Coordination Chemistry Reviews, 14 (1974) 269—285
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A PHENOMENOLOGICAL MODEL FOR REDOX REACTIONS IN SOLUTION APPLICATION TO AQUOCOBALT(III) SYSTEMS

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(Received April 8th, 1974)

CONTENTS

A. INTRODUCTION

Two broad categories of reaction mechanism have emerged from studies of redox reactions of metal complexes over the last twenty years. Reactions of inert complexes proceed via outer-sphere mechanisms, and theoretical models[1] have been applied with some success in these systems[2]. However, it has become apparent that most reactions of the transition metal ions involved in homogeneous enzymic catalysis[3], transport phenomena[3] and autoxidation processes[4] involve an inner-sphere process, in which the electron-transfer act occurs during the existence of some metal—substrate complex.

The development of good models for inner-sphere electron transfer seems a worthwhile goal, since, as is often pointed out[5], the use of model systems to simulate real biochemical processes often fails if the environment of the metal center in the two situations is radically different. In addition, some investigators[6] have noted the same types of free energy relationships in inner-sphere reactions as are predicted theoretically for outer-sphere processes[1,2]. This suggests that similar activation processes are required for electron transfer in the two types of mechanism, and that, at least in some cases, a general sort of mechanism might apply. The question of the development of general theories of mechanism for redox reactions is certainly of interest. Should we continue to study models in the hope of simulating highly specific catalytic systems, or

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might the most detailed possible decription of a given system be all that should realistically be hoped for? Perhaps the best approach would be to try to complement general quantitative theories of electron transfer with more qualitative (phenomenological) mechanisms having recognizable limits[7]. Endicott's recent work[8] has shown that in cobalt(III) systems, which have proved so valuable in providing the foundations of the field of inorganic reaction mechanism, the quantitative theories are inadequate even for redox reactions with a moderate overall free energy change[1,9]. Any phenomenological model is surely speculative, but it does offer the possibility of using complete kinetic data (activation parameters) rather than rate constants alone.

An inner-sphere mechanism requires the formation of a complex between the reactants prior to electron transfer

$$\mathrm{MX} + \mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{MXB} \quad K_1 \tag{1}$$

$$\mathrm{MXB} \xrightarrow{k_2} \text{products} \tag{2}$$

Here MX is a metal complex, B is the other reactant and X serves as a bridging group between the reaction partners in MXB. Evidence for an inner-sphere mechanism may take one of several forms, depending on the reaction type.

(1) When MX is inert, B is labile, and the product B′ (the oxidized or reduced form of B, a metal atom) is inert, then the incorporation of X into B′, i.e. a reaction product B′X which can analytically be characterized, constitutes proof of an inner-sphere mechanism[10]. Studies of reactions of inert cobalt(III) complexes L_5CoX^{n+} with labile reducing agents such as Cr^{2+}_{aq} have enabled assessment of the roles of different groups L and X in influencing the rate of electron transfer between metal centers[6,11]; in other cases, inner-sphere products which are moderately labile have been *kinetically* characterized[12].

(2) If M is a metal aquo-ion, i.e. contains at least one labile water molecule, then B may provide the bridging group or B may be directly linked to the metal center. These latter cases are obviously much more likely for non-metallic co-ordination at M in an inner-sphere mechanism[13]. Evidence for the involvement of a metal complex MB in such a system is usually obtained in reactions where it is sufficiently stable to allow deviations from simple reaction orders to occur, as in the familiar Michaelis—Menten kinetics of enzymatic reactions[3].

$$\text{rate} = \frac{k_2 K_1 [\mathrm{M}][\mathrm{B}]}{1 + K_1 [\mathrm{B}]} \tag{3}$$

This situation arises when step (1) is at equilibrium while step (2) is rate-determining. Although this type of rate law does not prove that reaction proceeds through such a complex[14], it is almost invariably taken to do so, based on the idea that electron transfer between the reactants is more likely within such a complex than between the separated reactants. This is a troublesome point, since strong coordination of metal centers often *decreases* their thermodynamic tendency to electron transfer[15].

In other cases, fast spectral changes accompany mixing of the reactants[16] and these sometimes allow confirmatory estimates of the equilibrium constant K_1 to be made.

Another line of evidence which is receiving increasing attention is the analysis of experimental activation parameters. In reactions involving a moderate or small overall free energy change there is usually a substantial enthalpy of activation ($\Delta H^{\ddagger}_{\text{obsd}}$ = 10—30 kcal mole^{-1}). Now

$$\Delta H^{\ddagger}_{\text{obsd}} = \Delta H^{\ddagger}_{\text{kin}} + \Delta H_1 \tag{4}$$

where $\Delta H^{\ddagger}_{\text{kin}}$ refers to the electron-transfer act and ΔH_1 is the enthalpy change in reaction (1). If $\Delta H^{\ddagger}_{\text{obsd}}$ is small or negative, then this is good evidence of discrete complex formation between the reactants in the overall reaction mechanism[17].

The high efficiency of enzymatic systems involving transition metal ions is often ascribed to some unusual "ground-state" stereochemistry at the metal center or its easy attainment in the catalytic mileu[3,5]. Thus, such centers may be much more active redox centers than are common coordination complexes of a particular element. Under some circumstances a single step may be rate-determining in the catalytic system, and for an inner-sphere mechanism this may be the setting up of equilibrium (1) or the electron-transfer act (2).

These possibilities may be explored analytically if the inner-sphere complex MXB is in a steady state [MXB]. If d[MXB]/dt = 0, then[13]

$$[\text{MXB}] = k_1k_2[\text{M}][\text{B}]/(k_{-1} + k_2) \tag{5}$$

and

$$k_{\text{obsd}} = k_1k_2/(k_{-1} + k_2) \tag{6}$$

Activation parameters for such systems are composite, and plots of log k_{obsd} vs. $1/T$ may be found to be non-linear over wide temperature ranges. Equation (6) suggests the consideration of two limits.

(i) $k_2 \ll k_{-1}$

and

$$k_{\text{obsd}} = K_1k_2 \tag{7}$$

which corresponds to rate-limiting electron-transfer (step (2)), the usual situation in most inner-sphere model systems. If

(ii) $k_2 \gg k_{-1}$ we have

$$k_{\text{obsd}} = k_1 \tag{8}$$

corresponding to rate-determining complex formation (step (1), forward). If this complex formation mechanism is dissociative, then the rates of electron-transfer will be largely determined by the identity of the metal center[13]. In other cases where the metal center is more labile, the rate constants will reflect a larger dependence on the nature of the other reactant[18], and such limits will be much harder to recognize.

There is one final point before we go on to consider this type of analysis in more detail. This concerns the involvement of solvent-separated precursors[19] in both complexation and redox processes. Step (1) of the above scheme can be broken down further

$$\mathrm{MX + B} \overset{\mathit{fast}}{\rightleftharpoons} \mathrm{(MX, B)} \quad K_0 \tag{9}$$

$$\mathrm{(MX, B)} \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}} \mathrm{MXB} \quad K'_1 \tag{10}$$

The measured equilibrium constant is actually $K_1 = K_0K'_1$, and the measured rate of complexation is given by $k_{\mathrm{obsd}} = K_0k'_1$ for limiting case (ii) above[20].

A recognition of the existence of such precursors in solution-phase reactions provides a starting point for the detailed analysis of redox systems where limiting behavior is apparent.

E. A PHENOMENOLOGICAL MECHANISM

(i) Theory

Consider a general mechanism for a solution-phase redox reaction between a solvated metal ion M and a substrate B*.

$$\mathrm{M + B} \rightleftharpoons \mathrm{M, B} \quad K_0\text{, fast} \tag{11}$$

$$\mathrm{M, B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{(M, B)^{\ddagger}} \quad K_1 \tag{12}$$

$$\mathrm{(M, B)^{\ddagger}} \xrightarrow{k_2} \text{products} \tag{13}$$

$$\mathrm{(M, B)^{\ddagger}} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{(M{-}B)^{\ddagger}} \quad K_3 \tag{14}$$

$$\mathrm{(M{-}B)^{\ddagger}} \xrightarrow{k_4} \text{products} \tag{15}$$

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* In this general case the coordination sphere and charge of the metal ion center have been omitted for clarity. Specific examples of interest are ions of the type $\mathrm{M(H_2O)_{6aq}^{3+}}$ and $\mathrm{M(H_2O)_5OH_{aq}^{2+}}$.

The first reaction involves a fast equilibrium between the reactants and a solvent-separated precursor. The existence of such equilibria is amply supported by thermodynamic[21] and kinetic[22] studies, and approximate theoretical models[17,23] (which depend on the formal charges on the reactants) and experimental data[21] are available for the estimation of K_0 and its thermodynamic components.

Reaction (12) involves the activation of the precursor prior to electron transfer. Theoretical models[1,9] for electron transfer associate this activation process with the rearrangement of the coordination spheres of metallic reactants to avoid violation of the Franck-Condon principle in the electron-transfer act[24]. Conversion of the activated complex to products is step (13) of the mechanism.

Steps (11—13) of the scheme are a phenomenological description of an outer-sphere electron-transfer process. If $[(\mathrm{M, B})^{\ddagger}]$ is in a steady state then

$$[(\mathrm{M, B})^{\ddagger}] = \frac{K_0 k_1 [\mathrm{M}][\mathrm{B}]}{k_{-1} + k_2} \tag{16}$$

and

$$\frac{\mathrm{d}[\text{products}]}{\mathrm{d}t} = \frac{K_0 k_1 k_2 [\mathrm{M}][\mathrm{B}]}{k_{-1} + k_2} = k_{\text{obsd}}[\mathrm{M}][\mathrm{B}] \tag{17}$$

where

$$k_{\text{obsd}} = \frac{K_0 k_1 k_2}{k_{-1} + k_2} \tag{18}$$

Under the conditions where eqn. (18) applies the rate constant and its activation parameters are evidently composite. However, two limiting cases of eqn. (18) are of interest.

(i) if $k_{-1} \gg k_2$, then step (12) is at equilibrium so that

$$k_{\text{obsd}} = K_0 K_1 k_2 \tag{19}$$

and the rate-determining step is the electron-transfer act within the activated complex (step (13)). One may expect under these circumstances that the reaction rate will be influenced by ΔG_0, the overall free energy change of the reaction, which is related to the ease with which M and B can accept or release electrons[1,6].

(ii) if $k_{-1} \ll k_2$, then

$$k_{\text{obsd}} = K_0 k_1 \tag{20}$$

and the rate-determining step is now the activation process, step (12). The overall free energy change of the reaction presumably will have to be comparatively large and negative to allow limit (ii) to be realized[8,25]. Thus, in studies involving a given metal center and a range of substrates B, the rate constant is

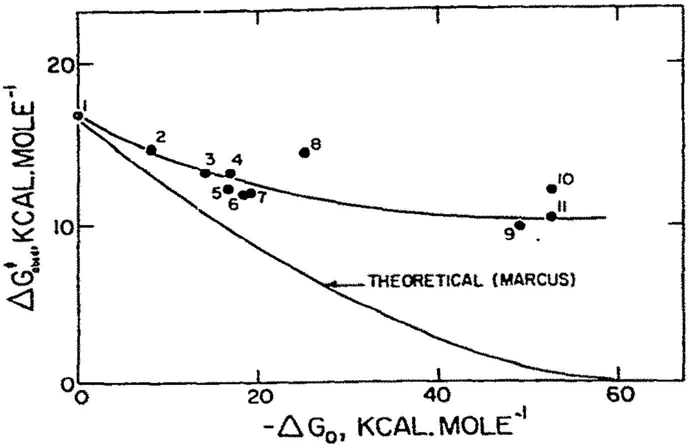

Fig. 1. Variation of $\Delta G^{\ddagger}_{\text{obsd}}$ with ΔG_0 for outer-sphere cobalt(III). Reactions: Data for $\text{Co}^{3+}_{\text{aq}}$. Reductants are as follows: 1, $\text{Co}^{2+}_{\text{aq}}$; 2, $\text{Mn}^{2+}_{\text{aq}}$; 3, tris(5-nitro 1, 10-phenanthroline)-iron(II); 4, Hydroquinone; 5, tris(5-chloro 1,10-phenanthroline)iron(II); 6, tris(1,10-phenanthroline)iron(II); 7, tris(5-methyl 1,10-phenanthroline)iron(II); 8, $\text{Fe}^{2+}_{\text{aq}}$; 9, $\text{V}^{2+}_{\text{aq}}$; 10, $\text{Cr}^{2+}_{\text{aq}}$; 11, $\text{Eu}^{2+}_{\text{aq}}$(est.). Data are from refs. 13 and 39.

expected to increase as the free energy change becomes more negative, ranging from conditions where eqn. (19) applies (ΔG_0 small) through the general case eqn. (17) and finally toward the situation represented by eqn. (20). However, smooth trends in free energy correlations will only be recognizable if k_1 and K_1 are approximately constant, implying that *activation of the metal center* M is the major factor in step (12)[8,25]. Equation (20) thus represents a "limiting" outer-sphere mechanism, which will prevent outer-sphere processes from becoming diffusion-controlled as the driving force for electron transfer increases.

Figure 1 illustrates data for a number of outer-sphere electron-transfer reactions of the strongly oxidizing $\text{Co}^{3+}_{\text{aq}}$ complex[13,25]. It is evident that the observed free-energy of activation, $\Delta G^{\ddagger}_{\text{obsd}}$, at first decreases as the overall free-energy change becomes more negative; however, when the free energy change is extremely negative the measured free energies of activation are essentially invariant, and some kind of "limiting" behavior seems to be indicated.

The Marcus relationship[1,2]*

$$\Delta G^{\ddagger}_{\text{obsd}} = \tfrac{1}{2}\,(\Delta G^{\ddagger}_{11} + \Delta G^{\ddagger}_{22}) + \tfrac{1}{2}\,\Delta G_0 + (\Delta G_0)^2/8(\Delta G^{\ddagger}_{11} + \Delta G^{\ddagger}_{22}) \qquad (21)$$

has previously been applied to outer-sphere reactions with a small or moderate

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[*] For example, $\Delta G^{\ddagger}_{\text{obsd}}$ would be the (observed) free energy of activation for the reaction $\text{Co}^{3+}_{\text{aq}} + \text{Fe}^{2+}_{\text{aq}} \rightarrow \text{Co}^{2+}_{\text{aq}} + \text{Fe}^{3+}_{\text{aq}}$, and $\Delta G^{\ddagger}_{11}$ and $\Delta G^{\ddagger}_{22}$ would be the (measured) free energies of activation for the processes $\text{Co}^{3+}_{\text{aq}} + \text{Co}^{2+}_{\text{aq}} \rightarrow \text{Co}^{2+}_{\text{aq}} + \text{Co}^{3+}_{\text{aq}}$ and $\text{Fe}^{3+}_{\text{aq}} + \text{Fe}^{2+}_{\text{aq}} \rightarrow \text{Fe}^{2+}_{\text{aq}} + \text{Fe}^{3+}_{\text{aq}}$, respectively.

overall free-energy change where the last term can justifiably be neglected. Under these circumstances a plot of $\Delta G^{\ddagger}_{\mathrm{obsd}}$ vs. ΔG_0 for reactions of a common oxidant with a series of similar reactants is a straight line of slope 0.5. This equation is derived from a harmonic oscillator model and higher order terms have been neglected. The factor ½ amounts to the assumption that the electron is "half-way" between the two metal centers in the transition state of the redox reaction, which is only reasonable for an electron exchange reaction involving identical nuclei, e.g., $Co^{3+} + Co^{2+} \rightarrow$ products, with $\Delta G_o = 0$. The lower line drawn in Fig. 1 is a plot of eqn. (21) for these Co^{3+}_{aq} reactions, and predicts that the free energy of activation will approach zero at $\Delta G_0 \approx -60$ kcal mole^{-1}, which is clearly not the case. It is worthwhile to consider possible reasons for this discrepancy.

The first point which should be made is that the rigorous application of eqn. (21) demands that free energies of activation should be corrected for the amount of work necessary to bring reactants and products together in the transition state[1]. However, theoretical and experimental considerations[1c] suggest that these terms are not altogether responsible for the non-zero values of $\Delta G^{\ddagger}_{\mathrm{obsd}}$ at very negative ΔG_0. In addition, the fastest reactions of Co^{3+}_{aq} are still orders of magnitude slower than the diffusion-controlled limit, indicating that some specific energy requirements obtain even under very extreme reaction conditions.

Recent work by Rosseinsky[9] suggests the application of a more general, but essentially empirical, form of eqn. (21), namely

$$\Delta G^{\ddagger}_{\mathrm{obsd}} = (1-\alpha)\,\Delta G^{\ddagger}_{11} + \alpha\Delta G^{\ddagger}_{22} + \alpha\Delta G_0 + (\Delta G_o)^2/16\{(1-\alpha)\Delta G^{\ddagger}_{11} + \alpha\Delta G^{\ddagger}_{22}\} \tag{22}$$

where the "unequal" distribution of the transferring electron in the transition state is accounted for by the term α. Minimization of this function gives

$$\Delta G^{\ddagger}_{\mathrm{obsd}} = (1-4\alpha^2)\{(1-\alpha)\Delta G^{\ddagger}_{11} + \alpha\Delta G^{\ddagger}_{22}) \tag{23}$$

and the experimental curve in Fig. 1 can be fitted to eqn. (22) if a minimum in the experimental curve has actually been reached at $\Delta G_0 = -60$ kcal mole^{-1}. This modified Marcus equation would then account for the data if α were allowed to vary from 0.5 at $\Delta G_0 = 0$ to ca. 0.3 at $\Delta G_0 \approx -60$ kcal mole^{-1}.

A second possible reason for the anomalously high "limiting" value for $\Delta G^{\ddagger}_{\mathrm{obsd}}$ is then as follows. A plot of $\Delta G^{\ddagger}_{\mathrm{obsd}}$ vs. ΔG_0 will only be meaningful if the first two terms of eqn. (22) are essentially constant. In principle, a knowledge of α for a given set of values of $\Delta G^{\ddagger}_{11}$, $\Delta G^{\ddagger}_{22}$ and ΔG_0 would enable a calculation of these two terms to be made and correction to a common intercept could then be applied in a plot of $\Delta G^{\ddagger}_{\mathrm{obsd}}$ vs. ΔG_0 for, say, reactions of a common oxidant with a series of very dissimilar reductants. Rearrangement of eqn. (22) gives a quadratic equation in α whose coefficients are functions of $\Delta G^{\ddagger}_{\mathrm{obsd}}$, $\Delta G^{\ddagger}_{11}$, $\Delta G^{\ddagger}_{22}$ and ΔG_0. The small variation of α observed (vide supra) and the reasonable fit of the data to a single line in Fig. 1 may mean that α depends largely on ΔG_0, although this remains to be proven.

The net result of these considerations is a functional form of the basic Marcus relationship which leads to approximate constancy for the term α at large ΔG_0 and provides an empirical description of the observed variations for outer-sphere reactions at fixed temperature. However, the apparent range of values for α is small enough to suggest considerable difficulty in rationalizing the enthalpic and entropic contributions to the free energy of activation for these outer-sphere processes on this basis alone and it seems worthwhile to explore an alternative approach in analyzing these terms. Consideration of this alternative suggests an approach based on the relationship between the energetic requirements of outer- and inner-sphere limiting mechanisms.

If electron transfer through an outer-sphere activated precursor (step (13)) is slow, then case (ii) applies and the possibility exists for reaction via an *inner-sphere* mechanism. Reaction (12) may be considered to be at equilibrium when $k_{-1} \gg k_2$. Step (14) involves the formation of an inner-sphere, activated complex $(MB)^{\ddagger}$, by loss of a solvent molecule (not shown in eqn. (14) from the inner coordination sphere of $(M, B)^{\ddagger}$. Since $[(M, B)^{\ddagger}]$ was postulated to be in a steady-state concentration, so too will $[(MB)^{\ddagger}]$, whose concentration is given by

$$[(MB)^{\ddagger}] = \frac{K_0 K_1 k_3 k_4 [M][B]}{k_{-3} + k_4} \tag{24}$$

thus

$$k_{obsd} = \frac{K_0 K_1 k_3 k_4}{k_{-3} + k_4} \tag{25}$$

and two limiting cases are again suggested.

(iii) if $k_{-3} \gg k_4$, then step (14) is at equilibrium and

$$k_{obsd} = K_0 K_1 K_3 k_4 \tag{26}$$

Under these conditions electron transfer takes place within an activated, inner-sphere complex $(MB)^{\ddagger}$, as is the case in most labile inner-sphere systems involving a moderate driving force for electron transfer (see page 271).

The final limit suggested by this general scheme is

(iv) $k_{-3} \ll k_4$, in which case

$$k_{obsd} = K_0 K_1 k_3 \tag{27}$$

In this limit the rate of the redox reaction is determined by the rate of formation of the inner-sphere complex, formulated here as $(MB)^{\ddagger}$. The reaction of a particular metal aquo-ion with a range of substrates will thus be comparatively constant if the slowest step in the overall electron-transfer act is solvent exchange at the metal center in $(M, B)^{\ddagger}$. This limit has been termed *substitution control*[26], and has so far been characterized unequivocally for reactions of V^{2+}_{aq} (ref. 26), $CoOH^{2+}_{aq}$ (ref. 13) and Ru^{2+}_{aq} (ref. 27), all of which are ions with a ground-state π-electronic configuration.

The evidence for the assignment of substitution-control in these compara- ively inert systems is two-fold.

(i) The rate constants for redox reactions of these ions with a range of videly different substrates B cover only a small range which appear to be haracteristic of the particular metal ion center M[13,26,27].

(ii) These electron-transfer rate constants are themselves similar to those or substitution of a range of substrates at the metal center in the absence of lectron transfer[13,26,27]. This indicates a dissociative interchange mechanism or both complex formation and substitution-controlled redox processes. In ne case, that for V^{2+}_{aq} reactions, the direct measurement of solvent exchange t the metal center confirms the conclusion that this is the slow step in both ypes of reaction[28].

It is useful at this stage to summarize the predictions of this general mech- nism (Table 1).

ii) Experimental evidence

Now if there are to be any links between the rate parameters for inner- and uter-sphere reactions of a particular metal center[6,7], then the most likely tarting point for establishing them would be at substitution-controlled, nner-sphere processes, since the rates of these reactions appear to be character- stic of the particular metal center concerned. As pointed out earlier, one nterpretation of the trends for outer-sphere reactions of Co^{3+}_{aq} and $CoOH^{2+}_{aq}$ is hat when the driving force for electron-transfer is sufficiently large, then imit (iv) applies, the rate again being characteristic of the metal center M and

ABLE 1

redictions of general mechanism

ssumption	k_{obsd}	$\Delta H^{\ddagger}_{obsd}$	$\Delta S^{\ddagger}_{obsd}$
. Outer-sphere reactions			
teady state in [M, B)$^{+}$]	$\frac{K_0k_1k_2}{k_{-1}+k_2}$	composite	composite
(i) $k_{-1} \gg k_2$	$K_0K_1k_2$	$\Delta H_0+\Delta H_1+\Delta H_2^{\ddagger}$	$\Delta S_0+\Delta S_1+\Delta S_2^{\ddagger}$
(ii) $k_{-1} \ll k_2$	K_0k_1	$\Delta H_0+\Delta H_1^{\ddagger}$	$\Delta S_0+\Delta S_1^{\ddagger}$
. Inner-sphere reactions			
teady state in [MB)$^{+}$]	$\frac{K_0K_1k_3k_4}{k_{-3}+k_4}$	composite	composite
iii) $k_{-3} \gg k_4$	$K_0K_1K_3k_4$	$\Delta H_0+\Delta H_1+\Delta H_3+\Delta H_4^{\ddagger}$	$\Delta S_0+\Delta S_1+\Delta S_3+\Delta S_4^{\ddagger}$
iv) $k_{-3} \ll k_4$	$K_0K_1k_3$	$\Delta H_0+\Delta H_1+\Delta H_3^{\ddagger}$	$\Delta S_0+\Delta S_1+\Delta S_3^{\ddagger}$

largely independent of the activation requirements of the other reactant B. This suggests that the most fruitful comparison would be that between the situations predicted by limits (ii) and (iv)*.

For substitution-controlled and limiting outer-sphere behavior we have respectively

$$(\Delta H^{\ddagger}_{\mathrm{obsd}})^{\mathrm{inner}} = \Delta H_0 + \Delta H_1 + \Delta H^{\ddagger}_3 \tag{28}$$

$$(\Delta S^{\ddagger}_{\mathrm{obsd}})^{\mathrm{inner}} = \Delta S_0 + \Delta S_1 + \Delta S^{\ddagger}_3 \tag{29}$$

$$(\Delta H^{\ddagger}_{\mathrm{obsd}})^{\mathrm{outer}} = \Delta H_0 + \Delta H^{\ddagger}_1 \tag{30}$$

$$(\Delta S^{\ddagger}_{\mathrm{obsd}})^{\mathrm{outer}} = \Delta S_0 + \Delta S^{\ddagger}_1 \tag{31}$$

Equations (28) and (30) predict that plots of $\Delta H^{\ddagger}_{\mathrm{obsd}}$ vs. ΔH_0 will both be linear with unit slope. Although estimates of ΔH_0 from theoretical models are very approximate[17], especially for substrates B which are not even crudely spherical, the values obtained for a series of reactions involving a given metal ion with a range of substrates of different formal charge enable such plots to be attempted. Figure 2 shows these plots for substitution-controlled and outer-sphere reactions of $\mathrm{CoOH}^{2+}_{\mathrm{aq}}$. The corresponding plots for eqns. (29) and (31) are shown in Fig. 3.

Although these plots are very much subject to the inherent experimental errors of the kinetic data and the uncertainty of predicting values of ΔH_0 and ΔS_0 for a given charge product, they do seem to divide the data into two broad reaction groups. It is evident that substitution-controlled reactions have higher enthalpies and entropies of activation than the corresponding outer-sphere processes involving the same formal charge product: this is reasonable, since the discrete bond-breaking required for dissociative substitution is not a feature of outer-sphere reactions, whose rates are faster and depend on the magnitude of the overall free-energy change[13]. It is somewhat surprising to note that the $\mathrm{CoOH}^{2+}_{\mathrm{aq}}/\mathrm{CoOH}^{+}_{\mathrm{aq}}$ exchange reaction is classified as a substitution-controlled redox reaction on the basis of its activation parameters. This emphasizes the point that *limiting behavior* has to be assumed in grouping these reactions, and this is almost certainly not valid for the exchange process. Thus, any tendency away from limiting behavior will lead to composite activation parameters, and, in the limit of rate-determining electron transfer, to greater activation enthalpies and entropies (see Table 1).

It should be pointed out that the actual values plotted in Figs. 2 and 3 are derived from the temperature dependence of $k_{\mathrm{obsd}} = kK_{\mathrm{h}}$, where k is the

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* Note that the identification of apparent limiting behavior depends on the same free-energy relationships as are used in testing more quantitative theory[1,2,6,8].

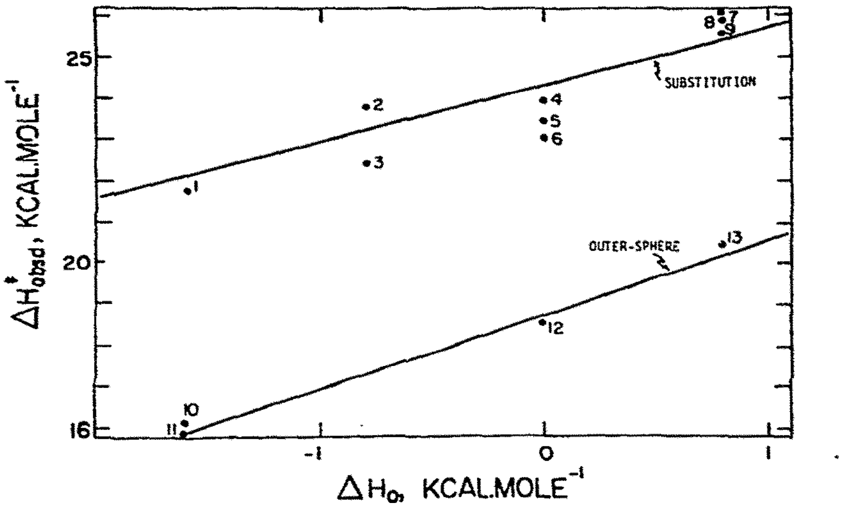

Fig. 2. Plot of $\Delta H^{\ddagger}_{obsd}$ vs. ΔH_0 for reactions of $CoOH^{2+}_{aq}$ at 25° and ionic strength 3 *M*. The reductants are numbered as follows: 1, Co^{2+}_{aq}; 2, $NH_3NH_2^+$; 3, NH_3OH^+; 4, $H_2C_2O_4$; 5, H_2O_2; 6, HN_3, 7, Br^-; 8, $HC_2O_4^-$; 9, SCN^-; 10, Mn^{2+}_{aq}; 11, Fe^{2+}_{aq}; 12, H_2Q; 13, I^-; Data are from ref. 13. (Errors in $\Delta H^{\ddagger}_{obsd}$ and ΔH_0 (not shown for clarity) are of the order of ±0.5 and ±0.3 kcal mole^{-1}, respectively (see refs. 13, 39 and 40).)

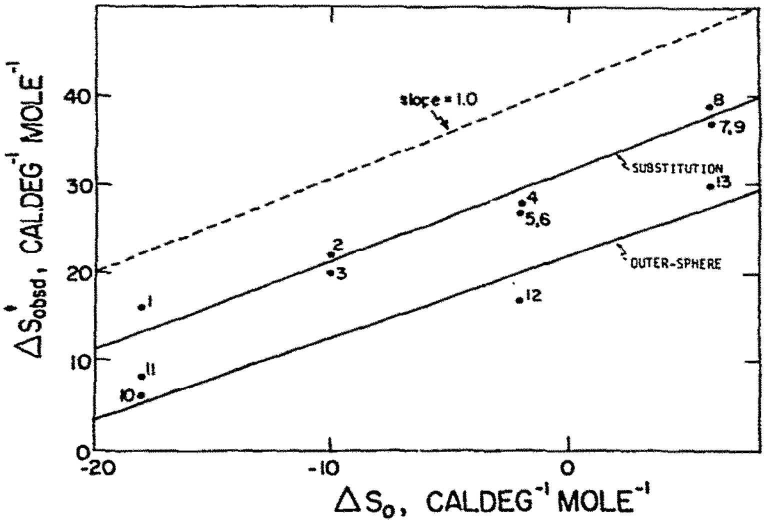

Fig. 3. Plot of $\Delta S^{\ddagger}_{obsd}$ vs. ΔS_0 for reactions of $CoOH^{2+}_{aq}$ at 25° and ionic strength 3 *M*. The reductants are numbered as in Fig. 2. A line of unit slope is shown for comparison. (Errors in $\Delta S^{\ddagger}_{obsd}$ and ΔS_0 (not shown, for clarity) are on the order of ±3 and ±1.5 cal deg^{-1} mole^{-1}, respectively (see refs. 13, 39 and 40).)

second-order rate constant for reaction of $CoOH^{2+}_{aq}$ with the substrate and K_h is the acid-dissociation constant of Co^{3+}_{aq} (ref. 13). Then we have

$$\Delta H^{\ddagger}_{obsd} = \Delta H^{\ddagger}_{kin} + \Delta H_h \tag{32}$$

and

$$\Delta S^{\ddagger}_{obsd} = \Delta S^{\ddagger}_{kin} + \Delta S_h \tag{33}$$

where the kinetic and thermodynamic components have been separated. Unfortunately, there are no accurate values of ΔH_h and ΔS_h available because of experimental difficulties connected with the instability of aquocobalt(III) species, although values of 10 kcal mole^{-1} and 20 cal deg^{-1} mole^{-1}, respectively, seem reasonable estimates[13].

The intercepts at $\Delta H_0 = 0$ in Fig. 2 and $\Delta S_0 = 0$ in Fig. 3 are ~ 19 kcal mole^{-1} and ~ 22 cal deg^{-1} mole^{-1}, respectively, for the outer-sphere reactions. Substitution into eqns. (32) and (33), respectively, gives $\Delta H^{\ddagger}_{kin} = \Delta H^{\ddagger}_1 \approx 9$ kcal mole^{-1} and $\Delta S^{\ddagger}_{kin} = \Delta S^{\ddagger}_1 \approx 2$ cal deg^{-1} mole^{-1} at 25°. This corresponds to a value of $k_1 \approx 4 \times 10^6$ sec^{-1} for $CoOH^{2+}_{aq}$ at 25°. Since k_{-1} is unlikely to be much greater than 10^{11} sec^{-1}, this corresponds to $K_1 \gtrsim 4 \times 10^{-5}$.

According to our analysis the spacings between the roughly parallel lines in Figs. 2 and 3 are given by

$$\Delta\Delta H^{\ddagger}_{obsd} = \Delta H_1 + \Delta H^{\ddagger}_3 - \Delta H^{\ddagger}_1 \tag{34}$$

$$\Delta\Delta S^{\ddagger}_{obsd} = \Delta S_1 + \Delta S^{\ddagger}_3 - \Delta S^{\ddagger}_1 \tag{35}$$

respectively. Since $\Delta H_1 = \Delta H^{\ddagger}_{-1} - \Delta H^{\ddagger}_1$ and $\Delta S_1 = \Delta S^{\ddagger}_1 - \Delta S^{\ddagger}_{-1}$ then $\Delta H^{\ddagger}_3 - \Delta H^{\ddagger}_{-1} \approx 6$ kcal mole^{-1} and $\Delta S^{\ddagger}_3 - \Delta S^{\ddagger}_{-1} \approx 11$ cal deg^{-1} mole^{-1} at 25° for these reactions of $CoOH^{2+}_{aq}$. The relationship between the requirements for outer-spin electron transfer (step (12) and substitution (step (14) is seen to be retained in these final expressions through the involvement of $\Delta H^{\ddagger}_{-1}$ and $\Delta S^{\ddagger}_{-1}$.

It is worthwhile speculating on the magnitude of $\Delta H^{\ddagger}_3$ and $\Delta S^{\ddagger}_3$, since such estimates would allow determination of ΔH_1 and ΔS_1 through the above relationships. Co^{2+}_{aq} and $FeOH^{2+}_{aq}$ are possible models for high-spin $CoOH^{2+}_{aq}$ since they both have two antibonding electrons. It is interesting to note that the observed enthalpies of activation for substitution by neutral ligands are in the region of 10—12 kcal mole^{-1} for both complexes[20b]. The corresponding entropies of activation are about —3 cal deg^{-1} mole^{-1}, and so values of $\Delta H^{\ddagger}_3 =$ 11 kcal mole^{-1} and $\Delta S^{\ddagger}_3 = 0$ may be approximated, leading to $\Delta H^{\ddagger}_{-1} \approx 5$ kcal mole^{-1} and $\Delta S^{\ddagger}_{-1} \approx -10$ cal deg^{-1} mole^{-1}. We may thus estimate that $\Delta H_1 = 4$ kcal mole^{-1} and $\Delta S^{\ddagger}_1 = 12$ cal deg^{-1} mole^{-1} at 25°. However, these values would predict that aquocobalt(III) complexes would be high-spin under normal conditions, which is contrary to observation[13]. Indeed, the lack of experimental evidence for any high-spin aquocobalt(III) species suggests that ΔG_1 is at least 4 kcal mole^{-1}, which might be explained if ΔS_1 is close to zero. It is unfortunate that so many assumptions concerning the values for ΔH_h, ΔS_h, $\Delta H_3^\ddagger$ and $\Delta S_3^\ddagger$ have to be made to arrive at an estimate of ΔG_1. However, it is interesting to note that if $\Delta H_{-1}^\ddagger$ and $\Delta S_{-1}^\ddagger$ are both close to zero, then, with the same assumptions for ΔH_h and ΔS_h, $\Delta H_1 \approx 9$ kcal mole^{-1} and $\Delta S_1 \approx 2$ cal deg^{-1} mole^{-1}, corresponding to $K_1 \approx 10^{-6}$; a more negative value of $\Delta S_{-1}^\ddagger$ would tend to make K_1 larger.

The Franck-Condon principle[24] requires that the coordination sphere of a metal ion which is accepting an electron from the substrate be expanded in the transition state. This also is required in a rate-determining dissociative interchange mechanism[20] for complex formation and so the identification of $(M, B)^\ddagger$ as the common intermediate for outer-sphere electron transfer and substitution is not so artificial as might first appear. Since $[(M, B)^\ddagger]$ is postulated to be in a steady state, then K_1 must be small. A better description of the activation process (12) might be

$$(M, B) \rightleftharpoons (M^*, B) \qquad K_s \tag{36}$$

$$(M^*, B) \rightleftharpoons (M^*, B)^\ddagger \quad K_{tr} \tag{37}$$

in which eqn. (36) now represents a thermal equilibrium between different spin states of the metal center and eqn. (37) describes the activation of the other spin state (M^*, B) for electron-transfer or substitution. Then $K_1 = K_s K_{tr}$ and

$$\Delta H_1 = \Delta H_s + \Delta H_{tr} \tag{38}$$

$$\Delta S_1 = \Delta S_s + \Delta S_{tr} \tag{39}$$

Thus the establishment of any limiting outer-sphere behavior (Fig. 1) still requires that net activation of the metal center be rate-determining. Since eqn. (36) may, to a first approximation, be considered to represent a thermal equilibrium whose extent is largely unaffected by the presence of B in the solvent-separated precursor complex, we are identifying this limit with the rate at which the thermal equilibrium is set up in the forward direction. If this limit is genuine then the rate constant derived above from eqns. (30) and (31) refers to this process.

Only two high-spin cobalt(III) complexes with simple monodentate ligands, viz. CoF_6^{3-} and $Co(H_2O)_3F_3$, are known[29]. The spectrochemical series predicts that the ligand field strengths of H_2O and OH^- are such that the aquocobalt(III) complexes may well be close to the spin crossover point from low to high spin[29]. A range of simple salts containing the $Co(H_2O)_6^{3+}$ unit is extremely difficult to obtain because of their high solubility and high oxidation potential (they oxidize water)[13]. Any high-spin form of Co_{aq}^{3+} will not only be more strongly oxidizing than the low-spin form but will also be considerably more labile because of increased electron density in the antibonding ϵ_g^* orbitals[25]. This may be the origin of the 10^7-fold increase in ligand exchange rate in the series $Co(NH_3)_6^{3+} - Co(H_2O)_6^{3+}$ (ref. 30).

Thermal spin equilibria with small equilibrium constants ($K_s \approx 10^{-5}$) are not detectable by bulk magnetic susceptibility measurements[31] or by emf measurements[32] but may, in principle, be determined quantitatively from the electronic spectrum.

A transition from the low-spin ($^1A_{1g}$) to high-spin ($^5T_{2g}$) states must involve an increase in metal-ligand bond distances since the population of the ϵ_g^* orbitals is thereby increased. Wherland and Gray[33] have recently made allowance for this "non-vertical" transition in their analysis of the spectrum of $CsCo(SO_4)_2.12H_2O$ by taking the Racah parameters 10 Dq, B and C from the electronic spectrum of the (low-spin) cobalt complex and assuming that the corresponding parameters for the high-spin form are identical to those of $Fe(H_2O)_6^{3+}$. This choice of model is reasonable, since, like the high-spin cobalt(III) species, $Fe(H_2O)_6^{3+}$ has two ϵ_g^* electrons. The value of the promotion energy is then obtained from the strong field diagonal element $E = 2(10Dq)-5B-8C$.

Although the choice of a realistic model for the high-spin form is crucial to these calculations[33], especially with respect to the Racah parameter C, and the expression for E is greatly simplified, the calculated values for the transition energy (0—13 kcal mole) are substantially smaller than those obtained by Johnson and Sharp[34] (15—20 kcal mole^{-1}, with no allowance for changes in metal—ligand distances). Wherland and Gray[33] have also calculated a spin-change activation energy of 13.4 kcal mole^{-1} for the $Co(NH_3)_6^{3+}/Co(NH_3)_6^{2+}$ electron-exchange reaction, which is more than 10 kcal mole^{-1} lower than that estimated by Stynes and Ibers[35] for the same system: this suggests that a thermal spin equilibrium is a realistic basis for explaining the origin of the kinetic effects noted earlier in the reactions of the pair $Co(H_2O)^{3+}_{6\,aq}/Co(H_2O)_5OH^{2+}_{aq}$.

As pointed out earlier, substitution control has only been firmly established for reactions $V^{2+}_{aq}(t^3_{2g})$, $Ru^{2+}_{aq}(t^6_{2g})$ (both of which are reducing ions) and for $CoOH^{2+}_{aq}(t^6_{2g})$, which is strongly oxidizing[13]. Limiting outer-sphere behavior is suggested by analysis of published data for the fastest redox reactions of V^{2+}_{aq} (ref. 36) and by the trends in rate constants for outer-sphere reactions of Co^{3+}_{aq} and $CoOH^{2+}_{aq}$; very few fast outer-sphere reactions of Ru^{2+}_{aq} have been studied so the establishment of limiting outer-sphere is an open question in this case. In addition, there is an indication of some kind of limiting behavior in reactions of $MnOH^{2+}_{aq}$, and although the rate constants for complexation by HF are similar to those for electron transfer in these faster reactions, indicating substitution control[15], the evidence is meager, particularly in the absence of accurate activation parameter data which would allow the application of analyses such as those suggested above.

Again, in the absence of any substantially quantitative theory, there is no simple correlation of electronic configuration (e.g. $Co^{3+}_{aq}(t^6_{2g})$ and $Mn^{3+}_{aq}(t^3_{2g}\epsilon_g)$) with the appearance of substitution control, although the final products in these two cases, $Co^{2+}_{aq}(t^5_{2g}\epsilon^2_g)$ and $Mn^{2+}_{aq}(t^3_2\epsilon^2_g)$ both have extra electrons in ϵ^*_g (antibonding) orbitals of σ-symmetry. The only obvious requirement would seem to be a moderate-to-large driving force for electron transfer coupled with a moderate or slow rate of inner-sphere solvent exchange[37].

Two considerations limit the applicability of any general mechanism for electron transfer. First, there is a general lack of experimental activation parameter data, which appears from the above discussion to be useful for analytical purposes, at least for cases where the reactants are sufficiently structureless to allow the calculation of K_0 and its thermodynamic components, as appears to be approximately true for reactions of aquocobalt(III) ions. The second difficulty is in rationalizing the application of the mechanism to both electron gain and loss at metal centers, for in the latter case activation for oxidation formally requires a contraction of the coordination sphere (Franck-Condon principle) while dissociative substitution formally requires a weakening of metal—ligand bonding as the solvent molecule is lost from the first coordination sphere. The model's predictions should perhaps first be investigated for reactions involving reduction of a metal center. It is for this reason that we would value further studies of complexation and oxidation reactions involving metal ions with a redox potentials for the couple

$$M^{3+} + e \rightleftharpoons M^{2+}$$

of the order of 1.4 V or greater, since the systems which exhibit substitution-control are evidently of this type. Recent evidence from studies of oxidation reactions of strongly oxidizing Np(VII) species, where narrow ranges of rate constants are also noted[38], might be explicable in terms of the nature of the overlap of potential energy surfaces[2,39], but the explanation in these terms is based on free energy considerations and no analysis of activation enthalpies and entropies has been put forward.

C. SUMMARY

The application of a phenomenological model which appears to link limiting cases of inner- and outer-sphere mechanisms has been investigated for aquocobalt(III) redox reactions, and the requirements for the interpretation of the apparent limits have been explored. Although the mechanism is speculative and relies on the existence of steady-state conditions without the necessity of distinct limits, it does offer the advantage of a classification of reaction series in terms of their activation parameters rather than in terms of their free-energy changes alone.

D. ACKNOWLEDGMENTS

We are very grateful to the Research Corporation and Imperial Chemical Industries, Limited, for supporting this work, and to several of our colleagues for very valuable discussions. We would particularly like to thank Drs. A.G.

Sykes and R.S. Taylor for contributing to the early work in this area (ref. 36) and Mr. Scott Wherland and Professor Harry Gray for providing details of their spectral analyses prior to publication.

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