Reduction of the Perchlorate Ion by Aquoruthenium(II)

By THOMAS W. KALLEN and JOSEPH E. EARLEY*

The kinetics of oxidation of $Ru(H_2O)_6^{2+}$ by ClO_4^- have been investigated. In excess $HClO_4$, the products are ClO_3^- and $Ru(H_2O)_6^{3+}$ and the rate law is $d[Ru(III)]/dt = 2k_1[ClO_4^-][Ru^{2+}](1 + K[Cl^-])^{-1}$. The rate is independent of $[H^+]$ in the range 0.088–0.297 M and decreases with increasing ionic strength to a limit near $\mu = 0.26$ M. Values of k_1 and K at 25° and $\mu = 0.30$ M (HBF_4) are $(3.2 \pm 0.1) \times 10^{-8}$ M^{-1} sec^{-1} and 1.2 ± 0.1 M^{-1}. Activation parameters for k_1 are $\Delta H^{\ddagger} = 19.4 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = -5.0 \pm 1.0$ eu in the interval from 20.0 to 35.0°. Comparison of these values with those for substitution of Cl^-, Br^-, and I^- on the Ru^{2+} substrate strongly suggests that the rate of oxidation by ClO_4^- is limited by slow substitution on Ru^{2+}. Comparison of the effectiveness of a number of cations as reductants for perchlorate indicates that polarizable d electrons (t_{2g}) on the reductant are required for this reaction.

Thermodynamically, ClO_4^- is a powerful oxidant, but the majority of common inorganic reductants react with this ion at rates so slow as to be negligible, under usual aqueous conditions. There are a few simple cations which do reduce perchlorate but their identity is not predicted by thermodynamic reducing power or kinetic lability. The fact of the sluggishness of ClO_4^- reductions is sufficiently familiar as not to seem remarkable and may be ascribed to the low charge density and substitution inertia of ClO_4^-. If this view is accepted, the more rapid reactions of the effective reductants seem anomalous.

Amineruthenium(II) species have been shown to reduce the perchlorate ion in a relatively rapid, smooth, second-order process at room temperature.[1,2] Aquo- and chlororuthenium(II) species also reduce ClO_4^-,[3,4] and the $RuCl^{2+}$ complex ion acts as an effective catalyst for the reduction of ClO_4^- by chromium(II) in a process initially independent of the chromium(II) concentration.[5] The relative values of the rate constants for ClO_4^- reduction by $Ru(NH_3)_5(H_3O)^{2+}$ and $Ru(NH_3)_6^{2+}$ suggest the need for a normal coordination position in the reduction mechanism, and rate constants for Ru(II)-catalyzed reduction of ClO_4^- by chromium(II) are similar to those for substitution on the $Ru(H_2O)_6^{2+}$ substrate.[6]

We now report the results of a study of the kinetics of the reduction of ClO_4^- by $Ru(H_2O)_6^{2+}$ which demonstrate the existence of a substitution limit to the rate of the reduction process and indicate that the reduction step is more rapid than dissociation of the $RuClO_4^+$ complex. Comparison of this result with other data provides some insight into the order of ClO_4^- reducing power of cations.

Experimental Section

Materials.—Reagents were prepared as described previously.[6] Aniline hydrochloride was prepared from Fisher "Certified grade" aniline which had been decolorized with activated charcoal. The product was twice recrystallized from water and dried under vacuum.

Rate Determinations.—The kinetics of the reaction of Ru^{2+} with ClO_4^- were studied polarographically by measuring the increase in diffusion current, I, at -0.45 V *vs.* a standard NaCl

calomel electrode. At this potential ruthenium(III)– and ruthenium(IV)–aquo and –chloro species are reducible to Ru(II)[3,4] and the diffusion current of the dominant species, the Ru^{3+} ion, obeys the Ilkovič equation.

Rate determinations were performed in a two-compartment polarographic cell immersed in a large-volume, constant-temperature bath which could be maintained within $\pm 0.1°$ of a given setting. Each run was initiated by adding 2.0 ml of a Ru^{2+} stock solution to 20.0 ml of argon-deaerated reactant solution. Solutions were mixed with a rapid stream of argon and measurements began 0.5 min after their combination. A stream of argon was maintained over the reaction mixture during the reaction.

Semilogarithmic plots of $I_\infty - I$ *vs.* t were linear for periods up to 4 half-lives, and infinite-time diffusion current measurements were stable and within 2% of that expected for Ru^{3+}. Induction periods were not noted in any of the rate determinations. These results indicate a first-order dependence of the reaction on Ru^{2+} and show the reaction of Ru^{3+} with ClO_4^- to be much slower than the Ru^{2+} reaction.

At the highest Cl^- concentrations infinite-time diffusion current measurements tended to drift slowly toward higher values. In this case the diffusion current at 10 half-lives was taken as I_∞.

Separate experiments showed that Ru^{3+} is oxidized by ClO_3^- at concentration levels attained during the Ru^{2+}–ClO_4^- reaction. However, this reaction has a long induction period which is dependent on the ClO_3^- concentration and influenced by light. Aniline suppresses the reaction, and in the presence of mercury, Hg_2Cl_2 is produced. It is possible that mercury and Ru^{2+} successfully scavenge the initiator of this reaction, thereby causing the observed stability of Ru^{3+} produced by ClO_4^- oxidation of Ru^{2+}.

Product Analysis.—Two milliliters of Ru^{2+} stock solution was added to 20.0 ml of deaerated $HClO_4$ and the mixture was allowed to react for 10 half-lives at 25°. The solution was then used to charge a 5-cm³ column of H$^+$ form Dowex 50W-X2, 100–200 mesh cation-exchange resin. The charged column was washed with two bed volumes of 0.1 F HBF_4 and all of the effluent to this point was collected for analysis of its oxidizing titer. The column was then developed with 1.0 F HBF_4 to remove $RuCl^{2+}$ and 2.0 F HBF_4 to remove Ru^{3+}. These fractions were diluted to a known volume and analyzed for ruthenium using the HIO_4–RuO_4 method.[7] Identities of the species were verified using known visible and uv spectra.[8] The amount of polymeric Ru(III) was estimated as the difference between taken and found quantities since $Ru(III)_n$ species are not eluted under the conditions described.[9] The spectrum of the spent reaction mixture prior to ion exchange agreed to within 2% of that of Ru^{3+} and cyclic voltammetric estimation of product concentrations indicated that $95 \pm 5\%$ of the total ruthenium was Ru^{3+}.

Chlorate in the effluent was determined by the method of Gordon and Feldman[10] after addition of sufficient concentrated HCl

(1) J. F. Endicott and H. Taube, *J. Amer. Chem. Soc.*, **84**, 4984 (1962).

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(8) H. H. Cady and R. E. Connick, *ibid.*, **80**, 2646 (1958).

(9) Polymeric ruthenium(III) species formed in the preparation of Ru^{2+} and Ru^{3+} are not eluted by 2 F HBF_4 and are only effectively removed by stirring the resin with hot 6 M HCl or with hydrogen peroxide in 0.1 M NaOH.

(10) G. Gordon and F. Feldman, *Inorg. Chem.*, **3**, 1728 (1964).

to bring the solution to 6 F in HCl. Using this method, blanks having an equivalent volume and containing 6.50×10^{-2} mmol of ClO₃⁻ were found to have an oxidizing titer equivalent to $(6.48 \pm 0.03) \times 10^{-2}$ mmol of ClO₃⁻. Treatment of the column effluent with starch and KI prior to the reduction of ClO₃⁻ indicated no measurable concentrations of Cl(III) or Cl(I). Results of the product analyses are given in Table I.

TABLE I
PRODUCT ANALYSIS FOR THE REDUCTION OF ClO₄⁻ BY Ru²⁺ AT 25° AND $\mu = 0.30$ M

[ClO₄⁻], M	Amt taken,ᵃ mmol × 10² Ru²⁺	Amt found, mmol × 10² Ru³⁺	RuCl²⁺	ClO₃⁻
0.214	2.60	2.55 ± 0.03	0.03 ± 0.01	…
0.0456	2.60	2.51 ± 0.01	0.03 ± 0.01	…
0.214	2.18	…	…	1.04 ± 0.02
0.838	4.36ᵇ	…	…	2.16 ± 0.04

ᵃ Reaction mixture volume 22.0 ml. ᵇ $\mu = 0.95$ M, volume 24.0 ml.

Hanging mercury drop cyclic voltammetry of Ru³⁺ solutions in HClO₄–p-toluenesulfonic acid mixtures indicated the formation of material which affected the normal mercury dissolution process. New anodic and cathodic current maxima (Figure 1) were ob-
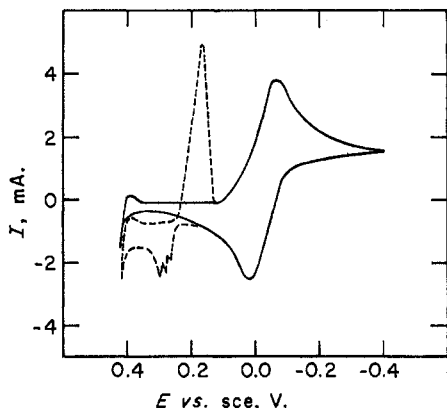

Figure 1.—Cyclic voltammogram of 3×10^{-3} M Ru³⁺ at 25°. Solid line indicates voltammogram in 0.10 M p-toluenesulfonic acid. Broken line indicates additional current maxima which occur when Ru³⁺ is produced by O₂ (or HClO₄) oxidation of Ru²⁺ in the same medium (sweep rate is 34 mV/sec at a Hg drop of 4.4-mm² surface area).

served near +0.2 V $vs.$ a saturated NaCl calomel electrode which did not appear during reductions of Ru³⁺ in either p-toluenesulfonic acid or HClO₄ and which did not influence the normal Ru³⁺–Ru²⁺ maxima centered about −0.03 V. These current maxima were not reproduced by adding H₂O₂, O₂, HSO₃⁻, S₂O²⁻, or S₂O₈²⁻ to the medium but were reproduced by oxygen oxidation of Ru²⁺ in H₂SO₄ or p-toluenesulfonic acid and by prolonged (overnight) electrolysis of the medium alone at −1 V. We believe that the new waves stem from some product (P) of the reaction of the p-toluenesulfonate ion with one or more strongly oxidizing intermediates formed during the Ru²⁺–ClO₄⁻ and Ru²⁺–O₂ reactions but not under other conditions and reflect the reversible process 2Hg + P ⇌ Hg₂P + 2e⁻.

Results

In excess perchloric acid, the stoichiometry of the Ru²⁺ reduction of ClO₄⁻ is

$$2Ru^{2+} + ClO_4^- + 2H^+ = 2Ru^{3+} + ClO_3^- + H_2O$$
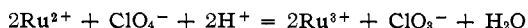
Small quantities of RuCl²⁺ found are consistent with the extent of reduction of ClO₃⁻ by Ru²⁺ and with rapid Ru²⁺ reduction of lower chlorine oxidation states to Cl⁻. The lack of more extensive reduction of ClO₃⁻ implies rate constants of similar magnitude for ClO₃⁻

and ClO₄⁻ reduction. Preliminary experiments permit an estimate of $k = 3 \times 10^{-2}$ M^{-1} sec⁻¹ for the oxidation of Ru²⁺ by ClO₃⁻ at 25° and $\mu = 0.3$ M.

The perchlorate ion is reduced to Cl⁻ by catalytic quantities of Ru³⁺ in chromium(II) solutions,[2,5] and it has been suggested that the catalytic activity of Ru³⁺ is decreased with time by production of a ruthenium(III) dimer which is more slowly reduced by Cr²⁺.[5] The stoichiometry and rate of the catalytic reaction are consistent with our result since Cr²⁺ is an excellent scavenger for ClO₃⁻ and lower chlorine oxidation rates.[11] However, extensive ion-exchange experiments indicate that less than 2% of the ruthenium(III) produced by ClO₄⁻ oxidation of Ru²⁺ exists as dimeric material.

Pseudo-first-order rate constants for the oxidation of Ru²⁺ by ClO₄⁻ are summarized in Table II. The

TABLE II
KINETIC DATA FOR THE OXIDATION OF Ru²⁺ BY PERCHLORATEᵃ

[ClO₄⁻], M	10³[Ru²⁺], M	[H⁺], M	[Cl⁻], M	10⁴k,ᵇ sec⁻¹
0.218	1.28	0.297		13.8 ± 0.1
0.214	1.45	0.297		13.8 ± 0.4
0.214	1.25	0.243		13.6 ± 0.2
0.214	1.25	0.188		13.4 ± 0.1
0.214	1.25	0.134		13.4 ± 0.1
0.214	1.25	0.088		13.6 ± 0.1
0.182	1.45	0.297		12.1 ± 0.1
0.160	0.287	0.297	0.117	9.37 ± 0.04
0.160	0.561	0.297	0.097	9.66 ± 0.10
0.160	0.499	0.204	0.094ᶜ	9.58 ± 0.10
0.160	1.07	0.297	0.058	10.0 ± 0.1
0.160	0.499	0.204	0.050ᶜ,ᵈ	9.70 ± 0.20
0.160	1.07	0.297	0.040	10.2 ± 0.1
0.160	1.07	0.297	0.020	10.4 ± 0.1
0.137	1.45	0.297		8.33 ± 0.04
0.0912	1.45	0.297		5.94 ± 0.12
0.0456	1.25	0.297		3.04 ± 0.01
0.0456	0.625	0.089	0.091ᵉ	3.98 ± 0.02
0.0456	1.25	0.129	0.133ᵉ	3.65 ± 0.07
0.0456	0.625	0.255	0.257ᵉ	3.05 ± 0.01
0.0456	1.25	0.297	0.301ᵉ	3.04 ± 0.01
0.0456	1.28	0.616	0.620ᵉ	3.02 ± 0.01
0.218	1.28	0.297	f	7.62 ± 0.02
0.218	1.28	0.297	g	24.6 ± 0.3
0.218	1.07	0.297	h	40.4 ± 0.8

ᵃ Ionic strength maintained with HBF₄ and NaBF₄. $\mu = 0.30$, [Cl⁻] = 0.0, 25.0°, unless otherwise specified. ᵇ Replicates. ᶜ Added as aniline hydrochloride. ᵈ [NaI] = 0.044 M. ᵉ μ, M; [Cl⁻] = 0.0 M. ᶠ Temperature 20.0°. ᵍ Temperature 30.0°. ʰ Temperature 35.0°.

rate law required by these data is

$$\frac{d[Ru(III)]}{dt} = \frac{2\,k_1[ClO_4^-][Ru^{2+}]}{1 + K[Cl^-]}$$

where K is 1.0 ± 0.2 M^{-1} and k_1 is $(3.2 \pm 0.1) \times 10^{-3}$ M^{-1} sec⁻¹ at 25° and $\mu = 0.30$ M. In the interval from 20 to 35°, $\Delta H^{\ddagger} = 19.4 \pm 0.3$ kcal mol⁻¹ and $\Delta S^{\ddagger} = -5.0 \pm 1.0$ eu.

Discussion

An excellent correlation exists between the kinetic parameters for oxidation of Ru²⁺ by ClO₄⁻ and those for the substitution of Cl⁻, Br⁻, and I⁻ on Ru²⁺. Activation enthalpies for substitution are in the range of 19.8 ± 0.4 kcal mol⁻¹ and activation entropies parallel the increasing absolute entropy of the solvated anion.[6] $\Delta H^{\ddagger}$ for ClO₄⁻ oxidation of Ru²⁺ is in this range and $\Delta S^{\ddagger}$ successfully extends the correlation of

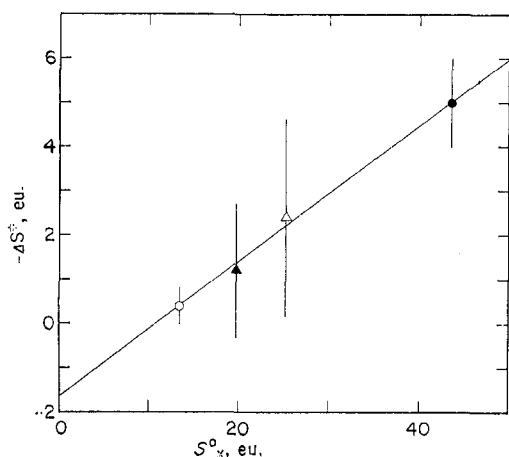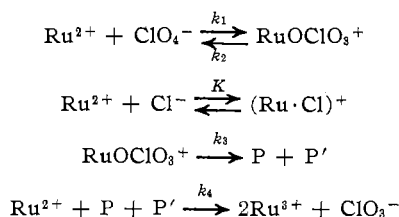(11) R. C. Thompson and G. Gordon, *Inorg. Chem.*, **5**, 562 (1966).

Figure 2.—Variation of $-\Delta S^{\ddagger}$ with the entropy of the solvated anion, $S^0{}_{x}$, for reactions of Ru^{2+} with various anions: O, chloride substitution; ▲, bromide substitution; △, iodide substitution;[6] ●, perchlorate reduction (this work).

$-\Delta S^{\ddagger}$ with S^0 (Figure 2). These points strongly support a redox mechanism in which substitution is rate determining

$$Ru^{2+} + ClO_4^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} RuOClO_3^+$$

$$Ru^{2+} + Cl^- \overset{K}{\rightleftharpoons} (Ru \cdot Cl)^+$$

$$RuOClO_3^+ \overset{k_3}{\longrightarrow} P + P'$$

$$Ru^{2+} + P + P' \overset{k_4}{\longrightarrow} 2Ru^{3+} + ClO_3^-$$

This mechanism yields the rate law

$$\frac{d[Ru^{3+}]}{dt} = \frac{2k_1k_3}{k_2 + k_3} \frac{[Ru^{2+}][ClO_4^-]}{1 + K[Cl^-]}$$

while $k_4 \gg k_1$ and reduces to the pure substitution-limited case when $k_3 > k_2 \approx k_1$. The latter condition is suggested by the entropy correlation which requires k_3 to be at least an order of magnitude greater than k_2.

Activation parameters for reduction of ClO_4^- by Ti(III) and Ru^{2+} are coincidentally very similar (for Ti(III) $\Delta H^{\ddagger} = 21.5 \pm 1.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -4 \pm 4$ eu).[12] However, Ti(III) is relatively labile[13] and therefore the observed second-order rate constants for Ti(III) reduction corresponds to k_1k_3/k_2 of our proposed mechanism. A free energy change of only 3 kcal mol^{-1} associated with k_1/k_2, the formation constant of $TiOClO_3{}^{2+}$, would be sufficient to make k_3 for the Ti(III) reaction 10 times greater than our measured rate constant, k_1. In this context, the requirement that $k_3 > k_2 \approx k_1$ for Ru^{2+} would not seem unreasonable if the interaction resulting in reduction of ClO_4^- also resulted in an increased formation constant for $MOClO_3{}^{(n-1)+}$ and a diminished $\Delta G^{\ddagger}(k_3)$ in going from Ti(III) to softer metal ions.

The value of the constant K associated with chloride inhibition is the same as the formation constant of $RuCl^+$ or a Ru^{2+}–Cl^- ion pair[6] but the nature of the complex involved in the inhibition is not established. Intermediates P and P' have not been identified, but

oxygen atom transfer to produce Ru(IV) and ClO_3^- has been previously suggested.[2] If Ru(IV) is produced in the rate-determining step, our stoichiometry requires that it react with Ru^{2+} almost exclusively, *via* outer-sphere electron transfer, to produce monomeric Ru^{3+}. Hydrolysis of any Ru(III) dimer would require scission of a Ru^{III}–O bond, a slow process.

The observed rate decreases with increasing ionic strength to a limit near $\mu = 0.267\ M$. (See lower portion of Table II, where μ is listed under column 4.) The decrease is consistent with an activated complex containing Ru^{2+} and ClO_4^- while the limit suggests a competitive interaction of Ru^{2+} with BF_4^-. Radical scavengers, aniline and I^-, have no effect on the rate.

Comparison of the rate constants for ClO_4^- oxidation of $Ru(H_2O)_6{}^{2+}$ at $\mu = 0.14$ and $0.62\ M$ with those for oxidation of $Ru(NH_3)_5(H_2O)^{2+}$ at $\mu = 0.14\ M^{1,2}$ and $Ru(NH_3)_6{}^{2+}$ at $\mu = 0.62\ M^2$ leads to the ratio 20:70:1. This is consistent with the proposed mechanism if, as in the case of Cr(III),[14,15] the coordinated water of $Ru(NH_3)_5(H_2O)^{2+}$ is more labile than that of the hexaaquo ion.

The relative rate of reduction of the perchlorate ion by various aquo ions is Ru(II) > Ti(III)[11] > Mo(III)[16] > V(II) $\approx$ V(III)[17] > Cr(II), Fe(II) $\approx$ 0. The Ru^{2+} reduction rate is limited by the rate of substitution and the reduction step must be more rapid than the observed rate. All other species are sufficiently labile that the observed rate must be that of the reduction step. Therefore this order is a measure of the interaction of the metal ion with ClO_4^-. The relative value of $10Dq$ for members of this group is Ru(II) > Ti(III) > Mo(III) > V(III) > Cr(II) > V(II) > Fe(II).[3,18] Since $10Dq$ is a measure of the polarizability of the metal ion d orbitals, the excellent correlation of the two series suggests that mutual deformation of metal ion d orbitals and ClO_4^- orbitals is necessary prior to electron or group transfer. Only Cr(II) is misplaced by the correlation, indicating that Jahn–Teller distortion and/or e_g orbital occupation is counterproductive to reduction. Slow dissociation of the perchlorato complex (k_2) should favor reduction by Ru(II).

Europium(II) and tin(II), which are f^7d^0 and $d^{10}s^2$ ions, fail to reduce ClO_4^- despite favorable free energy changes and rapid substitution rates. These observations support the suggestion that the metal ion acts as an electron donor using polarizable d orbitals.

The most favorable interaction would seem to be one which involves occupied metal ion t_{2g} orbitals and vacant 3d orbitals of the O–Cl bonding system. In such a case, the M–O bond would be strengthened by a synergic effect[19] while the O–Cl bond would be correspondingly weakened, resulting in a more stable $MOClO_3{}^{(n-1)+}$ complex and a lower $\Delta H^{\ddagger}$ for reduction of ClO_4^- by atom transfer. Evidence for an interaction of this sort is provided by the broadening of the ^{35}Cl resonance line which is caused by Mn^{2+} but not by

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(19) The magnitude of the synergic effect would be decreased by an e_g orbital occupancy. This may account for the failure of Cr(II), Fe(II), and Sn(II) to act as ClO_4^- reductants under normal conditions.

several other cations.[20] There is some evidence to suggest that, under some conditions, Mn^{2+} can reduce ClO_4^-.[21] We expect that the perchlorate complexes

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of Ti(III) and Ru(II) would also exhibit broadened ^{35}Cl resonance lines.

Kinetics and Mechanism of the Cobalt(III) Oxidation of Manganese(II) and Iron(II) in Acid Perchlorate Solution[1]

By GEOFFREY DAVIES

The stoichiometries and kinetics of the cobalt(III) oxidations of manganese(II) and iron(II) have been investigated in lithium perchlorate–perchloric acid and sodium perchlorate–perchloric acid mixtures at ionic strength 3.0 *M*. Stoichiometric measurements with excess reductant established that the products of oxidation are manganese(III) and iron(III), respectively, and kinetic measurements under the same conditions using the stopped-flow technique showed that the rate law for each reaction is given by $-d \ln (Co(III))/dt = [a + b/(H^+)](reductant)$, where a and b are interpreted in terms of rate constants for the reactions $Co_{aq}^{3+} + M_{aq}^{2+} \xrightarrow{k_0} Co(II)_{aq} + M(III)_{aq}$ ($a \equiv k_0$) and $CoOH_{aq}^{2+} + M_{aq}^{2+} \xrightarrow{k_{-1}} Co(II)_{aq} + M(III)_{aq}$ ($b \equiv k_{-1}K_h$), where K_h is the acid-dissociation constant of Co_{aq}^{3+}. Activation parameters for a and b in the two media are reported and the mechanisms of the reactions are discussed.

Introduction

A comparison of rate constants for complexation reactions of the type

$$MOH_{aq}^{2+} + B_{aq} \underset{k_{-1}}{\overset{}{\rightleftharpoons}} MOHB_{aq}^{2+} \qquad K_1 \qquad (1)$$

suggests that when M is Cr, Fe, or Co the forward rate of complexation is largely determined by the rate of water exchange on the metal ion.[2–4] When M is Co, the complexation reaction (eq 1). is generally followed by oxidative decomposition of the complex, and studies with B = Cl^-,[4a] malic acid,[4b] thiomalic acid,[4c] and cysteine[4d] have allowed the kinetics of these two processes to be studied separately.

By contrast, there is no direct spectrophotometric or kinetic evidence for intermediate complex formation in the majority of oxidation reactions involving $CoOH_{aq}^{2+}$.[5] However, in some of the faster reactions of this oxidant, notably those with B = H_2O_2,[6] HNO_2,[6] $H_2C_2O_4$,[7] HN_3,[8] Br^-,[6] SCN^-,[6] and $HC_2O_4^-$,[7] the rates of oxidation appear to be substitution controlled.[9] A comparison of activation parameters for these systems supports this view.[7]

The rate constants for reactions of aquocobalt(III)

with manganese(II)[10] and iron(II)[11,12] are of the same order of magnitude as those reported for substitution-controlled complexation[4,5] and redox[5–8] reactions. However, the data[10] for the reaction with manganese(II) refer only to 3 *M* perchloric acid at 25.0° and the reaction with iron(II) has only been investigated at 1 *M* ionic strength[11] ($HClO_4$, $NaClO_4$) in the temperature range 0–14° and in 3 *M* perchloric acid[12] at 25.0°. We need to study the effect of changing acidity, medium, and temperature in these reactions under the same conditions as used in the majority of fast redox reactions[5–8] of cobalt(III) in order to make a valid comparison of the rates of the constituent redox steps.[5]

In this paper we report an investigation of the stoichiometry and kinetics of the cobalt(III) oxidation of manganese(II) and iron(II) in 3 *M* lithium perchlorate–perchloric acid and 3 *M* sodium perchlorate–perchloric acid media in the temperature range 0–50°. A comparison with previous kinetic data[4–8] enables an assignment of the probable mechanisms of the constituent reaction pathways to be made.

Experimental Section

Reagents and Analytical Methods.—All chemicals, except for the Li_2CO_3 used in the preparation of lithium perchlorate solutions, were of reagent grade and triply distilled water was used throughout. The perchlorates of cobalt(III), cobalt(II), and sodium were prepared and standardized as described previously.[6] Lithium perchlorate was recrystallized three times from water and was made up into stock solutions which were standardized gravimetrically. Manganese(III) solutions in perchloric acid were prepared by oxidation of excess manganese(II) with manganese(VII) or at a Pt anode[10,13] and were standardized

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