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Ligand Interchange Controls Many Oxidations of Divalent First-Row Transition Metal Ions by Free Radicals

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Introduction

The intimate mechanism of reaction of divalent transition metal ions and complexes with aliphatic free radicals to produce unstable intermediates with metal–carbon σ bonds is of interest due to the role of such reactions in catalytic and biological systems. In these reactions the metal–carbon σ bond formation is formally accompanied by oxidation of the metal center and reduction of the radical as shown in (1). In order to optimize our mechanistic

$$M^{(n)} + {}^{\bullet}R \rightarrow (M^{(n+1)}\text{–}R) \qquad (1)$$

insight, we combined high-pressure and pulse-radiolysis techniques to obtain volumes of activation for such complex formation reactions.[2–4] Such data coupled to the construction of reaction volume profiles can significantly assist the elucidation of the underlying mechanism.[4–7] In the investigated systems, bond formation of Co(II) and Ni(II) complexes with $^{\bullet}CH_3$ to produce intermediate species with metal–carbon σ bonds was characterized by small positive $\Delta V^{\ddagger}$ values and interpreted in terms of an I_d type substitution mechanism.[2,3] Similar reactions of aquated Cr(II) ions with a series of 10 different aliphatic radicals[4] exhibited an average $\Delta V^{\ddagger}$ value of $+4.3 \pm 1.0$ cm^3 mol^{-1}, which was again taken as evidence for an I_d mechanism. The values of the volumes of activation of these reactions are similar to those reported for ligand exchange reactions of these complexes.[5–7]

In analogy it was found that also for the reaction

$$M^{(n)} + CH_3O_2^{\bullet} \rightarrow (M^{(n+1)}\text{–}O_2CH_3) \qquad (2)$$

where $M^{(n)}$ = Co(II) and Ni(II) complexes, the rate-determining step involves an I_d ligand exchange step.[2,3] The results even indicate that the rate-determining step of the oxidation of Cu_{aq}^{2+} by hydroxyl radicals is the ligand exchange of an aquo ligand by the oxidizing free radical.[8]

These studies suggest that the rate-determining step in the oxidation of a large variety of transition metal complexes by free radicals is the ligand exchange step. In other words it is proposed that free radicals behave in many reactions with transition metal complexes as incoming nucleophilic ligands. It seemed of interest to investigate this speculative statement in more detail. It was decided therefore to study the interaction of various Mn(II), Fe(II), and Co(II) complexes with a variety of free radicals. These ions were selected as it was shown that Mn(II) ligand exchange processes proceed usually via the I_a mechanism, whereas those of Fe(II) and Co(II) proceed usually via the I_d mechanism. The selected reactions are such that they were all suggested to proceed via the inner-sphere mechanism as their rates of reaction are nearly independent of the nature of the free radical[9] and can therefore be considered as typical complex formation reactions as shown in (3). The pressure dependence of the studied reactions

$$M^{(n)}(L)H_2O + {}^{\bullet}R \rightarrow (M^{(n+1)}(L)\text{–}R) + H_2O \qquad (3)$$

enables a detailed comparison with the volumes of activation for solvent exchange and complex formation reactions of these divalent first-row transition elements. Furthermore, it allows us to comment on the general behavior of free radicals during complex formation reactions with different metal centers.

Experimental Section

The sample preparation and the pulse-radiolysis experiments were carried out exactly as described earlier in detail.[10] Solutions of Fe(II) complexes which are air sensitive were prepared as follows: A solution containing all the required solutes, but the iron salt, was deaerated in a syringe by bubbling N_2O for 15 min. Then, while the solution was bubbling, the solid iron salt was added and the pH adjusted by adding deaerated NaOH or $HClO_4$ as required. The electrode of the pH meter was immersed in the solution during this procedure.

The high-pressure setup was identical to that described elsewhere in detail.[11] The window of the high-pressure cell through which the radiation penetrates the cell was however replaced by a thin-walled stainless steel window with a special design.[12] The internal pillbox-cell was placed immediately near the window so that the high-energy electrons will have a minimal path through the surrounding water medium. All experiments were performed at room temperature.

Preparation of Free Radicals. The radiolysis of water can be summed up by the following equation:[13]

$$H_2O \xrightarrow{\gamma,e^-} e_{aq}^- \,(2.65),\ {}^{\bullet}OH\,(2.65),\ H^{\bullet}\,(0.60),\ H_2\,(0.45),\ H_2O_2\,(0.75) \qquad (4)$$

The values in parentheses represent the relative yields of the different products.[13] In concentrated solutions the yield of the radical products is usually somewhat larger and that of the molecular products somewhat lower.[13]

In N_2O-saturated solutions, where $[N_2O] = 0.022$ mol dm^{-3}, the hydrated electrons are transformed into hydroxyl free radicals via reaction 5. $X_2^{\bullet-}$ free radicals, X = Br or SCN, are formed via reactions 6 and 7.

$$e_{aq}^- + N_2O \xrightarrow{H_3O^+} {}^{\bullet}OH + N_2 \qquad k_5 = 8.7 \times 10^9\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}\ {}^{14} \qquad (5)$$

$$X^- + {}^{\bullet}OH \rightarrow X^{\bullet} + OH^- \qquad k_6 > 2 \times 10^9\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}\ {}^{14} \qquad (6)$$

$$X^{\bullet} + X^- \rightarrow X_2^{\bullet-} \qquad k_7 > 2 \times 10^9\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}\ {}^{14} \qquad (7)$$

Methyl free radicals are formed via reactions 8 and 9. $CO_2^{\bullet-}$ free radicals are formed via reaction 10.

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$$^{\bullet}OH + (CH_3)_2SO \rightarrow (CH_3)_2\dot{S}OOH \qquad k_8 = 7.0 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}\ ^{15} \quad (8)$$

$$(CH_3)_2\dot{S}OOH \rightarrow {}^{\bullet}CH_3 + CH_3SOOH \qquad k_9 = 1.5 \times 10^7\ s^{-1}\ ^{15} \quad (9)$$

$$^{\bullet}OH + HCO_2^- \rightarrow CO_2^{\bullet-} \qquad k_{10} = 7.0 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}\ ^{14} \quad (10)$$

The concentration of the transition metal complex has to be low enough so that its reaction with the hydrated electron will not compete with reaction 5. The concentrations of the selected ligands were chosen so that complete complexation, >98%, of the M_{aq}^{n+} ion by them will be assured. The concentration of the reagent expected to react with the hydroxyl free radicals in reactions 6, 8, and 10 was chosen so that it will ensure that the free ligand and its complex will not be attacked by the hydroxyl free radicals.

Results and Discussion

Detailed kinetic studies of solvent exchange and complex formation reactions of divalent first-row transition metal ions clearly indicate a changeover in mechanism in going along the series V^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+}.[6,7] The earlier members of the series with the larger ionic radii, V^{2+} and Mn^{2+}, undergo substitution according to an I_a mechanism, whereas the later members of the series with the smaller ionic radii, Fe^{2+} to Ni^{2+}, follow an I_d mechanism. The size of the central metal ion, as well as the crowding caused by solvent or other bulky ligands, controls the nature of the ligand interchange process, which can either be more associative, I_a, or more dissociative, I_d, in nature.[6,7] These substitution mechanisms are characterized by small negative or small positive volumes of activation, respectively. The crucial changeover in mechanism occurs between Fe^{2+} and Mn^{2+} independent of whether solvent exchange or complex formation reactions are studied. Therefore, in the present study, selected typical reactions of Mn(II), Fe(II), and Co(II) complexes with a series of free radicals, *viz.* $^{\bullet}CH_3$, $CO_2^{\bullet-}$, $Br_2^{\bullet-}$, and $(SCN)_2^{\bullet-}$, were studied in order to be able to compare the kinetic parameters of these reactions with those found for ligand exchange reactions by normal nucleophiles.

The reactions of a series of free radicals with transition metal complexes, which have all been suggested to proceed via the inner-sphere mechanism,[9] were studied. The results obtained in this study are summarized in Table 1 along with those available from literature data. The reactions of aquated Mn(II) and Fe(II) with $Br_2^{\bullet-}$ exhibit small negative and positive volumes of activation, respectively, in line with the general changeover in mechanism observed for ligand exchange processes.[6,7] Water exchange reactions on Mn(II) and Fe(II) are characterized by $\Delta V^{\ddagger}$ values of −5.4 and +3.8 $cm^3\ mol^{-1}$, respectively, whereas complex formation reactions with 2,2′:6′,2″-terpyridine exhibit values of −3.4 and +3.6 $cm^3\ mol^{-1}$, respectively.[7] These data were interpreted as evidence for the operation of I_a and I_d substitution mechanisms, respectively. Our value for the reaction of Fe(II) with $Br_2^{\bullet-}$ is in close agreement with the solvent exchange and complex formation data and underlines the operation of an I_d mechanism in which bond breakage with the leaving water molecule accounts for the small positive $\Delta V^{\ddagger}$ value. The data for the reaction of Mn(II) with $Br_2^{\bullet-}$ are significantly more positive than for the exchange of coordinated water on Mn(II), but the overall value is still slightly negative in line with an I_a mechanism. Since the $Br_2^{\bullet-}$ radical carries a negative charge, bond formation in terms of an I_a mechanism will be accompanied by partial charge neutralization, which will result in a decrease in solvent electrostriction *i.e.* a small increase in volume which might offset partially the negative contribution arising from bond formation. Thus the two reactions studied in the absence of a chelating ligand result in $\Delta V^{\ddagger}$ values that correspond very well with the changeover in mechanism found for substitution by various nucleophiles.

Table 1. Summary of $\Delta V^{\ddagger}$ Data for Reactions of the Type

$$(L)M^{(n)}(H_2O) + {}^{\bullet}R \xrightarrow{k} (L)M^{(n+1)}\text{–}R + H_2O$$

M	L	$^{\bullet}R$	k (20 °C), $M^{-1}\ s^{-1}$	$\Delta V^{\ddagger}$, $cm^3\ mol^{-1}$ [a]
Co^{II}	NTA[c]	$^{\bullet}CH_3$	4×10^7	+6.0[b]
		$^{\bullet}O_2CH_3$	1×10^8	+6.0[b]
		$Br_2^{\bullet-}$	1×10^8	+3.4
		$(SCN)_2^{\bullet-}$	1×10^8	+2.4
Fe^{II}	H_2O	$Br_2^{\bullet-}$	4×10^6	+2.6
	NTA[c]		1×10^8	−0.4
	metaphosphate[d]		3×10^6	+0.25
	ATP[e]		$\sim 5 \times 10^6$	+0.7
	HEDTA[f]		1×10^8	−2.9
	EDTA[g]		1×10^8	−4.2
	NTA[c]	$^{\bullet}CH_3$	1×10^7	−0.3
		$^{\bullet}CO_2^-$	2×10^7	−1.3
		$(SCN)_2^{\bullet-}$	1×10^8	−1.8
Mn^{II}	H_2O	$Br_2^{\bullet-}$	1×10^7	−0.9
	NTA[c]	$Br_2^{\bullet-}$	2×10^7	−1.9
		$(SCN)_2^{\bullet-}$	2×10^7	+2.8

[a] Accuracy ±1.0 $cm^3\ mol^{-1}$. [b] Data from ref 3. [c] NTA = nitrilotriacetate. [d] Mainly *cyclo*-trimetaphosphate. [e] ATP = adenosine triphosphate. [f] HEDTA = *N*-(2-hydroxyethyl)ethylenediamine-*N*,*N′*,*N′*-triacetate. [g] EDTA = ethylenediaminetetraacetate.

The volumes of activation of the reactions of the $M(NTA)(H_2O)_2^-$ complexes, (M = Mn(II), Fe(II), Co(II)) with the radicals $^{\bullet}CH_3$, $Br_2^{\bullet-}$, and $(SCN)_2^{\bullet-}$ were determined. The data in Table 1 show some interesting trends in that $\Delta V^{\ddagger}$ changes from negative to positive along the series of metal complexes for $^{\bullet}CH_3$ and $Br_2^{\bullet-}$ as entering nucleophiles. A similar trend is seen for the reaction of $(SCN)_2^{\bullet-}$ with Fe(II) and Co(II), but the value for the reaction with Mn(II) seems to fall out of the expected sequence. It seems reasonable to attribute this discrepancy to the small free energy gain of the latter reaction. $(SCN)_2^{\bullet-}$ is a weaker oxidizing agent than $Br_2^{\bullet-}$, $E^{\circ}_{1/2}$ $((SCN)_2^{\bullet-}/2SCN^-)$ = 1.33 V and $E^{\circ}_{1/2}(Br_2^{\bullet-}/2Br^-)$ = 1.63 V.[16] On the other hand $Mn(NTA)(H_2O)_2^-$ is probably the weakest reducing agent of the complexes studied.[17] Thus the reaction of $Mn(NTA)(H_2O)_2^-$ with $(SCN)_2^{\bullet-}$ has the lowest free energy gain of all those studied, with the probable exception of the reaction $Mn(H_2O)_6^{2+} + Br_2^{\bullet-}$. Therefore it seems reasonable to suggest that this reaction has a "late", productlike, transition state; *i.e.*, in the transition state the bond between the two SCN units is elongated and probably causes some increase in volume. This could account for the difference of a ~5 $cm^3\ mol^{-1}$ between $\Delta V^{\ddagger}$ for the reactions of $Mn(NTA)(H_2O)_2^-$ with $Br_2^{\bullet-}$ and $(SCN)_2^{\bullet-}$.

Variation of the ligand on the Fe(II) center was studied for the reaction with $Br_2^{\bullet-}$. The $\Delta V^{\ddagger}$ values observed exhibit an interesting trend from small positive to significantly negative with increasing rate of complex formation. This means that an increased labilization of the coordinated water facilitates stronger binding of the entering nucleophile, *i.e.* a systematic changeover from I_d for the slower to I_a for the faster reactions. This could also be due to a change in the location of the transition state along the reaction coordinate in terms of "early", reactantlike, or "late", productlike, for the fast and slow reactions, respectively. Bond formation will contribute more in the former and bond breaking more in the latter case toward the observed $\Delta V^{\ddagger}$, presumably also partially due to the breakage of the Br–Br bond.

The other free radicals studied *viz.* $^{\bullet}O_2CH_3$ and $^{\bullet}CO_2^-$ result in $\Delta V^{\ddagger}$ values that are in good agreement with those observed for the other investigated radicals. All in all, the complex formation reactions are mainly controlled by solvent, water, exchange on

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(17) The redox potentials of the complexes can be calculated from the known redox potentials of the aquo complexes and the stability constants for the binding of the ligands to the metal ions; see for example: Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum Press: New York. However the stability constant for the formation of $Co^{III}(NTA)(H_2O)_2$ is not known.

the metal complex, which will strongly depend on the nature of the ligands present in the coordination sphere. The results of this study clearly indicate that complex formation reactions of metal ions and complexes with free radicals can be treated mechanistically in a similar way as developed for conventional ligand substitution processes.

Recently Akesson *et al.*[18] have shown that a linear correlation is obtained between the calculated gas-phase dissociation energies and the logarithm of the experimentally determined rate constants for water exchange reactions of the divalent ions of the first transition period. They interpret their results as indicating that though a seventh water molecule always penetrates somewhat the inner coordination sphere, leading in some systems to a negative volume of activation, the reactions are all dissociative in nature. In principle this interpretation would also be in accord with those reported herein which point out that free radicals behave in their reactions with transition metal complexes as ordinary, though powerful, nucleophiles. However a detailed analysis of the present results seems difficult to reconcile with this explanation: 1. According to the calculations of Akesson *et al.*[18] one would predict a large negative volume of activation for the reactions with Cr_{aq}^{2+} and Cu_{aq}^{2+} in contrast to observations.[4,8] 2. The effect of the rate of reaction of $Br_2^{\bullet -}$ with the different Fe(II) complexes on the observed volumes of activation which was interpreted "in terms of "early", reactantlike, or "late", productlike, for the fast and slow reactions, respectively" cannot be explained by the mechanism proposed by Akesson *et al.*[18] 3. The explanation offered for the unexpected volume of activation for the reaction of $(SCN)_2^{\bullet -}$ with Mn(II) cannot be explained by the mechanism proposed by Akesson *et al.*[18] 4. It is difficult to envisage that perfect square-pyramidal or trigonal-bipyramidal descriptions, as used in the calculations of Akesson *et al.*,[18] correctly describe the transition states after a seventh water molecule has significantly penetrated the inner coordination sphere. We therefore propose that the ligand exchange reactions of V(II) and Mn(II) indeed proceed via the I_a mechanism in which bond formation is more important than bond breakage.

The volumes of activation for the homolysis of the metal–carbon σ bond in $(NTA)Mn^{III}\text{–}CH_3^-$ and $(NTA)Fe^{III}\text{–}CH_3^-$ were also determined. The observed values are –4.0 and ~ 0 cm^3 mol^{-1}, respectively. These values are considerably less positive than those reported earlier for analogous reactions for Co(III),[3] Cr(III),[19] and Ni(III)[2] complexes for which typical values of *ca.* +20 cm^3 mol^{-1} were reported. The major difference between the $(NTA)Mn^{III}\text{–}CH_3^-$ and $(NTA)Fe^{III}\text{–}CH_3^-$ and the analogous Co(III),[3] Cr(III),[19] and Ni(III)[2] complexes is that the equilibrium constant for the reaction

$$M^{(n)} + {}^{\bullet}R \rightleftharpoons (M^{(n+1)}\text{–}R) \qquad (11)$$

is *ca.* 10^3 M^{-1} for the Mn and Fe systems[20] and $>10^6$ M^{-1} for the systems previously reported. In addition, the $\Delta V^{\ast}$ values for the formation and homolysis reactions of $(NTA)Fe^{III}\text{–}CH_3^-$ are both close to zero, which means that the overall reaction volume is also close to zero. Similarly, we expect an almost zero reaction volume for the Mn case. Thus the formation of a relatively weak metal–carbon σ bond, as reflected by the significantly lower stability constants, involves relatively small volume changes. This is quite realistic since bond formation in reaction 11 will be accompanied by desolvation of the methyl radical. The results thus point out that the volumes of activation for homolysis processes, and therefore also the volumes of reaction, depend strongly on the metal–carbon bond strength and are not always very large as previously proposed.[2,3,19]

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