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THE MECHANISTIC ASSIGNMENT OF TERMS IN EMPIRICAL RATE LAWS FOR COMPLEXATION AND REDOX REACTIONS OF METAL IONS IN AQUEOUS SOLUTION: ACID DEPENDENCES IN PERCHLORATE MEDIA

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CONTENTS

A. INTRODUCTION

There has been a tremendous increase in the extent of our knowledge of the kinetics of ionic reactions in solution in recent years[1]. Most of these studies have been carried out in predominantly aqueous media and its special relationship to water makes the hydroxide ion unique among the ligands commonly involved in these reactions.

As far as substitution of a ligand into the inner coordination sphere of an aquometal ion is concerned, the hydroxide group can be produced there without the need for replacement of a water molecule.

$$\mathrm{Fe(H_2O)_5H_2O^{3+}_{aq} + H_2O \rightleftharpoons Fe(H_2O)_5OH^{2+}_{aq} + H_3^{+}O_{aq}} \quad K_h \tag{1}$$

$$\mathrm{Fe(H_2O)_5H_2O^{3+}_{aq} + X^{-}_{aq} \rightleftharpoons Fe(H_2O)X^{2+}_{aq} + H_2O} \tag{2}$$

Thus the $\mathrm{Fe(H_2O)_5OH_{aq}}^{2+}$ species in eqn. (1) is produced by fast[2] proton transfer to a base (the solvent) and in eqn. (2) the replacement of a water molecule is necessary at some stage of the reaction in order for substitution to occur. The extent to which equilibria in eqns. (1) and (2) are distributed between the various coordinated and free species depends on the enthalpy and entropy changes associated with transfer of the complexing ligand from the bulk solvent to the inner coordination sphere of the metal ion. The hydroxide ion is more "water-like" than any other ligand except water itself, and the relative values of the equilibrium constants for eqns. (2) and (3) reflect these intrinsic differences

$$Fe(H_2O)_{6aq}{}^{3+} + OH^- \rightleftharpoons Fe(H_2O)_5OH_{aq}{}^{2+} + H_2O \qquad (3)$$

Thus, when X is Cl, the equilibrium constants for iron(III) complexes are $(5.2 \pm 0.4)M^{-1}$ (ref. 4) and $6.4 \times 10^{11}M^{-1}$ (ref. 3) in eqns. (2) and (3), respectively at 25°C and ionic strength 1*M*.

Since the self-dissociation of water is so fundamental to studies in aqueous solution, we shall present examples of the technique of mechanistic analysis applied to reaction rate laws which have experimentally observable acid-concentration dependences. It will be shown that independent equilibrium data are an obvious necessity for the establishment of mechanism, by means of which realistic statements can confidently be made concerning the relative reactivities of the species present under the reaction conditions. It is also intended that the manner in which mechanistic predictions are compared with empirical rate laws be made clear so that further attempts at complete analysis of kinetic acid-dependences will be encouraged in other systems. The experimental constraints of most aqueous systems make the choice of a constant ionic medium mandatory, and the basic assumptions inherent in this constraint will also be outlined.

Certain redox reactions of hydroxoaquocobalt(III) appear to exhibit limiting behavior when the driving force for electron transfer becomes large. With the involvement of ion-aggregate precursors as part of the description of the pathway for both complexation and reduction as a basis, it is possible to make rough estimates of the influence of the other reactant in determining the configurational distribution of the hydroxyl group in these reactions. These effects appear to be related to the π character of the OH^- ligand and to its relationship to the aqueous environment; however, the assessment of the importance of any distributional properties of activated complexes or transition states for complexation or redox reactions is made difficult not only by a distinct lack of detailed structural information concerning the separate energetics of each step in the activation process, but also by a fundamental problem of adequately describing the thermodynamics and structure of the ion-aggregate precursors which precede the actual substitution or electron-transfer act.

B. EQUILIBRIUM CONSIDERATIONS

Obviously, it is important to know the proportion of a metal ion present as the hydroxo complex in eqn. (1) so that a measure of the influence of the OH^- ligand in the reactions of the aquo complex can be obtained: the quantitative description of equilibria such as in eqn. (1) is thus fundamental to the study of the kinetics of reactions of metal ions in aqueous solution. Molecular properties of the hydroxo complexes, such as their spectral characteristics[5], are potentially useful in rationalizing these effects.

We might expect the oxidation state of the central metal ion to have a considerable influence on the position of equilibrium (1). This is found experimentally, in that the equilibrium constant for an ion with formal oxidation state III is, in general, several orders of magnitude greater than that for the ion of the same element in a lower oxidation state[6]. Indeed, higher formal charges in some metal aquo complexes lead to extensive acid-dissociation through further loss of protons, e.g. for vanadium (V)[6] the relevant equilibria are believed to be

$$V(H_2O)_5OH_{aq}{}^{4+} + H_2O \rightleftharpoons V(H_2O)_5O_{aq}{}^{3+} + H_3{}^+O_{aq} \tag{4}$$

$$V(H_2O)_5O_{aq}{}^{3+} + H_2O \rightleftharpoons V(H_2O)_4(OH)O_{aq}{}^{2+} + H_3{}^+O_{aq} \tag{5}$$

$$V(H_2O)_4(OH)O_{aq}{}^{2+} + H_2O \rightleftharpoons V(H_2O)_4O_{2aq}{}^{+} + H_3{}^+O_{aq} \tag{6}$$

with eqn. (6) the most important equilibrium at moderate acidities[6], while for aquovanadium(III), with an acid-dissociation constant $K_h = 7.1 \times 10^{-4}$ at 25°C and ionic strength 3 M, equilibrium (1) is sufficient to describe the situation except at very low acid concentrations[7].

Having developed the idea that acid dissociation is an important part of our understanding of chemical reactions in aqueous solution, we must make two further points clear before proceeding. These are concerned in general terms with the interpretation of equilibrium constants themselves for equilibria as in eqns. (1) or (2). The first point to be made is that, as in any reaction involving ionic species, a changing ionic environment will shift the position of the equilibrium (1) through specific solvation, outer-sphere complex formation and other effects, as reflected by changes in activity coefficients[1,4,6]. Perchlorate media, in which the complexing tendency of the anion is apparently small, are generally employed in contemporary investigations of inorganic reactions[1]. Perchloric acid itself has been shown by Raman measurements[8] to be fully dissociated up to concentrations near 6 M, and this observation allows the operational definition $(HClO_4) = [H^+]$ to be applied in the constant ionic medium.

In principle, there are two solutions to the problem of variations in activity coefficients: one is to work near infinite dilution, where molar and molal activity coefficients both approach unity, and the other is to choose a constant ionic medium in which the activity coefficients are essentially constant, despite shifts in the position of the equilibrium involving the dilute species of interest. In order to derive equilibrium constants at infinite dilution we must obtain data at relatively low metal ion and acid concentrations in order to make a reliable extrapolation to $\mu = 0$. Aside from the general difficulty of working at low concentrations, there is the possibility that extensive hydrolysis and even precipitation may occur at low acidities. Examples from the chemistries of aqueous manganese(III) and cobalt(III) species serve to illustrate the impracticability of this procedure.

The manganese(III) ion Mn_{aq}^{3+} is a relatively strong acid (eqn. (1)) in aqueous solution ($K_h \sim 1$ at 25°C and ionic strength 4 M)[9]: attempts to reduce the acidity below ($HClO_4$) ≈ 0.1 M result in the rapid formation of suspended material followed by precipitation; reducing the manganese(II) concentration at constant (low) acidity also results in turbidity followed by precipitation[9]. These effects are connected with (1) further hydrolysis of $MnOH_{aq}^{2+}$ (through reactions as in eqns. (4)—(6)), and (2) the disproportionation equilibrium[9,10]

$$2Mn(III)_{aq} \rightleftharpoons Mn(II)_{aq} + Mn(IV)_{aq} \qquad (7)$$

with manganese(IV) even more strongly hydrolyzed[10] than manganese(III). The precipitates which are formed are presumably hydrated manganese(III)—manganese(IV) oxides[9—11]. Even in the absence of precipitation, other systems show well-defined polymer formation (e.g. $Fe(OH)_2Fe_{aq}^{4+}$ (ref. 12) and $Cr(OH)_2Cr_{aq}^{4+}$ (ref. 13) at low acidities, particularly in labile systems at relatively high metal concentrations.

The cobalt(III)—cobalt(II) couple in perchlorate media is strongly oxidizing[14], and the rate of oxidation of solvent water is measurable even at acid concentrations of 3 M. Moreover, the rate increases as the inverse square of the acidity[15], and becomes extremely rapid at acidities in the region of $10^{-3}\,M$. This precludes kinetic measurements at low acid concentrations.

The constant ionic medium principle has been used for many years in the study of the equilibria and kinetics of inorganic reactions. Usually, relatively concentrated perchlorate solutions are used to maintain a constant ionic strength: the possibility of perchlorate complex formation, especially with cations[4,16], and indications that this situation does not, in fact, result in even approximately constant activity coefficients[4] are omnipresent in these studies. However, there is no practical alternative especially if we wish to restrict hydrolysis to reactions as in eqn. (1) or in eqns. (4)—(6) for cations in high oxidation states. For weak acids the activity coefficients do approach unity at high ionic strength[17] and it seems that the best compromise to the situation is to ensure that all the equilibria involved in a reaction are, if possible, studied in the same ionic environment as are used for kinetic studies.

C. KINETIC CONSIDERATIONS

The presence of species which are related by acid—base equilibria makes itself felt in the variations of the rates of reactions as the acid concentration is varied. Superimposed on the "real" kinetic effects are changes in activity coefficients which occur, say, on replacing sodium or lithium perchlorate by perchloric acid at constant ionic strength[15,18]. The environmental requirements of any activated complexes formed in a chemical reaction cannot be accurately predicted from a knowledge of the properties of the separate reactants because of an absence of any direct structural evidence (except the stoichiometry) and our lack of knowledge of the structural features of the environment itself, and so we must be very careful indeed in making any predictions concerning the enthalpy, entropy and volume of activation for a given reaction. Again, the only sensible approach seems to be to compare the effects of acidity on a group of reactions which involve one common species with a series of similar reactants in the same reaction environment. An example from transition metal chemistry will again serve to illustrate our point about the mechanistic implications of acid dissociation.

A typical case of studies of the effect of concentration variables on rates is found in the rate law for aquocobalt(III) oxidation reactions in perchloric acid solution: in the aquocobalt(III) oxidation of hydrogen peroxide[19] the empirical rate law is, within rather narrow limits of experimental error,

$$\frac{-\mathrm{d}[\mathrm{Co^{III}}]}{\mathrm{d}t} = \left(a + \frac{b}{[\mathrm{H^+}]}\right)[\mathrm{Co^{III}}]_\mathrm{T}[\mathrm{H_2O_2}]_\mathrm{T} \tag{8}$$

Here a and b are constants at constant temperature and ionic strength and subscript T represents total stoichiometric concentration. This type of rate law is very common in reactions of aquocobalt(III) species[15]. A possible mechanism for the reaction with hydrogen peroxide is as follows.

$$\mathrm{Co_{aq}}^{3+} \rightleftharpoons \mathrm{CoOH_{aq}}^{2+} + \mathrm{H_{aq}}^{+} \quad K_\mathrm{h} \tag{9}$$

$$\mathrm{Co_{aq}}^{3+} + \mathrm{H_2O_2} \xrightarrow{k_0} \mathrm{Co^{II}} + \text{other products} \tag{10}$$

$$\mathrm{CoOH_{aq}}^{2+} + \mathrm{H_2O_2} \xrightarrow{k_{-1}} \mathrm{Co^{II}} + \text{other products} \tag{11}$$

$$\mathrm{Co^{III}}_\mathrm{aq} + \text{other products} \xrightarrow{\text{fast}} \mathrm{Co^{II}} + \mathrm{O_2} \tag{12}$$

Here the subscript "aq" indicates that the complex is part of the solvent structure (i.e. is "aquated") and "other products" indicates that we do not definitely know the immediate products of the rate-determining steps (10) and (11). Strictly speaking, we have no kinetic evidence that cobalt(II), as either $\mathrm{Co_{aq}}^{2+}$ or $\mathrm{CoOH_{aq}}^{+}$ (both in their ground state?) is formed as a primary product in this reaction, since increases of the concentration of cobalt(II) up to the point where it can no longer be ignored as part of the general solution environment have no detectable effect on the observed rate[19]. "Other products" presumably include radical species (perhaps $\mathrm{H_2O_2}^{+\bullet}$ in this example)[20], since cobalt(III) is a one-electron oxidant and hydrogen peroxide needs to lose two electrons in order to be converted to oxygen.

$$\mathrm{Co^{III}}_\mathrm{aq} + \mathrm{e} \rightleftharpoons \mathrm{Co^{II}}_\mathrm{aq} \tag{13}$$

$$\mathrm{H_2O_2} \rightleftharpoons \mathrm{O_2} + 2\mathrm{H^+} + 2\mathrm{e} \tag{14}$$

In this non-complementary redox process, step (12), involving the reaction between aquocobalt(III) complexes and highly reactive "other products", is assumed to be at least ten times faster than in either eqn. (10) or eqn. (11). The assumption is also made that the hydrolysis equilibrium (9) is rapid[2] and that any other acid—base equilibria involving peroxide species are likewise too fast to be concerned in the rate-determining steps.

We can derive the rate law for this mechanism in a very straightforward manner.

(a) Stoichiometric concentrations of reactants.

$$[\mathrm{Co^{III}}]_T = \mathrm{Co_{aq}}^{3+} + \mathrm{CoOH_{aq}}^{2+} \tag{15}$$

$$K_h = \frac{[\mathrm{CoOH_{aq}}^{2+}][\mathrm{H_{aq}}^+]}{[\mathrm{Co_{aq}}^{3+}]} \tag{16}$$

Therefore

$$[\mathrm{Co^{III}}]_T = [\mathrm{Co_{aq}}^{3+}]\ (1 + K_h/[\mathrm{H}^+]_{aq}) \tag{17}$$

$$\mathrm{H_3O_{2\,aq}}^+ \rightleftharpoons \mathrm{H_2O_2} + \mathrm{H_{aq}}^+ \quad K_{1a} \tag{18}$$

$$\mathrm{H_2O_{2\,aq}} \rightleftharpoons \mathrm{HO_{2\,aq}}^- + \mathrm{H_{aq}}^+ \quad K_{2a} \tag{19}$$

$$[\mathrm{H_2O_2}]_T = \mathrm{H_3O_{2\,aq}}^+ + \mathrm{H_2O_{2\,aq}} + \mathrm{HO_{2\,aq}}^- \tag{20}$$

$$K_{1a} = \frac{[\mathrm{H_2O_2}][\mathrm{H_{aq}}^+]}{[\mathrm{H_3O_{2\,aq}}^+]} \approx 10^3\ M \qquad \text{(ref. 21)} \tag{21}$$

$$K_{2a} = \frac{[\mathrm{HO_{2\,aq}}^-][\mathrm{H_{aq}}^+]}{[\mathrm{H_2O_{2\,aq}}]} \approx 2 \times 10^{-12}\ M \qquad \text{(ref. 21)} \tag{22}$$

Therefore

$$[\mathrm{H_2O_2}]_T = [\mathrm{H_2O_{2\,aq}}]([\mathrm{H_{aq}}^+]/K_{1a} + 1 + K_{2a}/[\mathrm{H_{aq}}^+]) \tag{23}$$

(b) Rate law. The observed rate law is

$$\frac{-\mathrm{d}[\mathrm{Co^{III}}]_T}{\mathrm{d}t} = k_{\mathrm{obsd}}\,[\mathrm{Co^{III}}]_T[\mathrm{H_2O_2}]_T \tag{24}$$

Here k_{obsd} is the acid-dependent second-order rate constant for the reaction (cf. eqn. (8)). If we are going to admit to the existence of the species $\mathrm{HO_{2\,aq}}^-$ and $\mathrm{H_3O_{2\,aq}}^+$ in these solutions, then we must also consider possible rate-determining steps involving these species

$$\mathrm{Co_{aq}}^{3+} + \mathrm{H_3O_{2\,aq}}^+ \xrightarrow{k_2} \text{products} \tag{25}$$

$$\mathrm{CoOH_{aq}}^{2+} + \mathrm{H_3O_{2\,aq}}^{+} \xrightarrow{k_{-2}} \text{products} \tag{26}$$

$$\mathrm{Co_{aq}}^{3+} + \mathrm{HO_{2\,aq}}^{-} \xrightarrow{k_3} \text{products} \tag{27}$$

$$\mathrm{CoOH_{aq}}^{2+} + \mathrm{HO_{2\,aq}}^{-} \xrightarrow{k_{-3}} \text{products} \tag{28}$$

The rate law for the mechanism consisting of steps (9)—(12) and (25)—(28) has the form of eqn. (24) with

$$\tfrac{1}{2}\, k_{\mathrm{obsd}} = \frac{k_2[\mathrm{H_{aq}}^+]/K_{1\mathrm{a}} + [k_{-2}K_\mathrm{h}/K_{1\mathrm{a}} + k_0] + [k_{-1}K_\mathrm{h} + k_3K_{2\mathrm{a}}]/[\mathrm{H_{aq}}^+] + k_{-3}K_{2\mathrm{a}}K_\mathrm{h}/[\mathrm{H_{aq}^+}]^2}{(1 + K_\mathrm{h}/[\mathrm{H_{aq}}^+])\,([\mathrm{H_{aq}}^+]/K_{1\mathrm{a}} + 1 + K_{2\mathrm{a}}/[\mathrm{H_{aq}}^+])} \tag{29}$$

The stoichiometric factor 1/2 comes from the non-complementarity of the reaction. Note the grouping of the rate terms in the numerator: this is the result of the kinetic indistinguishability of pairs of reactions such as in eqns. (10)—(26), which are linked by fast acid—base equilibria (for this pair of reactions the relevant equilibria are eqns. (9) and (18)).

We now have the task of approaching the empirical rate law (eqn. (8)) from consideration of the individual terms of this complicated expression. It must be borne in mind that the observed rate law is the simplest expression which is consistent with the concentration dependences over the experimental range, taking account of experimental error in the rate determinations themselves.

Let us first consider the terms in the denominator of eqn. (29). Remembering that, in the example chosen, we are considering perchloric acid concentrations in the range[19] 0.05—3.00 *M*, we may first of all put $K_{2\mathrm{a}}/[\mathrm{H_{aq}}^+] \ll 1$ (see eqn. (22)). After expansion, with neglect of this term, the denominator of eqn. (29) becomes

$$1 + K_\mathrm{h}/K_{1\mathrm{a}} + K_\mathrm{h}/[\mathrm{H_{aq}}^+] + [\mathrm{H_{aq}}^+]/K_{1\mathrm{a}} \tag{30}$$

which has two acid-dependent terms and two terms which will tend to cancel each other as the acidity is varied. Under appropriate conditions the full form of eqn. (29) can be observed experimentally[22].

Let us now consider the numerator of eqn. (29), which is really the *kinetic* part of the argument. In this particular example the equilibrium constant for reaction (19) is such that, in the experimental acidity range[19], reactions (27) and (28) would have to be faster than the diffusion-controlled limit of about 10^{10}—10^{11} M^{-1} s^{-1} in order to contribute appreciably to the observed reaction[2,23]. They can clearly be eliminated from consideration on this basis. Equation (29) now has the form

$$\tfrac{1}{2}\, k_{\mathrm{obsd}} = \frac{k_2[\mathrm{H_{aq}}^+]/K_{1\mathrm{a}} + [k_{-2}K_\mathrm{h}/K_{1\mathrm{a}} + k_0] + k_{-1}K_\mathrm{h}/[\mathrm{H_{aq}}^+]}{1 + K_\mathrm{h}/K_{1\mathrm{a}} + K_\mathrm{h}/[\mathrm{H_{aq}}^+] + [\mathrm{H_{aq}}^+]/K_{1\mathrm{a}}} \tag{31}$$

Note that, depending on the relative magnitudes of k_2/K_{1a} and $k_{-1}K_h$, the first and last terms of the numerator of eqn. (31) will tend to cancel each other as the acid concentration is varied. That we are not justified in treating eqns. (8) and (31) as identities is shown by the result that $bK_h \equiv 0$ if this is the case; clearly, b in eqn. (8) is experimentally non-zero, and therefore K_h must be very small for this identity to be valid*. Data for other trivalent metal ions suggest that K_h is[6,15,19,24] 10^{-2}—10^{-4} M. The identity $a = k_2$ also follows from such an identity argument, but if the first identity is accepted then the identity $b \equiv (k_{-2}K_h + k_0K_{1a})$—$k_2(K_h + K_{1a})$ follows, and the kinetic indistinguishability of reaction pairs (10)—(26) is demonstrated. The identification of eqns. (8) and (31) is not valid simply because eqn. (8) is empirical and eqn. (31) is exact. Clearly, if none of the equilibrium constants is known, then the empirical rate parameters cannot be separated and realistically assigned.

A more fruitful approach is to consider the relative magnitude of the terms in the rate law after substitution of known values of the equilibrium constants. In the example under discussion, K_{1a} is believed to be of the order of[21] 10^3 M, although $H_3O_{2\,aq}{}^+$ certainly cannot be regarded as a well-established entity. Substitution of this value for K_{1a} in eqn. (31) under the experimental conditions gives the rate law

$$\tfrac{1}{2}k_{obsd} = \frac{k_2[H^+_{aq}]K_{1a} + [k_{-2}K_h/K_{1a} + k_0] + k_{-1}K_h/[H^+_{aq}]}{1 + K_h/[H^+_{aq}]} \tag{32}$$

K_h for $Co_{aq}{}^{3+}$ cannot be measured directly because of the difficulties with solvent oxidation mentioned above, but in order to approach the empirical rate law (8) we have to make the assumption that $K_h/[H^+_{aq}] \ll 1$. This gives $K_h \ll 5 \times 10^{-3}$ M under the experimental conditions[15,19]. Note that the altenative assumption that $K_h/[H^+] \gg 1$ gives a rate law of the form

$$k_{obsd} = a'[H^+_{aq}]^2 + b'[H^+_{aq}] + c' \tag{33}$$

where a', b' and c' are constants, which is clearly incompatible with eqn. (8). It also follows from the above argument that the term $k_2[H^+_{aq}]/K_{1a}$ may be neglected under the experimental conditions.

So, by using equilibrium information, we have come to the conclusion that

$$a = k_0 + k_{-2}K_h/K_{1a} \tag{34}$$

$$b = k_{-1}K_h/[H^+_{aq}]$$

It is at this point that the value of considering a range of kinetic data for reactions of a particular metallic aquo complex becomes apparent. As it happens, the observed rate constants for complexation and redox reactions of aquocobalt(III) species with a number of non-metallic species, including

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* This is not a trivial point since quantities of the order of 10^{-6} (e.g. in K_h/K_{1a}) are involved in eqn. (31).

hydrogen peroxide, fall into a narrow range which indicates that the activation process for either center essentially consists of a dissociative interchange reaction[1], with water loss at the cobalt(III) center as the rate-determining step[15]. In particular, the rate constants for negatively charged ligands such as SCN^-, Br^- and $HC_2O_4^-$ are the largest of the group[15]. Now, if the second term in the expression for a were significant we would require that $k_{-2} \approx 10^5 k_0$, and this likelihood seems extremely remote if the reaction with $H_3O_{2aq}^+$ is also substitution-controlled. On this basis, we can put $a = k_0$.

Note that the identification of a constant K_h or its upper limit does not identify the species of cobalt(III) actually present, i.e. they could be any species AH/A^- linked by a proton equilibrium (35)

$$AH_{aq} \rightleftharpoons A_{aq}^- + H_{aq}^+, K_h \qquad (35)$$

However, it seems likely from a consideration of values for other metal-ion acid-dissociation constants[3,5,6,24] that equilibrium (9) connects the two species involved in the reaction. We have also illustrated the fallibility of treating an empirical rate law as an identity based on a supposed mechanism for a solution-phase reaction.

The analysis of rate laws of this type for series of relatively slow reactions of aquoiron(III) and aquocobalt(III) species has led to the conclusion that an inner-sphere OH^- ligand greatly increases the rates of complexation and redox reactions of these ions. The effect seems smaller for manganese(III)[5a] and silver(II)[16,25] reactions, although these more labile systems may well react through different mechanisms.

D. SPECIAL FACTORS CONCERNING COORDINATED HYDROXIDE LIGANDS IN INORGANIC REACTIONS

The identification of the origin of kinetic and thermodynamic variations with changing acidity in terms of shifts in the proportions of those aquometal species which are present as hydroxoaquocations is obviously a prerequisite to any detailed understanding of the role of OH^- in catalyzing both complexation and redox reactions of these complexes. The particular character of the OH^- ligand itself and its unique relationship to its aqueous environment would seem to be very important factors in determining the nature and magnitude of such effects.

Replacement of a water molecule with an OH^- ligand at a metal center often has a dramatic effect on the rate of substitution of X^- as in eqn. (2). For example, the similar effects of decreasing acidity on the rates of formation of halo complexes of iron(III)[1,4] and cobalt(III)[15] are well documented, and the effect is still quite dramatic even when there are other ligands besides water in the inner coordination of the metal. As an illustration, recent work[26] in our laboratory on the kinetics of the reaction

$$cis\text{-}Co(NH_3)_2(H_2O)_{4\,aq}{}^{3+} + X_{aq}{}^{-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co(NH_3)_2(H_2O)_3X_{aq}{}^{2+} \tag{36}$$

where X is Cl or Br, has revealed an empirical rate law, at constant temperature, of the form

$$\frac{d\ln[\text{complex}]}{dt} = \frac{A\,[X^-]}{[H^+]} + \frac{B}{[H^+]} \tag{37}$$

which is significant in that only terms which have an *inverse* acid dependence are found within rather narrow limits of experimental error. This indicates that hydroxo complexes are the reactive species in both the formation and the dissociation reactions.

$$(NH_3)_2Co(H_2O)_3OH_{aq}{}^{2+} + X_{aq}{}^{-} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} (NH_3)_2Co(H_2O)_2OHX_{aq}{}^{+} \tag{38}$$

the empirical parameters being given by

$$A = K_h k_f \tag{39}$$

and

$$B = k_d K_a \tag{40}$$

where K_h is the acid-dissociation constant of $cis\text{-}Co(NH_3)_2(H_2O)_{4\,aq}{}^{3+}$ and K_a is the corresponding parameter for the monohalo complex. Independent spectral evidence indicates that a proton is lost by the amminetetraaquocobalt(III) complex at $pH \sim 2.5$, although the system is complicated by a tendency towards dimerization (μ-hydroxobridge formation) in all but very dilute solutions at $pH \sim 3$, as evidenced by a substantial increase in absorbance in the 300—350 nm region[27].

It is worth while considering in general terms how the OH^- ligand might influence the making and breaking of bonds at a metal coordination center.

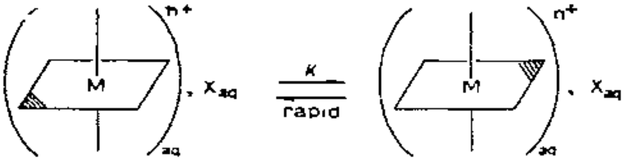
Spectral evidence, together with both observed kinetic and thermodynamic effects suggest that monodentate OH^- is a much more effective π donor or acceptor than is[5,15,28] H_2O, and the marked spectral changes which often occur at lower acidities at moderate or high metal concentrations are consistent with dimer or polymer formation in which any π character at a transition metal center is extended through space. In several systems, notably those of cobalt(III)[29], stoichiometric complexes can be isolated and high extinction coefficients can be assigned to these bridging hydroxyl groups. Thus, aside from its formal mononegative charge, the hydroxo ligand can, by π donation, further reduce the effective nuclear charge at the metal center. If this is the case, the net effect is a weakening of the bonds to the other ligands. There is, however, another particular effect which is important for hydroxoaquometal complexes, namely that, through proton transfer (perhaps involving the solvent itself), the hydroxo ligand can be produced at any aquo-coordinated site on the metal.

This means that, for a hydroxopentaaquo complex, the influence of the OH^- ligand could be regarded as resulting in an averaged coordination sphere (with effective spherical symmetry) provided that rotation of the species in the solvent is slower than is distributive proton transfer (see below).

One of the essential prerequisites to both substitution or redox reactions at metal centers is the existence of a precursor complex[30,31], usually thought of as some kind of solvent-separated ion aggregate.

$$M_{aq}{}^{n+} + X_{aq} \overset{\text{rapid}}{\rightleftharpoons} M_{aq}{}^{n+}, X_{aq} \tag{41}$$

In a dissociative interchange substitution process the rate-determining step is the collapse of this ion aggregate into a bona fide inner-sphere complex by the breaking of a bond between the metal center and a coordinated water molecule[1,4]. If the metal carries a hydroxo ligand and the ion aggregate has any one structure of lowest energy, then the nature of the incoming ligand will influence the relative position of the OH^- species in the ion aggregate

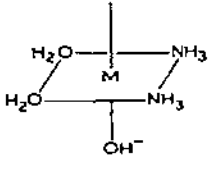


(42)

Two extreme situations are shown, the one on the left perhaps being more characteristic of an ion aggregate formed between a metal ion and a species with an excess of electrons (e.g. a halide ion), and the other being more reasonable for an ion aggregate of two electron-deficient species (e.g. two positively charged metal complexes). In the former case the π character of the OH^- ligand is relatively localized in the dimension which is *trans*- to the inner-sphere site closest to X in the ion aggregate and perhaps leads to preferential substitution at this site. The primary product of such a reaction, or even perhaps the transition state, would then contain the incoming anion and the hydroxo ligand at the maximum possible separation in the inner coordination sphere. (The possibility that the OH^- ligand is ever physically "lost" to the bulk solvent in the reaction of a hydroxo complex seems slight.)

It is worth while considering how these effects might be manifested in substitution reactions at aquometal centers which also carry non-aquo ligands such as the *cis*-diammineaquocobalt(III) species mentioned earlier.

If OH^- exerts a stronger *trans*-influence than does H_2O, and the ammonia molecules cannot be substituted in moderately acidic solution (as in undoubtedly the case[26]), then the following primary product of the reaction would be predicted where X is a halide ion. Cobalt(III) systems (π^6 ground state)



(43)

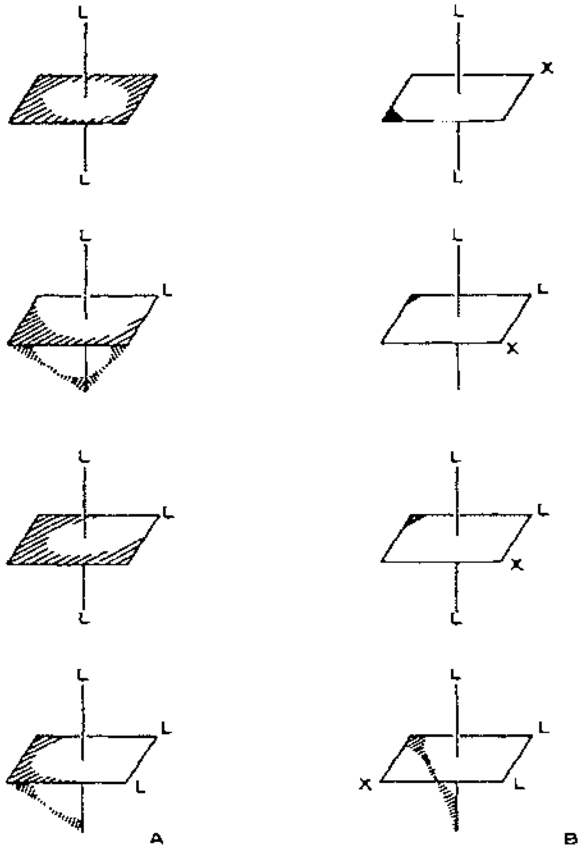


Fig. 1. A: aquo complex reactant. B: predicted primary monocomplex product from base-catalyzed path.

are likely candidates for manifestation of this *trans* influence of OH^-[1,32]. If it were possible to isolate and quantitate the isomeric products of substitution reactions of these lower amminoaquometal(III) systems, we would have a means of testing this distribution hypothesis, provided that isomerization were slow. The predictions are shown in Fig. 1, with possible coordination sites of OH^- shown shaded in the reactant and with the predicted OH^- coordination in the primary product indicated as in eqn. (42). It should be noted that only *cis*- and *mer*-substituted complexes would be suitable for any predictive distinction to be made on the basis of the distribution hypothesis. Any subsequent isomerization would negate the analysis, and coordinated groups L from multidentate ligands might help to eliminate this possibility[29b].

There has been remarkably little work on the substitution reactions of these lower aquoamminecobalt(III) complexes; studies of the isomeric distribution of triaquoamminehalocobalt(III) products $Co(NH_3)_2(H_2O)_3X^{2+}$ are hampered experimentally by their high solubility[26]. However, the aquotriamminecobalt(III) isomers seem much more likely to provide a test of this distribution—π-donation hypothesis in view of their lower solubility, and we would value such investigations. There is definite evidence for the influence of π character in determining the course of substitution reactions of other cobalt(III) systems, for example in systems involving coordinated thiourea[32] and carbonate ligands[33]; in general, π-donating ligands seem to increase substitutional lability[32,33].

These speculations place the onus for influencing the distribution of the OH^- ligand on the other reactant partner in the ion aggregate. Toppen and Linck[18c] and other workers agree that, in most systems which have been studied to date, the OH^- ligand appears to be a much better bridging ligand than is water in inner-sphere redox reactions. According to the above picture of the distributive character of OH^-, the observed catalytic effect of OH^- in promoting electron transfer must include, at least in part, a term which accounts for the influence of the other reactant in determining the fraction of the ion-aggregate precursors which have the OH^- ligand in the optimum configuration for bridge formation (right-hand side of eqn. (42)). We shall now attempt to estimate these distribution terms for aquocobalt(III) systems.

Recent work[15,26,34] indicates that the fastest reactions of aquocobalt(III) are base-catalyzed[15], appear to involve ion-aggregate precursors and also approach a limiting rate when the driving force becomes very large[31]. The limiting rate constant appears to be of the order of 2×10^6 s^{-1} for the species[31] $CoOH_{aq}{}^{2+}$. A possible mechanism to account for these effects is as follows.

$$CoOH_{aq}{}^{2+} + X \underset{}{\overset{\text{rapid}}{\rightleftharpoons}} [CoOH_{aq}{}^{2+},X]_{aq} \quad K_0 \tag{44}$$

$$\underset{A}{[CoOH_{aq}{}^{2+},X]_{aq}} \rightleftharpoons \underset{A^*}{[CoOH_{aq}{}^{2+},X]_{aq}{}^*} \quad K \tag{45}$$

$$\underset{A^*}{[CoOH^{2+},X]_{aq}{}^*} \xrightarrow{k_{\text{lim}}} \text{products} \tag{46}$$

Here A is a general description of the ion aggregate, A^* represents the configuration for optimum distribution of the OH^- ligand for bridging the two reactants in the activated complex for electron transfer and k_{lim} is the rate constant for electron transfer. According to this model the observed (second-order) rate constant for the reaction is given by

$$k_{\text{obsd}} = K_0 K k_{\text{lim}} \tag{47}$$

Since $CoOH_{aq}{}^{2+}$ is an extremely strongly oxidizing metal center[15,31], it seems likely, that electron transfer under optimum conditions would be very rapid* and so variations in the observed rate constants for these rapid reac-

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* This limiting behavior has been attributed to rate-determining thermal spin-crossover between the $^1A_{1g}$ and $^5T_{2g}$ states of aquocobalt(III)[31].

TABLE 1

Distribution parameters for $CoOH_{aq}^{2+}$ redox precursors [a]

Reductant	K	$10^{-11}\nu_{dist}$ (s^{-1})
Fe_{aq}^{2+} [b]	60	1
H_2Q [c]	0.8	50
I^- [d]	0.14	130

[a] The experimental data are from ref. 15, assuming $K_h = 2 \times 10^{-3}$ *M*.
[b] $k_{obsd} = 1.9 \times 10^5\ M^{-1}\ s^{-1}$, $K_0(\text{calc}) = 1.6 \times 10^{-3}\ M^{-1}$.
[c] $k_{obsd} = 6.4 \times 10^5\ M^{-1}\ s^{-1}$, $K_0(\text{calc}) = 0.4\ M^{-1}$.
[d] $k_{obsd} = 1.4 \times 10^6\ M^{-1}\ s^{-1}$, $K_0(\text{calc}) = 5\ M^{-1}$.

tions might primarily be determined by the magnitudes of K_0 (eqn. (41)) and of K (eqn. (42)). Although calculated values of K_0 are undoubtedly very crude[31], values of K may be obtained from the literature data[15] through eqn. 47 (Table 1).

It should be emphasized again that these estimates of the distribution constant are based on extremely crude spherical models for the ion-aggregate precursors[31], but, nevertheless, it is worth while examining their *relative orders of magnitude*. If X were H_2O, K would, of course, be unity, and it is perhaps fortuitous that the value for the formally neutral hydroquinone reactant (H_2Q) is close to this value. The calculated value for Fe_{aq}^{2+} corresponds to the situation where 98.5% of the ion aggregate is in the optimum configuration for bridged electron transfer, while the corresponding estimate for I_{aq}^- is 12.5%. According to the model, with its severe restriction that the actual electron-transfer act, within these three precursors, proceeds at much the same rate for all three reductants, the origin of the observed[15] sevenfold increase in going from Fe_{aq}^{2+} to I_{aq}^- as reductants for $CoOH_{aq}^{2+}$ is attributed to a compromise between the 3000-fold *increase* in the ion-association constant K_0 and a 400-fold *decrease* in the distribution coefficient K*. At the risk of carrying the analysis to imaginary limits, we can calculate the frequency of configurational change within the distribution manifold (third column of Table 1) from the Boltzmann equation

$$\nu_{dist} = \frac{-2.303kT}{h} \log_{10} \frac{K}{1+K} \tag{48}$$

The results are in the range 10^{11}—10^{13} s^{-1}, which is of the same order as thermal relaxation times in solution[35]. It should be pointed out that these estimates refer to proton distribution within the inner coordination sphere

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* The decrease in rate constant in going from I_{aq}^- to Fe_{aq}^{2+} as reductants is *opposite* to that expected theoretically for an increase in the driving force of ~ 10 kcal mol^{-1} (refs. 1, 31).

of the hydroxo complex and *not* to transfer of a proton from the inner coordination sphere to the bulk solvent, which is expected to be much slower. Thus, for the equilibria

$$(\mathrm{M(H_2O)_6})_{\mathrm{aq}}{}^{3+}, \mathrm{H_2O} \underset{k_\mathrm{p}}{\overset{k_\mathrm{h}}{\rightleftharpoons}} (\mathrm{M(H_2O)_5OH})_{\mathrm{aq}}{}^{2+}, \mathrm{H_3O^+} \tag{49}$$

$$(\mathrm{M(H_2O)_5OH})_{\mathrm{aq}}{}^{2+}, \mathrm{H_3{}^+O} + \mathrm{H_2O_{aq}} \underset{k_{-h}}{\overset{k_\mathrm{p}}{\rightleftharpoons}} (\mathrm{M(H_2O)_5OH})_{\mathrm{aq}}{}^{2+}, \mathrm{H_2O} + \mathrm{H_3O^+_{aq}} \tag{50}$$

we have, in a typical case

$$K_\mathrm{h} = \frac{k_\mathrm{h}}{k_{-h}} \approx 10^{-3}\,M \tag{50}$$

and with $k_{-\mathrm{h}} \approx 1 \times 10^9\ M^{-1}\ \mathrm{s}^{-1}$ (diffusion-controlled)^2 we obtain $k_\mathrm{h} = K_\mathrm{h}k_{-\mathrm{h}} \approx 2 \times 10^6\ \mathrm{s}^{-1}$, since k_p is likely to be very large (it corresponds to very rapid proton transfer within the bulk solvent[35]). This value for k_h is similar to estimates for thermal-spin crossover rates in the hexaaquocobalt(III) complex (p. 299) and it may mean that proton transfer to the solvent proceeds preferentially through the high spin ($^5T_{2g}$) electronic configuration.

Despite the approximate nature of the above analysis, particularly with regard to estimates of precursor stability constants from crude spherical models, the results are encouraging in that they illustrate that ligand distribution in an extremely labile inner-sphere metal ion environment is a factor which should be taken into account, particularly in systems with a tendency to limiting behavior where a bridging mechanism for electron transfer is suggested by the relative magnitude of the parameters in the empirical rate law.

E. CONCLUSIONS

The mechanistic assignment of the acid dependence in the empirical rate law for the oxidation of hydrogen peroxide by aquocobalt(III) species in aqueous perchlorate media has been reviewed. The situation is less clear-cut when separate equilibrium data are *inferred* (see, for example, ref. 36), or where parallel mechanisms with similar rate parameters have to be assumed in series of reactions which involve acid indistinguishability[23]. The analysis is also beset by uncertainties of the extent of apparent kinetic dependencies caused by medium effects and some authors prefer not to carry kinetic analysis to the stage where single rate-determining or subsequent steps are postulated, but instead report only the rate law in terms of its empirical parameters (e.g. eqn. (8); see, for example, ref. 18b). This approach is certainly realistic, but it does leave the possibility of inferences regarding mechanism to be made when sufficient data on a series of reactions of a common reactant in a specific constant ionic medium have been accumulated[15,31].

The particular characteristics of coordinated hydroxide which lead to marked catalysis of complexation and redox reactions at metal centers in aqueous solution have been described, and the concept of inner-sphere hydroxyl distribution has been introduced; tentative conclusions about the influence of reductant partners in ion-aggregate precursors have been considered, based on approximate models for precursors involved in observations of apparent limiting behavior in reductions of hydroxoaquocobalt(III) systems by $\mathrm{Fe_{aq}}^{2+}$, hydroquinone and $\mathrm{I_{aq}}^{-}$; an optimum configuration for hydroxo-bridged electron transfer in the rate-determining step was assumed.

Although attempts to obtain detailed mechanisms for the reactions of hydroxo complexes will always be limited by the accuracy with which ion aggregation can be described, we hope that this work will encourage further consideration of the interesting effects caused by changing acidity of the medium in inorganic and biochemical systems.

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