expt	$10^2[Rh(C_2O_4)_3{}^{3-}]_0$	$10^2[Ce(IV)]_0$	10^3k, M^{-1} sec^{-1}
1	2.048	4.34	1.05
2	2.048	6.52	0.99
3	2.066	6.52	1.15
4	1.033	4.34	1.41
5	1.033	6.52	1.16
6	2.066	2.172	1.29
7	1.034	2.172	1.28
8	1.036	2.172	1.47
9	1.036	4.34	1.34
10	2.071	4.34	1.26
11	4.14	4.34	1.09
12	4.39	4.34	1.09
13	4.71	2.172	1.24
		Av	1.22 (±0.20)

B. At 35.0°

No. of expt	$10^2[Rh(C_2O_4)_3{}^{3-}]_0$	$10^2[Ce(IV)]_0$	10^3k, M^{-1} sec^{-1}
1	1.975	2.136	7.56
2	0.988	2.136	7.70
		Av	7.63

C. At 45.0°

No. of expt	$10^2[Rh(C_2O_4)_3{}^{3-}]_0$	$10^2[Ce(IV)]_0$	10^2k, M^{-1} sec^{-1}
1	1.127	1.086	5.56
2	0.266	1.084	4.44
3	0.322	4.34	5.80
4	0.543	1.086	5.36
		Av	5.29

D. At 25.0°, with Ce(III) Added

No. of expt	$10^2[Rh(C_2O_4)_3{}^{3-}]_0$	$10^2[Ce(IV)]_0$	$10^2[Ce(III)]_0$	10^4k, M^{-1} sec^{-1}
1	2.059	4.65	0.57	9.70
2	2.059	4.46	1.19	9.30
3	2.059	3.96	2.12	7.56
4	2.059	4.12	2.09	7.50

[a] Concentrations are in moles per liter, and rate constants refer to the consumption of Ce(IV).

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(15) See Discussion.

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

(17) C. A. Bunton, J. H. Carter, D. R. Llewellyn, A. L. Odell, and S. Y. Yih, *J. Chem. Soc.*, 4622 (1964).

$k = 0.20\ M^{-1}\ \text{sec}^{-1}$; $35.0°$, $k = 0.32\ M^{-1}\ \text{sec}^{-1}$. In comparison to reactions 5–7, reaction 8 is rapid and may be considered to proceed to completion without delay.[18] For the reactions which ensue upon addition of Ce(IV) to $Cr(C_2O_4)_3{}^{3-}$ we then write

$$-\mathrm{d}C/\mathrm{d}t = k_5AC + k_7BC + 2k_6A \qquad (9)$$

where A, B, and C are the concentrations of $Cr(C_2O_4)_3{}^{3-}$, *cis*-$Cr(H_2O)_2(C_2O_4)_2{}^{-}$, and Ce(IV), respectively, and the subscript on each rate constant is the number of the reaction to which it refers. Also we have

$$-\mathrm{d}A/\mathrm{d}t = {}^{1}/_{2}k_5AC + k_6A \qquad (10)$$

$$\mathrm{d}B/\mathrm{d}t = k_6A + {}^{1}/_{2}k_5AC - {}^{1}/_{2}k_7BC \qquad (11)$$

In addition it is necessary to consider the stoichiometric relationships which are summarized by the equations

$$A = A_0 - w - u \qquad (12)$$

$$B = B_0 - v + (w + u) \qquad (13)$$

$$C = C_0 - 2(w + u + v) \qquad (14)$$

where subscript zero denotes zero time, w is the concentration of $Cr(C_2O_4)_3{}^{3-}$ consumed by reaction 5, u is the concentration of $Cr(C_2O_4)_3{}^{3-}$ consumed by reaction 6, and v is the concentration of *cis*-$Cr(H_2O)_2(C_2O_4)_2{}^{-}$ consumed by reaction 7. Exact mathematical solutions to the set of differential eq 9–11 cannot be obtained.[19] Plots of Ce(IV) concentrations against time were therefore used to estimate values of $-\mathrm{d}C/\mathrm{d}t$ for successive closely spaced times (0.5-min intervals were in general used). These values together with the known values of k_6 and k_7 and equations 9, 10, 12–14 were then used in an iterative procedure which allowed values of k_5 to be calculated for each of the time intervals. The $Cr(C_2O_4)_3{}^{3-}$–Ce(IV) reaction was followed in this way for about the first 20% or the reaction. Reasonable constancy of the k_5 values was obtained over this portion of the reaction, and the values also appeared to be independent of the initial concentrations of the reactants. Results for two typical reaction runs are summarized in Table II. The average value of k_5 for four reaction runs[20] at 25.0° in 1 M sulfuric acid is $8.0\ (\pm 1.0) \times 10^{-2}\ M^{-1}\ \text{sec}^{-1}$. With comparable studies at other temperatures in 1 M sulfuric acid we find at 15.0°, $k_5 = 3.2 \times 10^{-2}\ M^{-1}\ \text{sec}^{-1}$ and at 35.0°, $k_5 = 2.5 \times 10^{-1}\ M^{-1}\ \text{sec}^{-1}$.

TABLE II

SECOND-ORDER RATE CONSTANTS FOR REACTION 5 IN 1 M SULFURIC ACID[a]

Expt 1, $[Cr(C_2O_4)_3{}^{3-}]_0 = 4.62 \times 10^{-3}$, $[Ce(IV)]_0 = 2.172 \times 10^{-2}$		Expt 2, $[Cr(C_2O_4)_3{}^{3-}]_0 = 2.31 \times 10^{-3}$, $[Ce(IV)]_0 = 2.172 \times 10^{-2}$	
Time, sec	10^2k_5, M^{-1} sec^{-1}	Time, sec	10^2k_5, M^{-1} sec^{-1}
30	8.3	30	6.7
60	8.5	60	7.3
90	7.5	90	7.2
120	7.0	120	7.8
150	7.7	150	7.7
180	7.5	180	6.0
Av	7.8	Av	7.2

[a] Concentrations are in moles per liter, and rate constants refer to the consumption of Ce(IV); temperature is 25.0°.

Studies in Other Media.—Several reaction media in addition to 1 M sulfuric acid were used to obtain information on the roles of hydrogen ion and sulfate ion on the reactions. The compositions of these additional media, which were computed from the data of Baes,[5,21] are given in Table III. The rate constants obtained for these media at 25.0° are summarized for the $Cr(C_2O_4)_3{}^{3-}$ system and for the initial $Rh(C_2O_4)_3{}^{3-}$–Ce(IV) reaction in Table IV.

TABLE III

COMPOSITIONS OF THREE AQUEOUS SULFURIC ACID–SODIUM SULFATE MEDIA

Designation of media	Stoichiometric concn, M		Equilibrium concn, M			Ionic strength, M
	$[H_2SO_4]$	$[Na_2SO_4]$	$[HSO_4{}^{-}]$	$[H^{+}]$	$[SO_4{}^{2}]$	
I	0.950	. . .	0.675	1.225	0.276	1.50
II	0.555	0.238	0.518	0.592	0.276	1.34
III	0.641	0.020	0.492	0.790	0.169	1.00
IV	0.691	0.207	0.597	0.785	0.301	1.50

TABLE IV

RATE CONSTANTS[a] FOR VARIOUS MEDIA AT 25.0°

Reaction no.[c]	Medium[b]			
	I	II	III	IV
6[d]	3.5×10^{-5}	8.4×10^{-6}	1.6×10^{-5}	1.7×10^{-5}
7[e]	0.19	0.13	0.21	0.14
5[e]	8.0×10^{-2}	4.3×10^{-2}	9.0×10^{-2}	4.9×10^{-2}
3[e]	1.0×10^{-3}	0.20×10^{-3}	0.75×10^{-3}	0.20×10^{-3}

[a] Values based on duplicate measurements. [b] For compositions see Table III. [c] Reference is to number designated to reaction in text. [d] First-order rate constant in sec^{-1}. [e] Second-order rate constant in M^{-1} sec^{-1}.

Discussion

The $Rh(C_2O_4)_3{}^{3-}$–Ce(IV) redox reaction and the second-order path for the $Cr(C_2O_4)_3{}^{3-}$–Ce(IV) redox reaction may be interpreted most simply as involving rate-determining one-electron oxidations of the tris-oxalato complexes, followed by rapid one-electron oxidation of the metal–oxalato intermediates by additional Ce(IV). This type of mechanism has been previously outlined and supported[5] in relation to the Ce(IV) oxidations of $Cr(C_2O_4)_3{}^{3-}$, $Cr(H_2O)_4(C_2O_4)^{+}$, and especially *cis*-$Cr(H_2O)_2(C_2O_4)_2{}^{-}$, and the general arguments presented for these chromium complexes apply also to the inert $Rh(C_2O_4)_3{}^{3-}$ ion. The *essentials* of the suggested common mechanism, as applied to the tris-oxalato complexes, can be specified without reference to residual coordination positions in the bis-oxalato products or to details of the coordination sphere about the cerium. For the rhodium system slight reversibility of reaction 15 is indicated by the data, implying that

$$M^{III}(C_2O_4)_3{}^{3-} + Ce^{IV} \overset{\text{slow}}{\rightleftarrows} M(C_2O_4)_3{}^{2-} + Ce^{III} \qquad (15)$$

$$M(C_2O_4)_3{}^{2-} + Ce^{IV} \longrightarrow M^{III}(C_2O_4)_2{}^{-} + Ce^{III} + 2CO_2 \qquad (16)$$

the intermediate is efficient as both an oxidizing and a reducing agent. Cerium(III) inhibition of this type was clearly evident[5] in the Ce(IV) oxidation of *cis*-$Cr(H_2O)_2(C_2O_4)_2{}^{-}$. For $Cr(C_2O_4)_3{}^{3-}$ the kinetic analysis is more difficult, and a clear conclusion on the

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(18) Y. El-Tantawy and G. A. Rechnitz, *Anal. Chem.*, **36**, 1774 (1964).

(19) See, for example, S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 42.

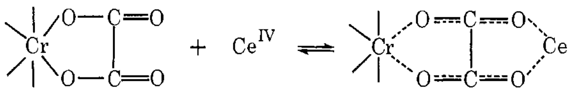
(20) Additional experiments in a medium of 1.83 M sulfuric acid reinforce the view that the initial direct reaction is first order in each of $Cr(C_2O_4)_3{}^{3-}$ and Ce(IV).

(21) C. F. Baes, *J. Am. Chem. Soc.*, **79**, 5611 (1957).

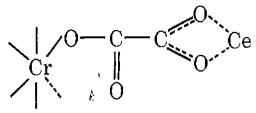
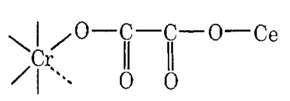
reversibility of reaction 15 for this complex has not at this time been drawn.

Before comparing the redox reactivities of $Rh(C_2O_4)_3^{3-}$ and $Cr(C_2O_4)_3^{3-}$ in further detail, it may be instructive to refer to the redox reactivity of the latter complex in relation to observations which have been made on *cis*-$Cr(H_2O)_2(C_2O_4)_2^-$, $Cr(H_2O)_4C_2O_4^+$, and free oxalate. Observed rate constants, in 1 M sulfuric acid at 25° for the Ce(IV) one-electron oxidations, are: $Cr(C_2O_4)_3^{3-}$, $4.0 \times 10^{-2}\ M^{-1}\ sec^{-1}$ (k_{15}, this work); *cis*-$Cr(H_2O)_2(C_2O_4)_2^-$, $1.0 \times 10^{-1}\ M^{-1}\ sec^{-1}$;[22] $Cr(H_2O)_4C_2O_4^+$, $1.5 \times 10^{-2}\ M^{-1}\ sec^{-1}$;[22] and $H_2C_2O_4$, $28\ M^{-1}\ sec^{-1}$.[18] For free oxalic acid and the three chromium complexes it is apparent that one cannot correlate the rates in any simple way with the charges carried by the principal oxalato species.[23,24] The relatively high reactivity of free oxalic acid is most likely related to the facility with which Ce(IV) and oxalic acid combine rapidly to form cerium(IV)–oxalato complexes. Evidence has been presented[18] that the predominant transient complex formed in sulfuric acid media[25,26] is $Ce(SO_4)_2(C_2O_4)^{2-}$, and this has the same composition as the transition state for the initial and rate-determining redox process. The apparent facilitation of the oxidation by direct coordination of oxalate to the cerium is similar to the situation which has been long recognized for the Mn(III) oxidation of oxalic acid.[27]

The Ce(IV) oxidations of the chromium(III)–oxalato complexes also almost certainly proceed *via* the initial formation of Ce(IV) complexes. For the $Cr(C_2O_4)_3^{3-}$–Ce(IV) system direct evidence for a rapidly established preequilibrium reaction is provided by the observed differences between measured and calculated absorbances for zero redox reaction time. These spectral differences are not large, and we have not at this point been able to make a detailed investigation of the preequilibrium reactions. Such rapid associations between any of these oxalato complexes and Ce(IV) could be achieved, without chromium–oxygen bond cleavage, if oxalate functions as a double bidentate ligand


(17)

Such a bridging function for oxalate was proposed a number of years ago as a means to interpreting the effectiveness of metal ions in catalyzing the racemization of the $Cr(C_2O_4)_3^{3-}$ ion,[28] and more recently direct evidence for such similarly bridging oxalate in the solid phase has been noted for $[\{Ni(en)_2\}_2C_2O_4](NO_3)_2$ on the basis of ir and X-ray studies.[29] On the other hand, evidence has accumulated which suggests that in aqueous acidic solution both $Cr(C_2O_4)_3^{3-}$ and *cis*-$Cr(H_2O)_2(C_2O_4)_2^-$ are in rapid equilibrium with forms in which an oxalate is coordinated to the chromium by a single oxygen.[24,30] It is therefore not unreasonable to suggest alternatively that binuclear Cr–Ce complexes could be rapidly formed in which oxalate is coordinated to one or both metal centers by a single oxygen. Likely structures are


or


where the sixth coordination position about the chromium could possibly accommodate a water molecule.

In the chosen medium one would not anticipate that the concentrations of any of the above binuclear types would be large, because of the high concentrations of sulfate and its considerable affinity for cerium(IV)[26] and because an already coordinated oxalate would not be expected to have a particularly high affinity for a second metal center. The significantly greater reactivity of free oxalate compared to the several chromium complexes may be at least partially attributable to higher concentrations of rapidly formed complexes in which the cerium(IV) and oxalate are brought into close association. Rationalization of the relative oxidation rates for the several different chromium complexes is a more difficult proposition. It cannot be assumed, for example, that the presumed reactive binuclear intermediates (and likewise transition states for the initial redox step) will necessarily have identical compositions in SO_4^{2-} and H^+. Unraveling the precise role of SO_4^{2-} and H^+ is an intricate matter and as a minimum necessitates examination of various media together with consideration of the way that the equilibrium quotient for bisulfate dissociation can depend on the specific composition of the medium.[5] Some studies of this type have been carried out in relation to the Ce(IV) oxidation of each of $Cr(H_2O)_4C_2O_4^+$ ion,[22] *cis*-$Cr(H_2O)_2(C_2O_4)_2^-$ ion,[5] and $Cr(C_2O_4)_3^{3-}$ ion (this study). The reactions for these three complexes show different specificities toward different media, implying transition states of differing compositions in relation to the components of the solvent electrolyte. It might be anticipated that complexities of the above type would be minimized, however, as one compares the redox reactivities of the identically charged and otherwise similar complexes, $Cr(C_2O_4)_3^{3-}$ and $Rh(C_2O_4)_3^{3-}$.

For 25° and 1 M sulfuric acid we obtain the following values for the rate constants for the forward reaction, eq 15: with M = Cr, $k_{15} = 4.0\ (\pm 0.5) \times 10^{-2}\ M^{-1}\ sec^{-1}$; with M = Rh, $k_{15} = 6.1\ (\pm 1.0) \times 10^{-4}\ M^{-1}$

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[22] M. W. Hsu and R. M. Milburn, unpublished results.

[23] In the 1 M sulfuric acid medium the principal oxalato species will correspond to the formulas as written above. For a discussion of the basicity of $Cr(C_2O_4)_3^{3-}$, see ref 24.

[24] H. Kelm and G. M. Harris, *Inorg. Chem.*, **6**, 1743 (1967).

[25] In 1 M sulfuric acid the predominant cerium(IV) species is, presumably,[26] $Ce(SO_4)_3^{2-}$.

[26] T. J. Hardwick and E. Robinson, *Can. J. Chem.*, **29**, 828 (1951).

[27] H. Taube, *J. Am. Chem. Soc.*, **70**, 1216 (1948).

[28] J. H. Carter, Doctoral Thesis, University College, London, England, 1956.

[29] N. F. Curtis, *J. Chem. Soc., A*, 1584 (1968).

[30] J. Aggett, I. Mawston, A. L. Odell, and B. E. Smith, *ibid., A*, 1413 (1968); also references therein.

$\sec^{-1}$. Thus, for the given conditions there is an approximately 70-fold difference in the rates observed for the two metal complexes.

In accord with the above discussion we suggest that reaction 15, rather than being a concerted process, is likely to involve equilibrium complexation reactions which precede the rate-determining redox step. In simple terms a likely set of initial reactions is

$$\mathrm{M(C_2O_4)_3^{3-} + Ce^{IV} \rightleftharpoons M(C_2O_4)_3^{3-}\cdot Ce^{IV}} \qquad (18)$$

$$\mathrm{M(C_2O_4)_3^{3-}\cdot Ce^{IV} \overset{slow}{\rightleftharpoons} M(C_2O_4)_3^{2-}\cdot Ce^{III}} \qquad (19)$$

$$\mathrm{M(C_2O_4)_3^{2-}\cdot Ce^{III} \rightleftharpoons M(C_2O_4)_3^{2-} + Ce^{III}} \qquad (20)$$

Reaction 18 is written to represent the rapid equilibrium formation of a binuclear complex, as discussed above for $\mathrm{Cr(C_2O_4)_3^{3-}}$, in which the cerium is immediately adjacent to oxalate which remains coordinated to M. Reaction 19 is the rate-determining electron-transfer process. Both $\mathrm{M(C_2O_4)_3^{2-}\cdot Ce^{III}}$ and $\mathrm{M(C_2O_4)_3^{2-}}$, formed by rapid equilibrium dissociation of this species, would be expected to react rapidly with additional Ce(IV) to consummate the redox process.

It cannot be assumed automatically that the greater reactivity of $\mathrm{Cr(C_2O_4)_3^{3-}}$ compared to $\mathrm{Rh(C_2O_4)_3^{3-}}$ at 25° is a reflection of the greater ability of the chromium center to facilitate electron transfer in reactions of type 19. A simple comparison between chromium and rhodium in these terms would be justified only if the compositions, stabilities, and structures of the binuclear complexes (formed according to reactions of type 18) and the compositions and structures of the transition states (for reactions of type 19) are identical or very similar. Although from a simple electrostatic point of view close similarities for chromium and rhodium would seem reasonable, since the $\mathrm{Cr(C_2O_4)_3^{3-}}$ and $\mathrm{Rh(C_2O_4)_3^{3-}}$ ions must be of quite similar size, this simplicity is not completely borne out by the results of our studies in the several media. Thus, as one moves from medium II to I, which involves doubling the hydrogen ion concentration while $[\mathrm{SO_4^{2-}}]$ remains constant (at the same time $[\mathrm{HSO_4^-}]$ increases by $\sim 30\%$ and the ionic strength increases by $\sim 12\%$), the observed rate constant for the direct Ce(IV) oxidation of $\mathrm{Cr(C_2O_4)_3^{3-}}$ (k_5) increases by a factor of 1.85; a similar medium change for $\mathrm{Rh(C_2O_4)_3^{3-}}$ results in an increase in the observed rate constant (k_3) by a factor of 5. Also, as one moves from medium IV to III, which involves essentially halving the sulfate ion concentration while $[\mathrm{H^+}]$ remains constant (at the same time $[\mathrm{HSO_4^-}]$ decreases by $\sim 18\%$ and the ionic strength decreases by $\sim 33\%$) k_5 for $\mathrm{Cr(C_2O_4)_3^{3-}}$ again increases by a factor of 1.85; whereas a similar medium change for $\mathrm{Rh(C_2O_4)_3^{3-}}$ results in an increase in the observed rate constant k_3 by a factor of 3.7. For both complexes, medium changes which involve increases in hydrogen ion concentration or decreases in sulfate ion concentration enhance the reaction rate, and on this basis it appears reasonable to ascribe specific roles to $\mathrm{H^+}$ and $\mathrm{SO_4^{2-}}$ in the reactions.[31] The quantitative effects of the medium changes are, however, rather different for $\mathrm{Cr(C_2O_4)_3^{3-}}$ and $\mathrm{Rh(C_2O_4)_3^{3-}}$. This observation illustrates the important point that the activated complexes for the initial and rate-determining redox reactions (reaction 19) are not identical.

If one accepts the view of Hardwick and Robinson[26] that the principal species of Ce(IV) in these media is $\mathrm{Ce(SO_4)_3^{2-}}$, the inverse dependences on sulfate ion are consistent with the view that cerium is coordinated to oxalate in the transition state for the rate-determining step. Possibly the greater sensitivity which the $\mathrm{Rh(C_2O_4)_3^{3-}}$ reaction exhibits toward sulfate implies a transition state in which bridging oxalate is still *chelated* to the rhodium center, while for the $\mathrm{Cr(C_2O_4)_3^{3-}}$ reaction the transition state could involve bridging oxalate coordinated to the chromium through a single oxygen, as suggested above. It would be expected that efficient coordination of cerium to an already "fully coordinated" (*i.e.*, chelated) oxalate would be significantly aided by more extensive loss of sulfate from the cerium(IV). This possible difference in the nature of the transition states for the $\mathrm{Cr(C_2O_4)_3^{3-}}$ and $\mathrm{Rh(C_2O_4)_3^{3-}}$ reactions is in accord with the relative labilities of the Cr–O and Rh–O bonds in the two complexes.[8,12,17,24,32–35] The role of hydrogen ion is even more difficult to ascribe with assurance, but it seems reasonable that protonation of sulfate, coordinated to the cerium, would facilitate electron transfer to the cerium(IV) center.

From the temperature dependences of the $\mathrm{Rh(C_2O_4)_3^{3-}}$–Ce(IV) and direct $\mathrm{Cr(C_2O_4)_3^{3-}}$–Ce(IV) redox reactions in 1*M* sulfuric acid we calculate the following apparent enthalpies of activation: rhodium, $\Delta H^{\ddagger} = 35.0\ (\pm 1.5)$ kcal mol^{-1} (at 35°); chromium, $\Delta H^{\ddagger} = 17.6\ (\pm 1.5)$ kcal mol^{-1} (25°). For each reaction the $\Delta H^{\ddagger}$ values exhibit temperature dependences which are likely to be an indication of changing compositions in transition states with temperature. For comparison purposes we calculate for the one-electron oxidations at 30°: chromium, $\Delta H^{\ddagger} \approx 20$ kcal mol^{-1}, $\Delta S^{\ddagger} \approx +2$ eu; rhodium, $\Delta H^{\ddagger} \approx 32.5$ kcal mol^{-1}, $\Delta S^{\ddagger} \approx +35$ eu. The measured $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values will include contributions from preequilibrium reactions, and these contributions will presumably differ for the $\mathrm{Cr(C_2O_4)_3^{3-}}$ and $\mathrm{Rh(C_2O_4)_3^{3-}}$ systems. Because of the nonidentity in compositions of transition states, detailed interpreta-

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(31) It might be argued that the different kinetic behaviors for the several media may be due principally to differences in ionic strength. This view is less appealing than ascribing a specific role to $\mathrm{H^+}$ and $\mathrm{SO_4^{2-}}$ in view of the types of observations made in extended studies of medium effects for the cerium(IV)–*cis*-$\mathrm{Cr(H_2O)_2(C_2O_4)_2^-}$ system[5] and because changing the medium leads to significant quantitative differences in the kinetic behavior exhibited by $\mathrm{Cr(C_2O_4)_3^{3-}}$ and $\mathrm{Rh(C_2O_4)_3^{3-}}$.

(32) L. Damrauer and R. M. Milburn, *J. Am. Chem. Soc.*, **90**, 3884 (1968).

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

(34) The formulation of $\mathrm{K_3Rh(C_2O_4)_3\cdot 4.5H_2O}$ proposed by Porte, *et al.*,[35] would suggest, however, that half of the rhodiums would initially contain a monodentate oxalate.

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

tion of these values is scarcely possible. However, the values are consistent with the suggestions that $\Delta H^{\ddagger}$ for the rhodium system may include a significant contribution from energy terms of a type common to substitution at the metal center, such as rhodium–oxygen bond stretching, and that the difference in the $\Delta S^{\ddagger}$ values for the two reactions could in part be a reflection of a lower charged transition state for rhodium, with consequent greater freedom for solvent, and in part an indication for chromium of rather specific geometric requirements for the transition state. If it were not for the relatively large positive value of $\Delta S^{\ddagger}$ for the $Rh(C_2O_4)_3^{3-}$–Ce(IV) system, this reaction would proceed many orders of magnitude more slowly than the corresponding $Cr(C_2O_4)_3^{3-}$ reaction.

It is relevant to inquire if the components $M(C_2O_4)_3^{2-}$, produced on electron transfer to the Ce(IV), are most appropriately described as complexes in which M remains in oxidation state +3 (*i.e.*, d^3 or d^6 complexes, each containing a coordinated oxalate radical ion) or complexes where M is in the oxidation state +4 (*i.e.*, d^2 or d^5 complexes). These distinctions are chemically meaningful, although, for the transient species under consideration, not easily made.[36] Detailed consideration of electrode potentials for Cr(IV)–Cr(III) and Rh(IV)–Rh(III) couples,[37–41] while not leading to unambiguous conclusions, suggests that the one-electron oxidations of the Cr^{3+} and Rh^{3+} metal centers are unlikely to be particularly favorable from a thermodynamic standpoint. Free oxalate is efficiently oxidized in sulfuric acid by both Ce(IV) and Mn(III), however, and it seems to us more likely that the initial one-electron oxidations of $Cr(C_2O_4)_3^{3-}$ and $Rh(C_2O_4)_3^{3-}$ will involve oxidation of a coordinated oxalate to a radical ion. Undoubtedly coordination to the chromium and rhodium centers would polarize the oxalate electrons and make it more difficult, in both a thermodynamic and a kinetic sense, for an external oxidant to be effective. For identical coordination such polarization should be greater in the case of rhodium where metal–ligand bonds are likely to have more covalent character. The difference in polarization would certainly be greater still if bridging oxalate is chelated to the rhodium and coordinated to the chromium by only a single oxygen. Also, for an electron transfer from an oxalate, as for transfer from an inert metal center, some prior metal–oxygen bond adjustment may be required which would involve larger energy requirements in the case of the rhodium. In view of these likely contributions the observed order of reactivity $Cr(C_2O_4)_3^{3-} > Rh(C_2O_4)_3^{3-}$ is not surprising.

[36] It is recognized that in some cases the oxidation state of a central atom in a complex may be difficult to specify in other than an arbitrary way. This situation arises especially where electrons may be considered to be delocalized over a large part of the complex. For most isolable complexes of chromium and rhodium there is little ambiguity in the oxidation state of the metal, but the situation is less clear for highly reactive intermediates, such as $Cr(C_2O_4)_3^{2-}$, etc. In certain cases direct distinctions between extreme possibilities are, at least in principle, feasible. Thus the number of unpaired electron spins for $Cr(C_2O_4)_3^{2-}$ would depend on whether it is a complex of Cr(IV) or of Cr(III) associated with an oxalate radical ion.

[37] F. P. Dwyer and H. N. Schafer, *J. Proc. Roy. Soc. N. S. Wales*, **82**, 294 (1948).

[38] J. Y. P. Tong and E. L. King, *J. Am. Chem. Soc.*, **82**, 3805 (1960).

[39] E. A. M. Wetton and W. C. E. Higginson, *J. Chem. Soc.*, 4890 (1965).

[40] J. Feldman, R. S. Nyholm, and E. Watton, *ibid.*, 4724 (1965).

[41] C. S. G. Phillips and R. J. P. Williams, "Inorganic Chemistry," Vol. II, Oxford University Press, London, 1966, Chapter 23.

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Substitution Reactions of the Sterically Hindered *trans*-Bis(triethylphosphine)chloro(mesityl)platinum(II)

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Kinetic data for substitution reactions of *trans*-$Pt(P(C_2H_5)_3)_2(ms)Cl$ (ms = mesityl) with various nucleophiles in methanol and dimethyl sulfoxide are reported. The results are discussed in terms of a balance between steric factors and electronic structure in determining the reaction mechanism. Depending on the solvent and nucleophile, the kinetic behavior is similar either to that found for "pseudooctahedral" complexes or to the associative mechanism typical of square-planar substitution reactions.

Introduction

In substitution reactions of low-spin d^8 systems, both steric factors and electronic structure favor an associative mechanism. Thus, the central metal atom is exposed for attack above and below the (square) plane and has a vacant p_z orbital, of relatively low energy, available for a σ bond in forming the transition state.[1,2]

It has recently been pointed out that in sterically

[1] F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1967.

[2] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter II.