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High-Pressure Pulse-Radiolysis Study of the Formation and Decomposition of Complexes with Iron−Carbon σ Bonds: Mechanistic Comparison for Different Metal Centers

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Volumes of activation for the formation and homolysis of the transient complexes (hedta)$Fe^{III}-CO_2^{2-}$ and (hedta)-$Fe^{III}-CH_3^-$ ($HOCH_2CH_2N(CH_2CO_2^-)CH_2CH_2N(CH_2CO_2^-)_2$ = hedta) were determined using high-pressure pulse-radiolysis techniques. A comparison of the results with those for analogous complexes with other central transition-metal cations (M^{n+}) and ligands (L) point out that (i) the reaction of M^nL_m with aliphatic radicals ($R^\bullet$) proceeds via an interchange ligand substitution mechanism, i.e. $M^nL_m + R^\bullet \rightarrow L_{m-1}M^{n+1}-R + L$, (ii) the homolysis of the metal−carbon bonds naturally follows the same mechanism, and (iii) the volume of activation for the homolysis reaction depends strongly on the nature of the central cation, i.e. larger for $M^{n+1} = Cr^{III}$, Co^{III}, Ni^{III} and smaller for Fe^{III}. The volume of activation for the reaction (hedta)$Fe^{III}-CO_2^{2-} + CO_2^{\bullet-} + 2H^+ \rightarrow Fe^{II}$(hedta)$(H_2O)^- + CO + CO_2$ was measured, and the results enable a tentative proposal for the nature of the transition state of this interesting reaction.

Introduction

Complexes with metal−carbon σ bonds are important intermediates in a variety of catalytic, synthetic, and biochemical processes.[1−3] It is therefore of interest to study the factors which affect the chemical properties of these transient complexes. Previous studies pointed out that the formation reactions of these transient complexes (reaction 1) may be considered as ligand

$$M^nL_m + R^\bullet \rightleftharpoons L_{m-1}M^{n+1}-R + L \qquad (1)$$

substitution processes which proceed through an interchange mechanism.[4−6]Measurements of the volumes of activation for reaction 1 suggest an I_d mechanism for $M^n = Co^{II}$,[4] Ni^{II},[5] Cr^{II},[6] Cu^{II},[7] an I mechanism for Fe^{II},[8] and an I_a mechanism for Mn^{II}.[8] On the other hand, large volumes of activation were reported for the homolysis of $L_{m-1}M^{n+1}-R$ (reaction −1) for $M^{n+1} = Cr^{III}$, Co^{III}, Ni^{III}; i.e. $\Delta V^\ddagger(k_{-1}) = 15-26$ cm^3 mol^{-1}.[4−6,9] It was proposed that these large volumes of activation are due to the bond breakage, i.e. an S_H1 mechanism, and to the breakup of the solvent cage as the aliphatic radicals separate from the $L_{m-1}M^n$ center.[9] These two mechanistic proposals are incompatible due to the microreversibility principle. It seemed therefore of interest to measure analogous reactions with other central metal cations in order to elucidate whether these observations are due to special properties of the central metal cations.

For the present study Fe^{II}(hedta)$(H_2O)^-$ was chosen for the following reasons (a) The reactions of $Fe^{II}L(H_2O)_n$ (L = poly(aminocarboxylate)) with $^\bullet CH_3$ and $CO_2^{\bullet-}$ were studied in netural aqueous solutions.[10,11] The results indicate that the transient complexes $L(H_2O)_{n-1}Fe^{III}-CO_2^{2-}$ are more stable than $L(H_2O)_{n-1}Fe^{III}-CH_3^-$.[10,11] (b) The electronic configuration of both $Fe^{II}L(H_2O)_n$ and $L(H_2O)_{n-1}Fe^{III}-R$ is high-spin, and therefore, no intrinsic volume changes due to changes in the electronic configuration are expected.[12,13] (c) The transient complexes $L(H_2O)_{n-1}Fe^{III}-CO_2^{2-}$ have been shown to decompose via reactions −2 and 3;[11] i.e. the iron complexes catalyze

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$$\mathrm{L(H_2O)_{\mathit{n}-1}Fe^{III}{-}CO_2^{\,2-} + H_2O \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} Fe^{II}L(H_2O)_{\mathit{n}}^{\,-} + CO_2^{\bullet-}} \quad (2)$$

$$\mathrm{L(H_2O)_{\mathit{n}-1}Fe^{III}{-}CO_2^{\,2-} + CO_2^{\bullet-} \xrightarrow[k_3]{2H^+} Fe^{II}L(H_2O)_{\mathit{n}}^{\,-} + CO_2 + CO} \quad (3)$$

the disproportionation of the $CO_2^{\bullet-}$ radical anions, which in their absence in neutral solutions dimerize to yield oxalate.[14]It was hoped that measuring the volume of activation of reaction 3 would shed light on the nature of the transition state of this interesting reaction.

Experimental Section

Chemicals. All solutions were prepared from AR grade chemicals in distilled water, or ion-exchanged water, which was further purified by passing through a Milli-Q Millipore setup, final resistivity >10 MΩ/cm. All solutions were N_2O-saturated, using the syringe technique.[15] All experiments were repeated with at least two independently prepared samples.

Methods. Pulse radiolysis experiments were carried out with the Varian 7715 linear accelerator delivering 5 MeV electron pulses of 1.5 μs and 200 mA at the Hebrew University of Jerusalem. The experimental setup was identical with that described in detail before.[11,16] Briefly, a small pillbox optical cell made of Suprasil (optical path length ∼0.8 cm) is placed with its flat surface against the thin stainless steel window of the high-pressure cell, so that the high-energy electrons would have a minimal path through the surrounding water-pressurizing medium. Measurements at ambient pressure were also carried out in a 4 cm Spectrosil cell using three light passes. A 150 W Xe lamp produced the analyzing light, and appropriate filters were used to minimize photochemistry. The reported rate constants are the mean values of at least five kinetic runs. The pH was adjusted by addition of $HClO_4$ and/or NaOH. The experiments were performed up to 1500 atm at room temperature (20 °C). Measurements between 1 and 1500 atm were performed only when a large effect upon increasing the pressure from 1 to 1500 atm was found, since otherwise the size of the effect is too small to be measured accurately at intermediate pressures. The activation volume was determined either from the slope of ln *k* vs P or using the equation $\ln(k_2/k_1) = (\Delta V^{\ddagger}/RT)(P_1 - P_2)$. The linear fit of the data was done using weighed least-squares analysis by applying the Origin 6.0 software.

Results

Volumes of Activation for the Formation and Decomposition of (hedta)$\mathbf{Fe^{III}{-}CO_2^{2-}}$. When N_2O-saturated solutions containing 1−4 mM $FeSO_4 \cdot 7H_2O$, 0.1 M sodium formate, and 6 mM hedta (pH 7.0) are irradiated, all the primary radicals formed by irradiation of water are converted into the $CO_2^{\bullet-}$ radical.[11] The formation and decomposition of (hedta)$Fe^{III}{-}CO_2^{2-}$ were followed at 420 nm ($\epsilon = 950 \pm 100$ M^{-1} cm^{-1}).[11] The formation of (hedta)$Fe^{III}{-}CO_2^{2-}$ obeyed pseudo-first-order kinetics, and k_{obs} was linearly dependent on the initial concentration of the ferrous complex, resulting in $k_2 = (7.1 \pm 0.3) \times 10^6$ M^{-1} s^{-1} at ambient pressure and $(6.3 \pm 0.3) \times 10^6$ M^{-1} s^{-1} at 1500 atm. The former value is in good agreement with data reported earlier.[11] Thus, the volume of activation for reaction 2 was determined from this pressure dependence to be $\Delta V^{\ddagger}(k_2) = 2 \pm 1$ cm^3 mol^{-1} .

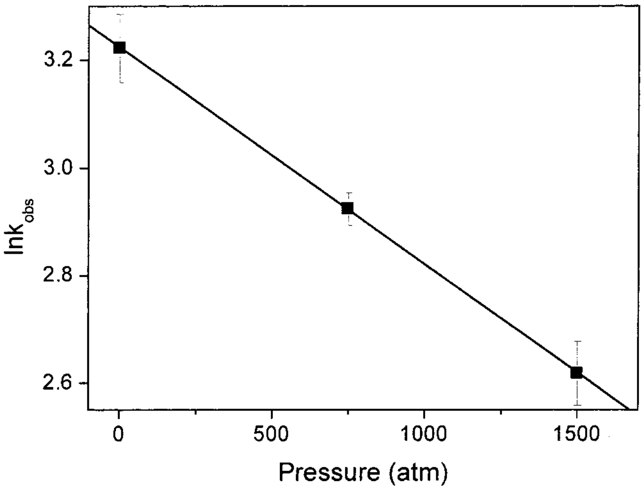

Figure 1. Pressure dependence of the observed second-order rate constant for (hedta)$Fe^{III}{-}CO_2^{2-}$ decomposition in the presence of 1 mM Fe^{II}(hedta)$(H_2O)^-$.

The decomposition of (hedta)$Fe^{III}{-}CO_2^{2-}$ obeys second-order kinetics, and the observed second-order rate constant decreases upon increasing the concentration of Fe^{II}(hedta)$(H_2O)^-$. It has already been shown that the decomposition process at ambient pressure takes place via reactions −2 and 3.[11] Under our experimental conditions, rate law 4 is obtained by assuming a

$$-\mathrm{d[(hedta)Fe^{III}{-}CO_2^{\,2-}]/d}t = 2k_3\mathrm{[(hedta)Fe^{III}{-}CO_2^{\,2-}]^2}/K_2\mathrm{[Fe^{II}(hedta)(H_2O)^-]} \quad (4)$$

fast equilibrium for reaction 2, and k_{-2} and k_3 were determined at ambient pressure to be 25 ± 5 s^{-1} and $(4.5 \pm 0.5) \times 10^6$ M^{-1} s^{-1}, respectively.[11] The observed second-order rate constant, i.e. $k_{obs} = 2k_3/K_2[Fe^{II}(hedta)(H_2O)^-]$, decreases upon increasing the pressure (Figure 1), resulting in $\Delta V^{\ddagger}_{app} = 9.7 \pm 1.2$ cm^3 mol^{-1}, which equals $\Delta V^{\ddagger}(k_3) - \Delta V^{\circ}(K_2)$.

The volume of activation for reaction −2 was measured by adding $Co(NH_3)_6^{3+}$, which is an efficient scavenger of $CO_2^{\bullet-}$. Under these conditions reaction 3 is replaced by reaction 5 and

$$\mathrm{Co(NH_3)_6^{\,3+} + CO_2^{\bullet-} \rightarrow Co(NH_3)_6^{\,2+} + CO_2} \qquad k_5 = 4 \times 10^7\ \mathrm{M^{-1}s^{-1}}\,^{17} \quad (5)$$

the decomposition of (hedta)$Fe^{III}{-}CO_2^{2-}$ turns from second order to first-order kinetics; i.e., the rate equation (6) is obtained

$$\frac{-\mathrm{d[(hedta)Fe^{III}{-}CO_2^{\,2-}]}}{\mathrm{d}t} = \frac{k_{-2}k_5\mathrm{[Co(NH_3)_6^{\,3+}][(hedta)Fe^{III}{-}CO_2^{\,2-}]}}{k_2\mathrm{[Fe^{II}(hedta)(H_2O)^-]} + k_5\mathrm{[Co(NH_3)_6^{\,3+}]}} \quad (6)$$

assuming the steady-state approximation for $[CO_2^{\bullet-}]$. Rearrangement of eq 6 yields eq 7, which predicts a linear plot of

$$1/k_{obs} = 1/k_{-2} + \mathrm{K_2[Fe^{II}(hedta)(H_2O)^-]}/k_5\mathrm{[Co(NH_3)_6^{\,3+}]} \quad (7)$$

$1/k_{obs}$ vs $1/[Co(NH_3)_6^{3+}]$. The double-reciprocal plots of k_{obs} vs $[Co(NH_3)_6^{3+}]$ are given in Figure 2 at 1 and 1500 atm. From the intercept of these plots one calculates $k_{-2} = 18 \pm 2$ s^{-1} at 1 atm and 12 ± 1 s^{-1} at 1500 atm; hence, $\Delta V^{\ddagger}(k_{-2}) = 6.5 \pm 2$

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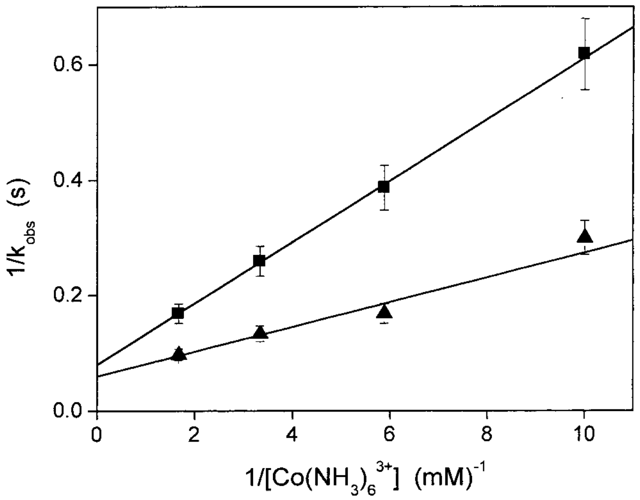


Figure 2. Double-reciprocal plots of the observed first-order rate constant for the decomposition of (hedta)Fe^{III}−CO$_2$$^{2-}$ vs [Co(NH$_3$)$_6$$^{3+}$] at (▲) 1 and (■) 1500 atm. N$_2$O-saturated solutions contained 0.1−0.6 mM FeSO$_4$, 6 mM hedta, and 0.1 M formate at pH 7.

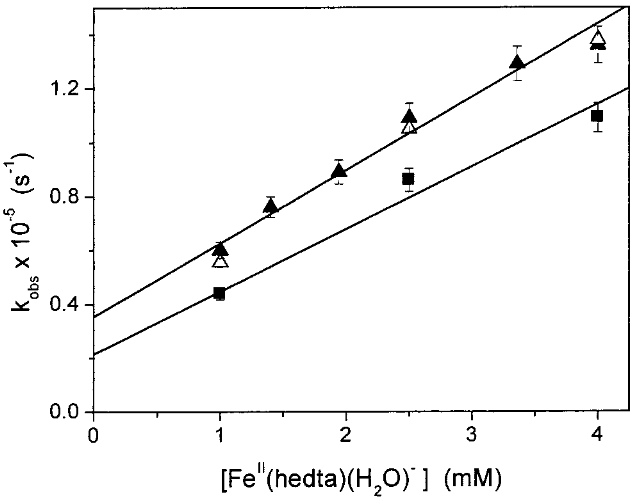


Figure 3. Observed first-order rate constants for the formation of (hedta)Fe^{III}−CH$_3$$^-$ vs [Fe^{II}(hedta)(H$_2$O)$^-$] at (▲, △) 1 atm and (■) 1500 atm. The rate constants were measured at 1 atm using the 4 cm optical cell (▲) and the 0.8 cm pillbox optical cell (△). N$_2$O-saturated solutions contained 1−4 mM FeSO$_4$, 6 mM hedta, and 0.1 M DMSO at pH 7.

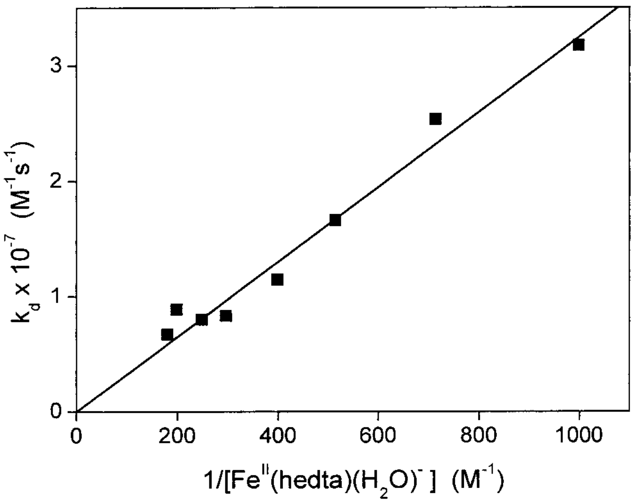


Figure 4. Observed second-order rate constants for the decomposition of (hedta)Fe^{III}−CH$_3$$^-$ vs 1/[Fe^{II}(hedta)(H$_2$O)$^-$] at pH 7.

cm^3 mol^{-1}. As $\Delta V^{\ddagger}(k_2) = 2 \pm 1$ cm^3 mol^{-1} and $\Delta V^{\ddagger}_{app} = \Delta V^{\ddagger}(k_3) - \Delta V^{\circ}(K_2) = 9.7 \pm 1.2$ cm^3 mol^{-1}, one obtains $\Delta V^{\circ}(K_2) = -4.5 \pm 3$ cm^3 mol^{-1} and $\Delta V^{\ddagger}(k_3) = 5.2 \pm 3.4$ cm^3 mol^{-1}.

From the pressure dependence of the slopes of the lines in Figure 2, one calculates $\Delta V^{\ddagger}_{app} = \Delta V^{\circ}(K_2) - \Delta V^{\ddagger}(k_5) = -15 \pm 2$ cm^3 mol^{-1}. As $\Delta V^{\circ}(K_2)$ was derived above, one can evaluate $\Delta V^{\ddagger}(k_5) = 10.5 \pm 5$ cm^3 mol^{-1}.

Volumes of Activation for the Formation and Homolysis of the Transient Complex (hedta)Fe^{III}−CH$_3$$^-$. The results obtained in the previous section indicate that $\Delta V^{\circ}(K_2)$ is considerably less negative than that observed for analogous complexes.[4−6] Since in all previous studies alkyl radicals, and not CO$_2$$^{\bullet-}$, were studied, it was decided to repeat the study with $^{\bullet}$CH$_3$ radicals. The same solution as described in the previous section was used, but 0.1 M formate was replaced with 0.1 M DMSO. The formation and decomposition of the transient complex (hedta)Fe^{III}−CH$_3$$^-$ were followed at 310 nm ($\epsilon = 2030 \pm 200$ M^{-1}cm^{-1}). The kinetics of formation obeyed a first-order rate law, and the observed rate constant was proportional to the concentration of Fe^{II}(hedta)(H$_2$O)$^-$ (Figure 3). The large intercept in Figure 3 is considerably higher than the contribution of the dimerization of the $^{\cdot}$CH$_3$ radicals, and therefore indicates that reaction 8 is an equilibrium process. From the slope and

$$\mathrm{Fe^{II}(hedta)(H_2O)^- + {}^{\cdot}CH_3 \rightleftharpoons (hedta)Fe^{III}{-}CH_3^- + H_2O} \qquad (8)$$

intercept of the line at ambient pressure one obtains $k_8 = (2.7 \pm 0.2) \times 10^7$ M^{-1} s^{-1} and $k_{-8} = (3.6 \pm 0.4) \times 10^4$ s^{-1}, respectively, and hence, $K_8 = (7.5 \pm 1.5) \times 10^2$ M^{-1}. Both k_8 and k_{-8} decrease upon increasing the pressure to 1500 atm to the values $(2.3 \pm 0.2) \times 10^7$ M^{-1} s^{-1} and $(2.1 \pm 0.3) \times 10^4$ s^{-1}, respectively (Figure 3), and hence $\Delta V^{\ddagger}(k_8) = 2.5 \pm 0.5$ cm^3 mol^{-1}, $\Delta V^{\ddagger}(k_{-8}) = 8 \pm 2$ cm^3 mol^{-1}, and $\Delta V^{\circ}(K_8) = -5.5 \pm 2.5$ cm^3 mol^{-1}. The kinetics of the decomposition obeyed a second-order rate law with a rate which depended linearly on 1/[Fe^{II}(hedta)(H$_2$O)$^-$] (Figure 4), pointing out that the mechanism of the decomposition of this transient complex involves reaction −8 followed by reaction 9, and $k_{obs} = 2k_9/K_8$[Fe^{II}(hedta)(H$_2$O)$^-$] (see eq 4). Since K_8 is known, one calculates from the slope of the line in Figure 4 that $k_9 = (1.3 \pm 0.2) \times 10^7$ M^{-1} s^{-1}. However, in this case there was hardly any effect of the pressure on the decomposition rate; i.e., $\Delta V^{\ddagger}_{app} = \Delta V^{\ddagger}(k_9) - \Delta V^{\circ}(K_8) \approx 0$, and hence, $\Delta V^{\ddagger}(k_9) \approx \Delta V^{\circ}(K_8)$.

$$\mathrm{(hedta)Fe^{III}{-}CH_3^- + {}^{\bullet}CH_3 + H_2O \rightleftharpoons Fe^{II}(hedta)(H_2O)^- + C_2H_6} \qquad (9)$$

Discussion

The small positive volumes of activation for reactions 2 and 8 are in accord with previous reports for reactions of radicals with LM^n complexes,[4−6,8] which suggest that reaction 1 in general proceeds via a mechanism which is best described as an interchange ligand substitution process. For Fe^{II} complexes, this often involves very small volumes of activation, as the mechanism changes from an I$_a$ mechanism for Mn^{II} to an I$_d$ mechanism for Co^{II} and Ni^{II}.[8] However, the relatively small volumes of activation observed for reactions −2 and −8, and therefore the small overall reaction volumes, are at odds with the common notion for reactions involving the formation and homolysis of complexes with metal−carbon σ bonds.[16]

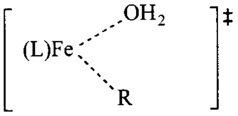
Table 1. Volumes of Activation and Reaction for the Formation and Homolysis of Transient Complexes with Metal−Carbon σ Bonds

complex	$\Delta V^{\ddagger}(k_1)$, cm^3 mol^{-1}	$\Delta V^{\ddagger}(k_{-1})$, cm^3 mol^{-1}	$\Delta V^{o}(K_1)$, cm^3 mol^{-1}	K_1, M^{-1}	ref
(hedta)Fe^{III}−CO$_2$$^{2-}$	2 ± 1	6.5 ± 3	-4.5 ± 2.2	$(3.6 \pm 0.3) \times 10^5$	this work
(hedta)Fe^{III}−CH$_3$$^{-}$	2.5 ± 2.5	8 ± 5	-5.5 ± 2.5	$(7.2 \pm 1.2) \times 10^2$	this work
(H$_2$O)$_5$Cr^{III}−C(CH$_3$)$_2$OH^{2+}	6 ± 1	15 ± 2	-9 ± 3	4.0×10^8	6
(nta)(H$_2$O)Co^{III}−CH$_3$$^{-}$ [a]	6 ± 2.5	19 ± 2	-13 ± 5.5	2.7×10^6	4
(cyclam)Ni^{III}−CH$_3$$^{2+}$ [b]	4 ± 1	24 ± 2	-20 ± 3	1.1×10^7	5

[a] nta = nitrilotriacetate. [b] cyclam = *trans*-III-1,4,8,11-tetraazacyclotetradecane.

All the measured volumes of activation for homolysis, $\Delta V^{\ddagger}(k_{-1})$, and the overall reaction volumes, $\Delta V^{o}(K_1)$, reported to date are summarized in Table 1. The results clearly demonstrate that the values of $\Delta V^{o}(K_1)$ do not correlate with the stability constants of these transient complexes. It is proposed that the main contributor to $\Delta V^{o}(K_1)$ is the electronic configuration of the central cation, and therefore the following is true.

(a) Both the Fe^{II} and the Fe^{III}−R complexes have the high-spin electronic configuration, and therefore the reaction involves a small $\Delta V^{o}(K_1)$. The transition state for these reactions is thus best described by



(b) The negative volume of reaction observed for the formation of (H$_2$O)$_5$Cr^{III}−C(CH$_3$)$_2$OH^{2+} is attributed mainly to the change in the inner coordination sphere of the central chromium cation from the Jahn−Teller distorted coordination sphere of Cr(H$_2$O)$_6$$^{2+}$ to the octahedral coordination sphere of (H$_2$O)$_5$Cr^{III}−C(CH$_3$)$_2$OH^{2+}.[6] Similar volumes of reaction were reported for other oxidations of Cr(H$_2$O)$_6$$^{2+}$.[6]

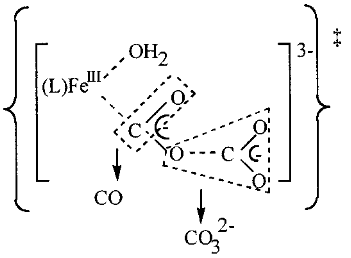
(c) The negative volume of reaction observed for the formation of (nta)(H$_2$O)Co^{III}−CH$_3$$^{-}$ is attributed mainly to the change of the electronic configuration of the central cobalt ion from high-spin d^7 for Co^{II}(nta)(H$_2$O)$_2$$^{-}$ to the low-spin d^6 for (nta)(H$_2$O)Co^{III}−CH$_3$$^{-}$.[4] It is well-known that redox reactions involving Co$^{III/II}$ couples have large volumes of reactions.[18,19]

(d) The very large negative volume of reaction observed for the formation of (cyclam)(H$_2$O)Ni^{III}−CH$_3$$^{2+}$ is attributed to the change in the coordination number of the central nickel ion from the planar low spin d^8 Ni(cyclam)$^{2+}$ to the octahedral d^7 (cyclam)(H$_2$O)Ni^{III}−CH$_3$$^{2+}$.[5,16]

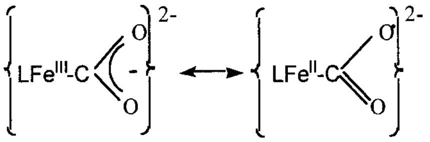
Thus, the results clearly demonstrate that the homolysis processes do not proceed via a S$_H$1 mechanism but, as expected, via an interchange "ligand substitution" mechanism, although these reactions also involve a redox step.

The kinetic results also indicate the following. (i) The stability constants of (hedta)Fe^{III}−R and (nta)(H$_2$O)Fe^{III}−R are similar for R = $^{-}$CH$_3$ and CO$_2$$^{2-}$; i.e., the ligands nta and hedta have a similar effect on the central Fe^{III} cation. (ii) The complexes formed with CO$_2$$^{\bullet-}$ are considerably more stable than those formed with $^{\bullet}$CH$_3$. This difference is attributed to the stronger electrostatic interaction between the central cation and the CO$_2$$^{2-}$ ligand and probably to some d−π^* interaction.

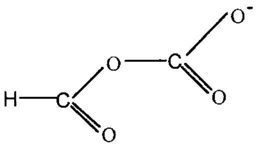
Volume of Activation of Reactions 3 and 9. The observed volumes of activation for reactions 3 and 9 were determined to be 4.2 ± 3.4 and -5.5 ± 2.5 cm^3 mol^{-1}, respectively. The former value is somewhat surprising, as it was expected that bond formation, Fe−C or C−O, in the transition state will lead to a negative $\Delta V^{\ddagger}$, as in the case for reaction 9, and that in addition $\Delta V^{\ddagger}$ should be more negative due to charge localization. The observed positive $\Delta V^{\ddagger}$ cannot be due to a homolytic partial release of the radicals, as C$_2$O$_4$$^{2-}$ was not detected as an end product.[11] It is therefore suggested that the transition state for reaction 3 is



This transition state involves the formation of an Fe−O bond, the formation of a C−O bond, the breaking of an Fe−C bond, the breaking of a C−O bond, and the reduction of the central Fe^{III} ion to Fe^{II}. It should be pointed out that probably not all these processes occur coherently, but if another transient product is formed in this process, its concentration is too low to be observed. The activation volume for reaction 3 is similar to that for the homolysis of (hedta)Fe^{III}−CO$_2$$^{-}$, suggesting that reaction 3 involves an attack of the CO$_2$$^{\bullet-}$ radical anion on the oxygen of the bound :CO$_2$ unit and not on the central iron cation. The formation of this transition state can be rationalized if one considers the resonance structures



which are analogous to the resonance structures of the CO$_2$$^{\bullet-}$ radical.[14b] The transition state is thus analogous to the transient formed in acidic solution in the disproportionation reaction of the CO$_2$$^{\bullet-}$ radical, which, however, decomposes into CO$_2$ + HCO$_2$$^{-}$:[14b]



The difference in the mechanisms of decomposition is attributed to the difference in the Fe−C and H−C bond strengths. Similarly, the transition state of reaction 9 involves the attack of the methyl radical on the ligated methyl and not on the central iron cation, in agreement with earlier suggestions.[16]

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Volume of Activation for Reaction 5. The volume of activation for reaction 5, $\Delta V^{\ddagger}(k_5) = 10.5 \pm 4.2$ cm^3 mol^{-1}, is in accord with expectations for the reduction of $Co(NH_3)_6^{3+}$.[18,19]

Conclusions

The results of this study have once again demonstrated the mechanistic discrimination ability of activation and reaction volume data as obtained from high-pressure kinetic and thermodynamic data. Furthermore, this study has illustrated the role of changes in the electronic environment in terms of the coordination number and spin state of the complexes during the formation and decomposition reactions of metal−carbon σ bonds.

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