soever is formed. In retrospect the report of the preparation of $TeCl_2$ by reaction of the element and $C_2Cl_2F_2$[23] in general did not clearly distinguish the assigned product from either the glassy or the finely crystalline mixture of Te and $TeCl_4$ one evidently gets on cooling the one-phase melt of the composition $TeCl_2$. The tetrachloroaluminate derivative $Te(AlCl_4)_2$ does not exist either.

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Inner-Sphere Mechanisms of Oxidation. Stoichiometry and Kinetics of the Cobalt(III) Oxidation of Oxalic Acid in Acid Perchlorate Solution

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The stoichiometry and kinetics of the reaction $2Co(III)_{aq} + H_2C_2O_4 \rightarrow 2Co(II)_{aq} + 2CO_2 + 2H^+$ have been investigated in perchloric acid–sodium perchlorate solutions. The stoichiometry was measured using standard analytical procedures and the kinetics were followed at ionic strength 3.0 *M* using stopped-flow and conventional spectrophotometry. Any intermediate complexes formed between the reactants could not be detected by kinetic or spectrophotometric means. The acid dissociation constants of $H_2C_2O_4$ were measured as a function of temperature and the results were used in an analysis of the empirical acidity dependence of the rate law. A comparison of the relative rate constants for the $CoOH_{aq}^{2+}$ reactions with $H_2C_2O_4$ and $HC_2O_4^-$ and of the individual rate constants themselves with those for other reductants suggests that intermediate complex formation is rate determining. The observed enthalpies and entropies of activation of a series of cobalt(III) oxidation reactions are consistent with this interpretation.

Introduction

The rate law for second-order redox reactions of cobalt(III) in aqueous perchloric acid solution generally takes the form $k_{obsd} = k_1 + k_2K_h/[H^+]$, where the rate constants k_1 and k_2 are defined by the reactions

$$Co_{aq}^{3+} + B \xrightarrow{k_1} \text{products}$$

$$CoOH_{aq}^{2+} + B \xrightarrow{k_2} \text{products}$$

Here B is the reductant and K_h is the acid dissociation constant of Co_{aq}^{3+}.[2,3] When B is H_2O_2, HNO_2, Br^-, or SCN^- the rate of the redox reaction appears to be controlled by the rate of substitution of the reductant in the inner coordination sphere of the cobalt(III).[4] By contrast, when B is hydroquinone or I^- the rates of oxidation are much higher and substitution on cobalt(III) is no longer rate determining.[4]

When cobalt(III) and oxalic acid are mixed in aqueous perchloric acid a redox reaction takes place at a notably higher rate than those observed with typical organic reductants.[2] In this paper we report a study of the stoichiometry and kinetics of this reaction. The stoichiometry was determined by standard analytical methods and the kinetics were studied at ionic strength 3.0 *M* using both conventional and stopped-flow spectrophotometry.

Experimental Section

Reagents.—All reagents used were of analytical grade and triply distilled water was used throughout. Solutions of cobalt(III) were prepared and standardized as described previously.[3,4] Sodium perchlorate solutions were prepared[5] by neutralization of sodium carbonate with perchloric acid and were standardized gravimetrically. Sodium oxalate was dried at 110–120° for 2 hr, allowed to cool in a desiccator, and then made up into stock solutions which were standardized by titration with manganese(VII) at 60°.

Determination of Acid Dissociation Constants of Oxalic Acid.—Solutions containing (1–4) × 10^{-2} *M* sodium oxalate and 3.0 *M* sodium perchlorate were titrated with perchloric acid at constant temperature under nitrogen using a Radiometer Model 4 pH meter fitted with a Type G200B glass electrode and a Type K100 calomel electrode in which the potassium chloride had been replaced with saturated sodium chloride solution.[5] The solutions were maintained at constant temperature to within ±0.1° over the range 1.5–47.8° in a jacketed titration vessel through which water was circulated from a thermostat. At least 1 hr was allowed for equilibration and pH measurements were obtained to within ±0.002 unit. The system was calibrated in the range $[H^+] = (0.02\text{–}1) \times 10^{-1}$ *M* by titration of 3.0 *M* sodium perchlorate solution with perchloric acid at the appropriate temperatures. Preliminary estimates of the acid dissociation con-

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(2) W. A. Waters and J. S. Littler in "Oxidation in Organic Chemistry," Vol. 5, K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, Part A, pp 186–241.

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stants defined in eq 1 and 2 were obtained by plotting the limiting forms of eq 3 for the titration curve at high and low pH,

$$H_2C_2O_4 \rightleftharpoons H^+ + HC_2O_4^- \qquad K_{1a} \tag{1}$$

$$HC_2O_4^- \rightleftharpoons H^+ + C_2O_4^{2-} \qquad K_{2a} \tag{2}$$

$$[H^+]_T = [H^+] + \frac{[H^+][Ox]_T(2[Ox]_T + K_{1a})}{[H^+]^2 + K_{1a}([H^+] + K_{2a})} \tag{3}$$

where the concentrations of total added acid, stoichiometric oxalate, and free acid are denoted by $[H^+]_T$, $[Ox]_T$, and $[H^+]$, respectively. The first estimates of K_{1a} and K_{2a} were then used in a refinement of the data using a nonlinear least-squares program.[6]

Stoichiometry.—The stoichiometry of the oxidation reaction was determined by addition of aliquots of a standardized cobalt(III) solution to a known excess of sodium oxalate in perchloric acid. The remaining oxalic acid was then determined by titration with manganese(VII) at 60°. The concentration ranges used were $[Co(III)] = (1.65\text{–}8.27) \times 10^{-3}$ *M* with $[Ox]_T = 1.013 \times 10^{-2}$ *M* and $[H^+] = 0.3\text{–}1.50$ *M* at 25°.

Kinetics.—A stopped-flow apparatus[7] was used for the majority of the kinetic runs, although it was found convenient in some cases to follow reactions on a Cary Model 14 spectrophotometer using conventional techniques. In all kinetic runs the rate of disappearance of cobalt(III) in the region 250–270 nm was monitored in the presence of excess oxalic acid. Each run was generally repeated four to six times with a sufficient excess of oxalic acid to ensure pseudo-first-order conditions. The rate constants obtained in replicate determinations generally agreed to within ±5%.

Results

Acid Dissociation Constants.—Typical observed and calculated[6] titration curves are shown in Figure 1, and the values obtained for the acid dissociation constants and their temperature coefficients are collected in Table I. The dissociation constants are in good agreement with previous data at high ionic strength.[5,8] The enthalpy and entropy of dissociation are of the same order of magnitude as found for other carboxylic acids.[9]

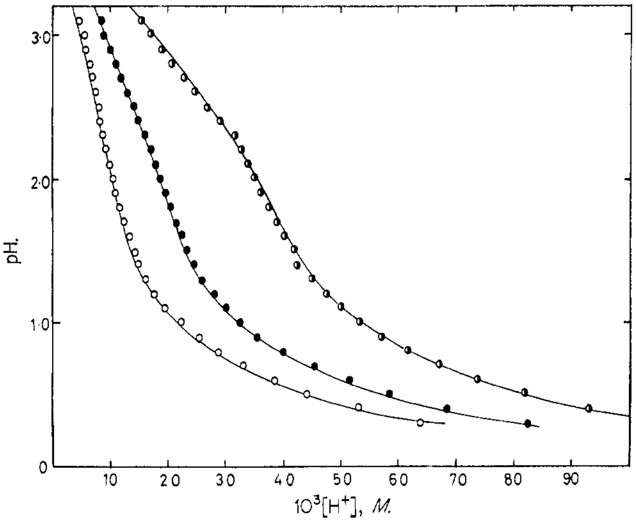

Figure 1.—Titration curves for oxalic acid at 1.5° and ionic strength 3.0 *M* at the following oxalic acid concentrations: ○, 9.9×10^{-3} *M*; ●, 19.8×10^{-3} *M*; ◑, 39.6×10^{-3} *M*. The points are experimental and the curves are calculated[6] using the data of Table I in eq 3.

TABLE I

ACID DISSOCIATION CONSTANTS OF OXALIC ACID IN 3.0 *M* SODIUM PERCHLORATE SOLUTION

Temp, °C	10^2K_{1a}[a,b]	10^4K_{2a}[a,b]	
1.5	6.48 ± 0.53	3.56 ± 0.06	$\Delta H_{1a} = 3.4 \pm 0.8$[c]
25.0	4.25 ± 0.35	3.15 ± 0.15	$\Delta S_{1a} = -14 \pm 2$[d]
34.5	3.51 ± 0.39	3.01 ± 0.13	$\Delta H_{2a} = 0.9 \pm 0.2$[c]
47.8	2.80 ± 0.37	2.85 ± 0.14	$\Delta S_{2a} = -4.8 \pm 0.2$[d]

[a] Units are *M*. [b] Errors quoted are standard deviations. [c] Units are kcal mol^{-1}. [d] Units are cal deg^{-1} mol^{-1}.

Stoichiometry.—The stoichiometric measurements showed that the overall redox reaction is

$$2Co(III)_{aq} + H_2C_2O_4 \longrightarrow 2Co(II)_{aq} + 2CO_2 + 2H^+ \tag{4}$$

within the experimental uncertainty of ±2%. This result is in agreement with previous stoichiometric determinations.[10]

Kinetics.—The disappearance of cobalt(III) was accurately first order for at least 4 half-lives, and the reaction is also first-order in total oxalic acid concentration. The kinetic data are collected in Table II. Observations at wavelengths in the region 270–400 nm led to the conclusion that any intermediate complexes which are formed either do not absorb in this region or are present at very low concentration levels (see Discussion). Competing photochemical reactions evidently play only a very minor role under the experimental conditions.

The rate law for the reaction is thus, within experimental error

$$\text{rate} = \frac{-d[Co(III)]}{dt} = k_{obsd}[Co(III)][Ox]_T \tag{5}$$

where the observed second-order rate constant, k_{obsd}, is a function of acidity.

Acidity Dependence.—A plot of k_{obsd} *vs.* $1/[H^+]$, shown in Figure 2, is approximately linear at the three temperatures employed.[11-14] However, in view of the fact that at least four potential reactants, *viz.*, Co_{aq}^{3+}, $CoOH_{aq}^{2+}$, $H_2C_2O_4$, and $HC_2O_4^-$, are present under the experimental conditions, it was considered desirable to test more complex forms of the empirical acidity func-

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(6) The computer program was based on the Los Alamos Scientific Laboratory Reports LA2367, by R. H. Moore and R. K. Zeigler, 1959, and LA2367 + Addenda, by P. McWilliams, 1962. This program was generously supplied by Dr. T. W. Newton.

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(11) The data in Table II give plots of $1/k_{obsd}$ *vs.* $[H^+]$ with negligible intercepts at each temperature: this observation contrasts sharply with the appreciable intercepts of such plots found in a recent study of the kinetics of complexation of Cr_{aq}^{3+} by oxalic acid.[12] The rapid equilibrium $H^+ + H_2C_2O_4 \rightleftharpoons H_3C_2O_4^+$ and a single rate-determining step $Cr_{aq}^{3+} + H_2C_2O_4 \rightarrow CrC_2O_4^+ + 2H^+$ were postulated to explain this observation. There is no evidence for the involvement of this additional acid–base reaction either in the present work or in recent studies of the kinetics of complexation of thallium(III)[13] and iron(III)[5] by oxalic acid in acid solution. Other considerations[14] indicate that the reactions of $CrOH_{aq}^{2+}$ should not be neglected in mechanisms of complexation of chromium(III).

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TABLE II

KINETIC DATA FOR THE OXIDATION REACTION IN PERCHLORIC ACID–SODIUM PERCHLORATE MIXTURES AT IONIC STRENGTH 3.0 M^a

10^4[Co(III)]	10^4[Co(II)]	[H^+]	$10^2[Ox]_T$	$10^{-2}k_{calcd}{}^{b,c}$	$10^{-2}k_{obsd}{}^{b}$
25.0°					
0.31	0.64	0.10	0.0278	6.17	5.75
0.15	0.32		0.00461		7.17
			0.00925		6.85
			0.0185		6.22
4.08	14.3	0.20	0.400	2.26	2.15
			0.600		2.20
			1.00		2.00
			2.00		2.13
8.90	0.90	0.50	0.426	0.665	0.704
			0.852		0.704
			1.90		0.641
			2.76		0.671
4.08	14.3	1.09	1.00	0.275	0.300
			2.00		0.295
			3.60		0.264
		2.00	2.00	0.156	0.168
			4.00		0.165
2.04	7.14	3.00	2.00	0.113	0.110
			4.00		0.105
35.0°					
2.67	1.33	0.50	0.140	2.33	2.29
			0.300		2.30
			0.500		2.14
			1.00		2.46
		1.00	0.140	0.917	1.04
			0.300		0.933
			0.500		1.02
			1.00		1.00
		1.50	0.140	0.567	0.586
			0.300		0.521
			0.500		0.500
			1.00		0.530
		3.00	0.300	0.300	0.277
			0.500		0.300
49.9°					
2.35	1.52	0.50	0.140	16.6	15.8
			0.300		17.2
			0.500		16.7
		1.00	0.140	7.56	7.79
			0.300		7.60
		1.50	0.140	4.97	5.00
			0.300		4.80
			0.500		4.54
		3.00	0.140	2.58	2.93
			0.300		2.60
			0.500		2.63

[a] All concentrations are M. [b] Units are M^{-1} sec^{-1}. [c] Calculated from the parameters in Table III.

tion using a computer procedure (nonlinear least squares).[6] These studies showed that the best fit of the kinetic data is obtained from an expression of the form

$$k_{obsd} = \frac{A + B/[H^+] + C/[H^+]^2}{1 + K_{1a}/[H^+]} \tag{6}$$

in which A, B, and C are constants. A comparison of observed and calculated rate constants is made in Table II using the values of A, B, and C in Table III.

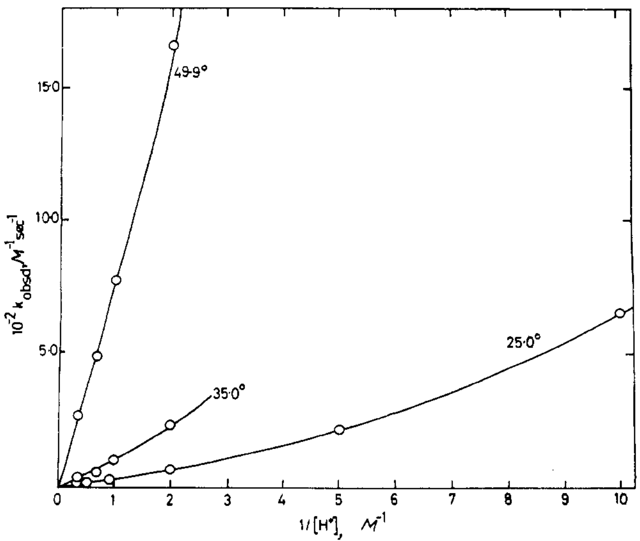

Figure 2.—Plots of k_{obsd} *vs.* $1/[H^+]$ from the data of Table II.

TABLE III

EMPIRICAL RATE PARAMETERS AT IONIC STRENGTH 3.0 M^a

Temp, °C	A^b	B^c	C^d
25.0	3.7 ± 1.1	21.1 ± 2.4	6.49 ± 0.52
35.0	5.7 ± 4.7	56.8 ± 12.9	32.0 ± 6.36
49.9	55.7 ± 32.6	565 ± 96.6	140 ± 49.9

[a] Errors quoted are standard deviations. [b] Units are M^{-1} sec^{-1}. [c] Units are sec^{-1}. [d] Units are M sec^{-1}.

Mechanism

The following mechanism, in which steps (8)–(13) are rate determining and Ox· is a radical species, is consistent with the observed kinetic dependencies

$$Co_{aq}{}^{3+} \rightleftharpoons CoOH_{aq}{}^{2+} + H_{aq}{}^{+} \qquad K_h \tag{7}$$

$$Co_{aq}{}^{3+} + H_2C_2O_4 \xrightarrow{k_1} Co(II) + Ox\cdot \tag{8}$$

$$CoOH_{aq}{}^{2+} + H_2C_2O_4 \xrightarrow{k_2} Co(II) + Ox\cdot \tag{9}$$

$$Co_{aq}{}^{3+} + HC_2O_4{}^{-} \xrightarrow{k_3} Co(II) + Ox\cdot \tag{10}$$

$$CoOH_{aq}{}^{2+} + HC_2O_4{}^{-} \xrightarrow{k_4} Co(II) + Ox\cdot \tag{11}$$

$$Co_{aq}{}^{3+} + C_2O_4{}^{2-} \xrightarrow{k_5} Co(II) + Ox\cdot \tag{12}$$

$$CoOH_{aq}{}^{2+} + C_2O_4{}^{2-} \xrightarrow{k_6} Co(II) + Ox\cdot \tag{13}$$

$$Co(III) + Ox\cdot \xrightarrow{\text{fast}} Co(II) + CO_2 \tag{14}$$

The rate law for this mechanism (eq 15) reduces to the empirical rate law (5) and (6) under the following conditions. (i) $K_h/[H^+] \ll 1$,[3,4] (ii) step 13 may be neglected,[3,15] and (iii) $K_{1a}K_{2a}/[H^+]^2 \ll 1 + K_{1a}/[H^+]$, as suggested by the data in Table I. With these assumptions the empirical expression (6) obtains, with $A = 2k_1$, $B = 2(k_2K_h + k_3K_{1a})$, and $C = 2K_{1a}(k_4K_h + k_5K_{2a})$. Parameter A has low precision, as found for analogous kinetic terms in other systems.[3] In addition, there is some uncertainty about its kinetic significance in rate laws of this type.[3,4] For this reason we have not cal-

$$k_{obsd} = 2 \times \left[\frac{k_1 + (k_2K_h + k_3K_{1a})/[H^+] + K_{1a}(k_4K_h + k_5K_{2a})/[H^+]^2 + k_6K_hK_{1a}K_{2a}/[H^+]^3}{(1 + K_h/[H^+])(1 + K_{1a}/[H^+] + K_{1a}K_{2a}/[H^+]^2)}\right] \tag{15}$$

culated activation parameters from the values of A in Table III. The identities for B and C represent the kinetic indistinguishability of the reaction pairs (9)–(10) and (11)–(12), respectively. On the basis of the available data,[3,4,15] it seems reasonable to suppose that $k_2K_h \gg k_3K_{1a}$ and $k_4K_h \gg k_5K_{2a}$, which suggests the assignments $B = 2k_2K_h$ and $C = 2k_4K_hK_{1a}$. Values computed for k_1, k_2K_h, and k_4K_h and the activation parameters for k_2K_h and k_4K_h are collected together with data for other cobalt(III) reactions in Table IV.

TABLE IV
KINETIC PARAMETERS FOR SOME OXIDATION REACTIONS OF COBALT(III) IN ACID PERCHLORATE SOLUTION AT IONIC STRENGTH 3.0 M

Reductant	k_1[a]	k_2K_h[b]	$\Delta H^{\ddagger}$[c]	$\Delta S^{\ddagger}$[d]	Ref
NH_3OH^+		3.26	22.5	+20	*e*
$NH_3NH_2^+$		1.06	23.8	+22	*e*
H_2O_2	<2	23.0	23.5	+27	*f*
HN_3	<2	35.2	23.1	+27	*g*
$H_2C_2O_4$	≃2	10.6	24.0	+28	*h*
Br^-	<5	30.4	26.1	+37	*f*
$HC_2O_4^-$		81.5[i]	25.9	+39	*h*
SCN^-	86.5	79.6	25.6	+37	*f*

[a] Units are M^{-1} sec^{-1} at 25°. [b] Units are sec^{-1} at 25°. [c] Units are kcal mol^{-1} (uncorrected for enthalpy of dissociation, reaction 7; parameters refer to the product k_2K_h. [d] Units are cal deg^{-1} mol^{-1} (uncorrected for entropy of dissociation, reaction 7); parameters refer to the product k_2K_h. [e] K. Jijie and M. Santappa, *Proc. Indian Acad. Sci.*, *Sect. A*, **69**, 117 (1969); ionic strength 2.10 M (nitrate media). [f] Reference 4. [g] R. K. Murmann, J. C. Sullivan, and R. C. Thompson, *Inorg. Chem.*, **7**, 1878 (1968); R. C. Thompson and J. C. Sullivan, *ibid.*, **9**, 1590 (1970); ionic strength 2.0 M. [h] This work. [i] This parameter is k_4K_h in the oxalate system.

Discussion

Tris(oxalato)cobalt(III) and bis(oxalato)cobalt(III) anions may be prepared by standard procedures.[16] Their decomposition, which is both acid and cation catalyzed,[17] results in the same products as those observed under the present conditions, *i.e.*, Co_{aq}^{2+} and CO_2 (eq 4). However, the rates of decomposition of these complexes are much lower than those observed in the present study, and the spectrophotometric and kinetic evidence given above suggests that such species are not formed in appreciable concentrations when the aquocobalt(III) complexes and oxalic acid are mixed in aqueous perchloric acid.

If the formation of intermediate complexes is the rate-determining process in this redox reaction, then the same kinetic trends might be expected for a series of similar redox reactions as are observed in a group of complexation reactions involving the same charge products.[3,18,19]

Studies of complexation reactions involving ligands which are acid–base pairs of the type H_2X,HX^- and HX^-,X^{2-} have been helpful in confirming the generality of an SN1 mechanism[18] for many complexation reactions involving divalent, first-row transition metal ions. In terms of this mechanism, represented by eq 16 and 17, the forward rate constant for complexation is

$$M_{aq}^{2+} + B_{aq}^- \rightleftharpoons M_{aq}^{2+},B_{aq}^- \qquad K_0 \tag{16}$$

$$M_{aq}^{2+},B_{aq}^- \xrightarrow{k_0} MB_{aq}^+ \tag{17}$$

given by $k_f = K_0k_0$, where K_0 is the equilibrium constant for the diffusion-controlled formation of an ion pair M_{aq}^{2+},B_{aq}^- which collapses in a rate-determining step[15] governed by a characteristic rate constant, k_0. This rate constant describes the process of water exchange on the particular metal ion involved. According to the mechanism any ligand dependence of k_f may be attributed to variations in K_0, which, for a simple, hard-sphere model,[20] increases as the charge product of the reactants becomes more negative.[18,21] The basis for the assignment of an SN1 mechanism and the use of the hard-sphere model as a means of estimating K_0 rests ultimately on an encouraging agreement between values for k_0 calculated from data for complexation reactions and those measured independently in the absence of B.[15,22]

However, factors other than the simple charge product undoubtedly determine the magnitude of K_0 for different ligands,[23] and it is here that the use of ligand pairs of the type H_2X,HX^- helps to minimize effects due to differences of structure, size, etc., which are important even for ligands with the same formal charge. These "nonelectrostatic" factors tend to cancel out when the ratios $K_0^{M^{2+},H_2X}/K_0^{M^{2+},HX^-}$, etc., are formed, and a more satisfactory comparison of rate constants for different reactions can thus be made.

Nancollas and Sutin[19a] have used this approach to confirm that an SN1 mechanism is appropriate to the formation of the monooxalate complex of nickel(II) *via* the reactions

$$Ni^{2+} + HC_2O_4^- \longrightarrow Ni(C_2O_4) + H^+ \tag{18}$$

$$Ni^{2+} + C_2O_4^{2-} \longrightarrow Ni(C_2O_4) \tag{19}$$

since in this case the forward rate constants for reactions 18 and 19 are in about the same ratio as are the values of K_0 computed[20] for the two charge products involved. An extension[5] of this line of reasoning to the more complicated iron(III)–oxalate system suggests that this model is also appropriate for reactions of Fe_{aq}^{3+} and $FeOH_{aq}^{2+}$ with the ligand pair $HC_2O_4^-,C_2O_4^{2-}$.

Inspection of the data for the group of oxidation reactions of $CoOH_{aq}^{2+}$ in Table IV indicates the same general trend of increasing rate with increasing negative

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charge product as is found in complexation reactions with an SN1 mechanism. Thus, the ratios of rate constants for different charge products are in reasonable agreement with those of the estimates[5,15,19,21] of the ion-pair association constant K_0. In particular, the ratio $k_4/k_2 = 7.7$ for the oxalate system is in good agreement with other experimental data[5,15,19,21] and a value for $K_0^{\mathrm{MOH^{2+},H_2X}}/K_0^{\mathrm{MOH^{2+},HX^-}}$ of about 10.[20,24]

Examination of the apparent enthalpies and entropies of the redox reactions in Table IV also lends some support to the assignment of an SN1 mechanism.[26] Enthalpies of activation increase as the enthalpy of ion-pair formation (eq 16) becomes more positive[18b] and the entropy of activation becomes increasingly positive as electrostriction of solvent in the transition state decreases.[23,25,26] The observed trends are in the direction expected from these considerations, the change being most marked in going from charge product 0 to charge product −2.

The large driving force[3,27] for reactions of cobalt(III) is evidently of primary importance[28] in determining the mechanism of its oxidation reactions in perchloric acid solution. It is also evident that the rates of decomposition of the mono(oxalato)cobalt(III) complexes are much greater than those of the higher oxalato complexes. Indeed, the rates of oxidation of oxalic acid by the weaker, labile oxidants cerium(IV),[29] chromium(VI),[30] and manganese(III)[31] would seem to be limited rather by the rates of decomposition of intermediate complexes than by the rates of their formation.

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(24) The use of the hard-sphere model[20] at high ionic strength is at best only semiquantitative even in cases involving acid–base pairs.[25]

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A Series of 1,3-Dioxolanes Derived from Dilithium Perfluoropinacolate[1]

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The ionic compound dilithium perfluoropinacolate, $Li_2[(CF_3)_2CO]_2$, can be prepared from lithium and perfluoroacetone in tetrahydrofuran. When this compound is allowed to react with a variety of labile dihalides such as $SOCl_2$, SO_2Cl_2, $COCl_2$, $C_6H_5BCl_2$, $C_6H_5PCl_2$, CrO_2Cl_2, $CF_3N{=}SF_2$, $CF_3CF_2N{=}SF_2$, or the tetrahalide of titanium, a series of 1,3-dioxolanes, $[(CF_3)_2CO]_2XY$, with the central atom of the halide in the 2 position, is produced. Thus X is S, C, B, P, Cr, or Ti and Y is O, O_2, C_6H_5, $=NR_f$, or Cl_2. The new substances prepared in this manner were identified by elemental and various spectral analyses.

Introduction

The chemistry of perfluoroacetone has been under serious investigation for several years and the more pertinent results have been well surveyed.[3] There exist also a vast number of examples of the preparation of a variety of 1,3-dioxolanes starting with a study by Fischer[4] and others,[5] who introduced atoms other than carbon into the 2 position of the five-membered ring. The known fluorine-containing analogous compounds have S, P, or Si atoms in the 2 position. These were obtained by the reactions of C_2F_4 and SO_3,[6] $(CF_3)_2CO$ and alkyl phosphines[7], and $(CF_3)_2CO$, Li, and $(CH_3)_2SiCl_2$,[8] respectively. The structure of the silicon-containing compound was reported initially as having the silicon atom in the 3 position. Subsequent studies[9] showed that the Si atom did in fact occupy the 2 position which was in accord with the structure of all other 1,3-dioxolanes reported.

The structures of 1,3-dioxolanes have been generally interpreted from nmr data. In at least one instance,[10] a half-chair configuration was assigned on the basis of

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