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Correlation of Activation Parameters and the Case for Substitution-controlled Reduction of $CoOH_{aq}{}^{2+}$ and $Co(NH_3)_2OH_{aq}{}^{2+}$. Implications for Electrocatalysis by Aquocobalt(III) and Other Strongly Oxidizing Metal Species

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Abstract

A correlation of the activation parameters for complexation and reduction of aquocobalt(III) species $CoOH_{aq}{}^{2+}$ by a wide range of substrates B indicates that the redox reaction rates are limited by substrate coordination at this metal center. The activation parameters are remarkably insensitive to the formal substrate charge. Although the rates of reduction of the homologue $Co(NH_3)_2OH_{aq}{}^{2+}$ by $Br_{aq}{}^-$, H_2O_2, $N_2H_{5aq}{}^+$ and $NH_3OH_{aq}{}^+$ also suggest a substitution-controlled rate-determining step, we agree with M.P. Hayward and C.F. Wells (*Inorganica Chimica Acta, 148* (1988) 241) that there are insufficient data available to make this conclusion as definite. The implications of substitution-controlled redox phenomena on electrocatalysis by the aquocations of cobalt(III), manganese(III) and silver(II) are considered.

Introduction

Solutions obtained by facile electrolytic oxidation of cobalt(II) perchlorate in 3 M aqueous perchloric acid at a Pt anode at 0–25 °C contain the mononuclear blue ion $Co_{aq}{}^{3+}$, which is of considerable interest because of its extremely strong oxidizing character ($E_{red}{}^\circ = 1.86$ V in 3.0 M $HClO_4$ at 23 °C) [1,2]. Good electrocatalytic oxidants have this property [3]. This implies that the aquocobalt(III)/(II) couple should be an excellent prospect for electrocatalyzed oxidation of a wide range of substrates [3b]. A major limitation in such applications might be the relative rates of competitive reduction of cobalt(III) by the target substrate and solvent water [1–3]. This paper addresses the rates and activation parameters of relatively slow substrate oxidation by aquocobalt(III) species.

The rates of slower known aquocobalt(III) reactions generally decrease with increasing experimental acidity [1,4,5]. Evidence for equilibrium (1) comes mainly from kinetic studies of aquocobalt(III) complexation and reduction by excesses of a wide range of molecules and ions B at different acidities. In these reactions, the characteristic second-order rate law for forward complexation of cobalt(III) or the only observable redox process is found to be eqn. (2) [1,4–7]. Rate law (2) accounts for complexation and redox reactions with species like $Cl_{aq}{}^-$ [6] and $Br_{aq}{}^-$ [7], respectively, that are not expected to be involved in significant acid–base equilibria of their own. For this reason experimental parameters a and b have been specifically associated with reactions of $Co_{aq}{}^{3+}$ and $CoOH_{aq}{}^{2+}$, with $a = k_3$ and $b = k_4K_h$, respectively, in rate-determining steps (3) and (4) of mechanisms for complexation and reduction of aquocobalt(III) [1,4–7].

$$Co_{aq}{}^{3+} + H_2O \rightleftarrows CoOH_{aq}{}^{2+} + H_3O^+ \quad \text{fast}, K_h \qquad (1)$$

$$\begin{aligned}\text{rate} &= k_{obs}[\text{Co(III)}][\text{B}] \\ &= (a + b/[H_3O^+])[\text{Co(III)}][\text{B}]\end{aligned} \qquad (2)$$

$$Co_{aq}{}^{3+} + B \longrightarrow \text{products} \quad \text{slow}, k_3 \qquad (3)$$

$$CoOH_{aq}{}^{2+} + B \longrightarrow \text{products} \quad \text{slow}, k_4 \qquad (4)$$

The goal of kinetic and mechanistic studies of complexation and redox reactions of metal ions is to account for the observed rate law and to associate empirical parameters like a and b with events occurring at specific metal ion centers [5].

Experimental Limitations

There are two well known experimental limitations in the assignment and discussion of kinetic data for reactions of aquocobalt(III) species $Co_{aq}{}^{3+}$ and $CoOH_{aq}{}^{2+}$.

First, it is commonly observed for relatively slow reactions of aquocobalt(III) (e.g. with B = H_2O_2 [7,8]) that the term $b/[H_3O^+]$ of eqn. (2) is so dominant that $a = k_3$ obtained from the intercepts of plots of the experimental second-order rate constant k_{obs} *versus* $1/[H_3O^+]$ at fixed temperature and ionic strength are small and subject to considerable

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uncertainty (see, for example, Fig. 1 of ref. 7). For this reason our present understanding of the variation of k_3 with B is restricted to the most rapid reactions of Co_{aq}^{3+} with species such as Fe_{aq}^{2+} and I^-, which have been discussed previously [1,4,7,9]. Because we have far less accurate information for the slower reactions of Co_{aq}^{3+} (eqn. (3)) than for those of $CoOH_{aq}^{2+}$ (eqn. (4)), we focus attention on the latter in this paper.

Second, the form of eqn. (2) indicates that K_h in eqn. (1) is smaller than the lowest practical acidity [5]. The latter is generally set at $[H_3O^+] = 0.05$ M because the rate of oxidation of solvent water increases very sharply at lower acidities. Attempts to estimate K_h spectrophotometrically are frustrated by cobalt(III) instability and the danger of forming polymeric aquocobalt(III) species [1,2]. Thus, we cannot derive accurate values of k_4 from the relationship $k_4 = b/K_h$. However, since K_h and its thermodynamic parameters are associated just with Co_{aq}^{3+}, eqn. (1), we can investigate the dependence of b and its associated activation parameters (eqns. (5) and (6)) on the characteristics (charge, oxidation potential, etc.) of B and try to see if some inherent property of $CoOH_{aq}^{2+}$ governs dominant term $b/[H_3O^+]$ of the rate law [1,4,5].

$$\Delta H_b^{\ddagger} = \Delta H_h + \Delta H_4^{\ddagger} \tag{5}$$

$$\Delta S_b^{\ddagger} = \Delta S_h + \Delta S_4^{\ddagger} \tag{6}$$

Reaction Mechanisms

Reactions with a large driving force, such as those involving reduction of aquocobalt(III) species, might, for a variety of reasons, proceed by outer-sphere or inner-sphere mechanisms.

Outer-sphere systems are identifiable from only one observable reaction with relatively large, comparable values of a and b and relatively small respective $\Delta H^{\ddagger}$. On this basis the reactions of Co_{aq}^{3+} and $CoOH_{aq}^{2+}$ with such species as I_{aq}^- and hydroquinone proceed by outer-sphere mechanisms (see Fig. 1 of ref. 4).

Most of the other reactions of aquocobalt(III) also proceed with only one observable step, no kinetic evidence for rapidly equilibrated precursors but at significantly lower rates. In these cases we observe small or negligible a, larger $\Delta H_b^{\ddagger}$ and relatively positive $\Delta S_b^{\ddagger}$ (see Fig. 3 of ref. 4). Although positive ΔS_h (indirectly estimated at 22 cal deg^{-1} mol^{-1} at 25 °C [1,5]) always contributes to these positive $\Delta S_b^{\ddagger}$ through eqn. (6), the latter already suggest a dissociatively-controlled rate-determining process.

In rare cases involving smaller driving forces one can monitor two slow but distinct processes at wavelengths where cobalt(III) absorbs (see, for example, Fig. 4 of ref. 1 for the observed (at 280 nm) two-step reaction of aquocobalt(III) with excess $B = Cl_{aq}^-$ at $[H_3O^+] = 1.00$ M and 25 °C) [6]. The first process must correspond to complexation of B by aquocobalt(II) because an absorbance increase is observed (aquocobalt(II) absorbs much more weakly than aquocobalt(III) [1]). The second must be due to cobalt(III) reduction because the absorbance decreases to that of aquocobalt(II). In such cases the kinetic data for the first process (complexation) are very valuable for comparison with data for systems exhibiting only one step but which are too slow to be outer-sphere. Similarity of b for slow one-step and the first of two-step complexation/redox processes is good evidence that many slow reactions of $CoOH_{aq}^{2+}$ are limited by the rate of substitution of B at this very strongly oxidizing cobalt(III) center [1,4,5]. We will now examine this conclusion in more detail.

Activation Parameter Correlation

We endorse the recent recommendation of Hayward and Wells [10] that rate constants and their associated activation parameters should be compared when trying to draw conclusions about a possible common rate-determining substitution step in reactions of a particular metal complex with different B. The question is how should the data be compared?

One approach is to see if the activation parameters vary in a predictable manner with the formal charge of B (rather than with its reductive power) as the most dominant contribution of B to either an inner- or outer-sphere rate. This expectation has been demonstrated for some reactions of $CoOH_{aq}^{2+}$ (see Figs. 2 and 3 of ref. 4, but note the following comments). It makes sense that the activation parameters for a series of reactions whose rates are governed by a common slow event should be correlated [11]. Thus, another approach is to plot $\Delta H_b^{\ddagger}$ *versus* $\Delta S_b^{\ddagger}$ to see if these parameters are correlated for reactions with widely different B, as might be expected for a series of reactions with a common rate-determining step [12,13]*.

Before presenting the result of the second approach for slower $CoOH_{aq}^{2+}$ reactions it is necessary to point out some inherent limitations. It has been observed in several laboratories [6,7,14–16]**

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*Figure 4 of ref. 12 shows an activation parameter correlation for fourteen isomerization reactions of heterotetranuclear nickel(II)–copper(II) complexes. Figures 4–6 of ref. 13 classify and correlate activation parameters for 35 monotransmetalations of dinuclear copper targets with $M(NS)_2$ transmetalators.

**Recalculated activation parameters from the data of ref. 15 (see Table 8 of ref. 1) have been plotted in Fig. 1 of the present work.

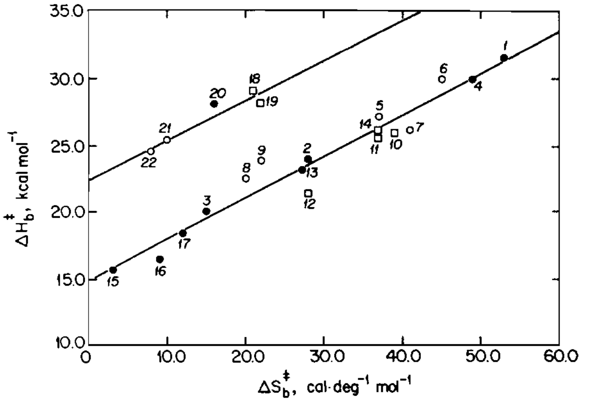

Fig. 1. Plots of $\Delta H_b^{\ddagger}$ vs. $\Delta S_b^{\ddagger}$ (at 25 °C) for complexation and reduction of $CoOH_{aq}^{2+}$ and *cis*-$Co(NH_3)_2OH_{aq}^{2+}$ by reagents B. The data for complexation and reduction of $CoOH_{aq}^{2+}$ are taken from refs. 1, 6, 7, 14, 15 and 16. The data for complexation and reduction of *cis*-$Co(NH_3)_2OH_{aq}^{2+}$ are taken from refs. 19 and 20. Key: 1, propionic acid; 2, oxalic acid; 3, malonic acid; 4, 2-ethylmalonic acid; 5, glycinium cation; 6, α-alaninium cation; 7, β-alaninium cation; 8, hydroxylammonium cation; 9, hydrazinium monocation; 10, binoxalate anion; 11, thiocyanate; 12, chloride; 13, H_2O_2; 14, bromide; 15, thiourea; 16, *N*,*N*′-diethylthiourea; 17, ethylenethiourea; 18, bromide; 19, chloride; 20, H_2O_2; 21, hydroxylammonium cation; 22, hydrazinium monocation. Formally anionic, neutral and cationic reactants B are distinguished by squares, closed circles and open circles, respectively. Typical standard deviations of $\Delta H_b^{\ddagger}$ and $\Delta S_b^{\ddagger}$ (not shown) are ±0.5 kcal mol^{-1} and ±4 cal deg^{-1} mol^{-1}, respectively, except for the data from ref. 15, which have about twice these standard deviations (see Table 8 of ref. 1). The respective slopes, intercepts and correlation coefficients of the lower and upper lines are as follows: 309 K, 14.9 kcal mol^{-1}, 0.972; 294 K, 22.4 kcal mol^{-1}, 0.939.

that the rate constants b for reactions of $CoOH_{aq}^{2+}$ with a range of complexing/reducing substrates B cover only a small range in rate law (2). As noted above, this is good but incomplete [10, 17] evidence for a common (ostensibly substitution-controlled) rate-determining step. However, it also results in similar $\Delta G_4^{\ddagger}$ in the reaction series. Thus, a plot of $\Delta H_b^{\ddagger}$ versus $\Delta S_b^{\ddagger}$ from eqn. (7) is expected to be linear provided that none of the reactions being considered has a distinctly different rate-determining step [18].

$$\Delta H_b^{\ddagger} = T\Delta S_b^{\ddagger} + \Delta G_b^{\ddagger} \qquad (7)$$

Figure 1 shows a plot of eqn. (7) which includes previous [1, 7] and more recent (complexation, [16]) data for relatively slow reactions of $CoOH_{aq}^{2+}$. Different symbols are used to distinguish between formally anionic, neutral and positively charged reductants B in Fig. 1.

The benefit of inclusion of new data [16] for monocomplexation by $CoOH_{aq}^{2+}$ of a range of carboxylic acids R-COOH that are either neutral (e.g. propionic acid, R = Et, point 1) or monopositive (e.g. α-alaninium, R = $(CH_3)(NH_3^+)CH-$, point 6) is a demonstration that the activation parameters for complexation of $CoOH_{aq}^{2+}$ actually are quite insensitive to the formal charge of reactant B (substitution-controlled redox reactions of $CoOH_{aq}^{2+}$ were expected to be faster for anions that form stronger ion-pair precursors than would cations [1, 4, 5]).

It is unlikely that the rate of water exchange at $CoOH_{aq}^{2+}$ will ever be measured directly because it invariable co-exists with Co_{aq}^{2+}, rapidly oxidizes solvent water [1] and is never present in significant concentrations at $[H_3O^+] \geqslant 0.05$ M because of the small value of K_h in eqn. (1) [1]. This information would help to prove that all the data in Fig. 1 refer to substitution-controlled redox processes, as is the case for several oxidations of V_{aq}^{2+} [17]. Nevertheless, we feel that the correlation of activation parameters in Fig. 1 very strongly suggests a common rate-determining substitution step in the cited substitution and redox reactions of $CoOH_{aq}^{2+}$. This classification and correlation of the data is all the more impressive when one considers that it (i) covers the wide ranges $\Delta H_b^{\ddagger}$ = 15.7–31.6 kcal mol^{-1} and $\Delta S_b^{\ddagger}$ = 3–53 cal deg^{-1} mol^{-1} at 25 °C; (ii) covers reactions with likely ligand donor atoms S (points 15–17 [15]), halide (but not I^-, which is oxidized in the outer sphere [1, 4]), N (from SCN^- [7] and $N_2H_5^+$ [14]) and O (from a variety of reductants); (iii) correlates kinetic data from six laboratories employing different monitoring instruments and reagent sources*.

Also included in Fig. 1 (upper line) are much more limited data for monocomplexation and reduction of the homologue *cis*-$Co(NH_3)_2OH_{aq}^{2+}$ [19, 20] by some of the B that also correlate for substitution-controlled reduction of $CoOH_{aq}^{2+}$. Hayward and Wells [10] are correct in their opinion that insufficient activation parameter data are available to allow their use to support a substitution-controlled mechanism for reduction of *cis*-$Co(NH_3)_2OH_{aq}^{2+}$ by Br_{aq}^- and H_2O_2 [19]. However, we note that $\Delta H_b^{\ddagger}$ appears to be larger (by about 7 kcal mol^{-1} at fixed $\Delta S_b^{\ddagger}$) and that $\Delta S_b^{\ddagger}$ apparently is smaller (by about 15 cal deg^{-1} mol^{-1} at 25 °C) than for the corresponding reaction of $CoOH_{aq}^{2+}$ with any one of the cited reductants. This indicates that *cis*-$Co(NH_3)_2OH_{aq}^{2+}$, while still a strong oxidant [19a], is more substitutionally inert than $CoOH_{aq}^{2+}$, which is in line with the expected trend on progressive replacement

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*Our attempts to detect discrete aquocobalt(III)–H_2O_2 complexes (as reported in ref. 8) with different stopped-flow instruments and different reagent sources have been unsuccessful at $[H_3O^+] \geqslant 0.05$ M and temperatures in the range 0.8–43.6 °C. The correlation in Fig. 1 suggests that the rates of formation and redox decomposition of such complexes are similar (if they differ at all).

of water in aquocobalt(III) species with ammine ligands [19].

The Need for Large Databases

We have long felt it necessary to collect a considerable amount of kinetic and other supporting data on the reactions of a particular metallic species before attempting to draw firm conclusions concerning a possible common metal-based rate-determining process [1,4,5,12,13]. We feel that the case for particular substitution-controlled redox reactions of $CoOH_{aq}^{2+}$ is made by the correlation of activation parameters in Fig. 1. The case for corresponding reactions of *cis*-$Co(NH_3)_2OH_{aq}^{2+}$ is supported by the rate constant data [19,20]. However, the conclusion is less compelling in the absence of activation parameters for a wider range of substrates that either form kinetically characterizable monocomplexes or are relatively slowly oxidized in one observable step.

Implications for Electrocatalysis

In principle, any strongly oxidizing cation that is easily generated at an anode can serve as an oxidizing electrocatalyst. Candidates include aquocobalt(III), Mn_{aq}^{3+} (E_{red}° = 1.56 V in 3.0 M $HClO_4$ [21, 22]), and aquosilver(II) (E_{red}° = 1.914 V in 1.0 M HNO_3 [23,24]). All these species are so highly unstable at low acidity that they are impractical as chemical oxidants under such conditions. The factors determining their potential usefulness as electrocatalysts are: (i) reasonable rates of anodic oxidation of Co_{aq}^{2+}, Mn_{aq}^{2+} and Ag_{aq}^{+}, respectively; (ii) any tendency or otherwise to disproportionate, e.g. via eqn. (8) [21] at low [25] levels; and (iii) the relative rates of substrate and solvent water oxidation.

$$2Mn(III) \rightleftarrows Mn(II) + Mn(IV) \qquad (8)$$

Benzene, with no obvious donor atoms, is oxidized very slowly by aquocobalt(III) [26]. This indicates that target organic substrates should have at least one ligand atom that can be coordinated by the oxidant [3], as do all the substrates B in Fig. 1. Under these circumstances it would appear that electrocatalysis by aquocobalt(III) would be most efficient at moderate acidities, could well be rate-limited by substitution of B at $CoOH_{aq}^{2+}$ and would therefore be non-specific. On the other hand, greater substitutional lability of strong oxidants $MnOH_{aq}^{2+}$ [21] and $Ag^{2+}/AgOH_{aq}^{+}$ [23,24] implies that they are better general electrocatalysts than aquocobalt(III). This supposition has been well demonstrated for aquosilver(II) in nitric and perchloric acid media [25].

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