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from the energy penalty associated with promotion of the central uranium atom from the tetravalent states in UF_4, UO, and UO_2 to the hexavalent states in UO_2F_2 and UOF_4. This is especially apparent in D(F_4U-O), which is only one-half the values *D*(OU-O) and *D*(U-O).

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Rates and Mechanisms of Reduction of Tris(phenanthroline)iron(III) by Various Radicals. Effect of Solvent[1]

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Tris(phenanthroline)iron(III) (Fe^{III}(phen)$_3$) is reduced to Fe^{II} complex by a wide variety of radicals in aqueous solutions. Reduction by α-hydroxyalkyl radicals takes place with nearly diffusion-controlled rate constants ($3-5 \times 10^9$ M^{-1} s^{-1}) and involves an outer-sphere electron transfer. Reduction by other substituted alkyl radicals, as well as methyl and ethyl, is less rapid to varying degrees ($k \sim 10^6-10^9$ M^{-1} s^{-1}) and may involve an inner-sphere mechanism, whereby the radical attaches to the iron center in an intermediate stage. Addition of alkyl radicals to a phenanthroline carbon, which occurs in acetonitrile solutions, becomes less likely in water, because it is slow relative to the other processes. In the case of the OH radical reaction, however, addition to carbon followed by an intramolecular electron transfer may be the only operative mechanism for reduction of Fe^{III}(phen)$_3$.

Introduction

Redox reactions of organic radicals often occur by an outer-sphere electron transfer, especially those reactions with a high driving force.[3-5] Oxidation of simple alkyl radicals, however, may be more complex, since these radicals do not typically reduce by electron transfer but rather by ligand substitution or ligand exchange.[4,5] The present study has been undertaken to investigate the rates and mechanism of reduction of tris(phenanthroline)-iron(III) (Fe^{III}(phen)$_3$) by various radicals.

Fe^{III}(phen)$_3$ is a very strong one-electron oxidizing agent ($E°$ = 1.06 V in water and 1.23 V in acetonitrile) and its reduction by different alkyl radicals has been studied in acetonitrile solutions.[4] The results have been interpreted in terms of two possible mechanisms for this reaction, i.e., addition of $\dot{R}$ to a phenanthroline ligand (1) or outer-sphere electron transfer (2).

$$\dot{R} + Fe(phen)_3{}^{3+} \rightarrow (R\text{-}phen)Fe(phen)_2{}^{2+} + H^+ \quad (1)$$

$$\rightarrow Fe(phen)_3{}^{2+} + R^+ \quad (2)$$

The estimated rate constants were in the range of 10^5-10^8 M^{-1} s^{-1} and increased in going from methyl to *tert*-butyl radical. This was also accompanied by a gradual change in mechanism from (1) to (2). In the present paper we investigate these processes in aqueous solutions using methyl, ethyl, and a variety of substituted alkyl radicals as reactants. We find a substantial difference between these results and those obtained in acetonitrile solutions.

Experimental Section

Materials. 1,10-Phenanthroline (Alpha Chemical Co.) was recrystallized from a mixture of hexane and toluene. The 5-methyl- and the 4,7-dimethyl-substituted phenanthrolines were obtained from G. F. Smith Chemical Co., and the 2,9-dimethyl derivative was obtained from J. T. Baker Chemical Co. The 4-methyl derivative was synthesized as follows. Lepidine (City Chemical Corp.) was nitrated in concentrated H_2SO_4 to a mixture containing mostly 8-nitrolepidine, which was reduced with iron powder in ethanol according to general methods.[6] The crude 8-aminolepidine was converted by the modified procedure of Richter and Smith[7] and Manske et al.[8] as follows. The aminolepidine (16 g) was added portionwise to 50 mL of concentrated H_2SO_4 with occasionally cooling. Anhydrous glycerol (40 mL) was added, and the mixture heated on a steam bath for 1 h. This premix was added in small portions with vigorous stirring to 17 g of As_2O_5 and 1.5 g of $FeSO_4$ in 20 mL of concentrated H_2SO_4 at approximately 130 °C. The mixture was heated for 3 h and then poured over ice. The reaction mixture was partially neutralized with NaOH and filtered, and 27 g of $FeSO_4 \cdot 7H_2O$ was added. After the mixture was stirred for 1 h, the iron(II) complex was precipitated with $HClO_4$, and collected on a glass frit (care!). After the complex was washed with alcohol and ether, it was decomposed with a solution of aqueous NaOH. The 4-methyl-1,10-phenanthroline was extracted with benzene several times and the combined extracts decolorized with charcoal and concentrated in vacuo: yield 11.6 g (61%), mp 143-145 °C. The ^1H and ^{13}C NMR data for these methylphenanthrolines are compared in Tables I and II, respectively.

2-Propanol, methanol, *tert*-butyl alcohol, and benzoic acid were Baker Analyzed reagents. Ethyl bromide, *tert*-amyl alcohol, and 2,3-dimethyl-2-butanol were from Aldrich, *n*-propyl alcohol from Mallinckrodt, isobutyric acid from Baker, pivalic acid from Eastman, acetic acid, benzene, ethylene glycol, potassium persulfate, and sulfuric acid from Fisher, and sodium perchlorate from G.F.S. The gases were obtained from Linde. Water was purified by a Millipore Milli-Q system.

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TABLE I: ^1H NMR Data for Some Methyl-Substituted 1,10-Phenanthrolines[a]

	assignments[b]								
substituent	2	3	4	5	6	7	8	9	Me
H	9.10 (dd) (4.5, 1.5)	7.51 (dd) (8.1, 4.5)	8.10 (dd) (8.1, 1.5)	7.64 (s)	7.64 (s)	8.10 (dd) (8.1, 1.5)	7.51 (dd) (8.1, 4.5)	9.10 (dd) (4.5, 1.5)	
4-Me	8.91 (d) (4.5)	7.28 (d) (4.5)		7.56 (d) (9.0)	7.75 (d) (9.0)	8.02 (dd) (8.1, 1.8)	7.44 (dd) (8.1, 4.5)	9.06 (dd) (4.5, 1.8)	2.59 (s)
5-Me	9.05 (dd) (4.2, 1.8)	7.50 (dd) (8.0, 4.4)	8.03 (dd) (8.0, 1.8)		7.46 (s)	8.25 (dd) (8.2, 1.8)	7.57 (dd) (8.2, 4.2)	9.12 (dd) (4.4, 1.8)	2.62 (s)
4,7-diMe	8.92 (d) (4.6)	7.30 (d) (4.6)		7.80 (s)	7.80 (s)		7.30 (d) (4.6)	8.92 (d) (4.6)	2.64 (s)
2,9-diMe		7.37 (d) (8.2)	7.98 (d) (8.2)	7.56 (s)	7.56 (s)	7.98 (d) (8.2)	7.37 (d) (8.2)		2.88 (s)

[a] In $CDCl_3$ with internal Me_4Si, using a Varian HR-220 spectrometer; probe temperature ≈ 16 °C. [b] Each position given in the following format: δ (splitting pattern) (upper) and (J) (lower figures) with d = doublet, dd = doublet of doublets, and s = singlet.

TABLE II: ^{13}C Chemical Shifts of Some Methyl-Substituted 1,10-Phenanthroline Hydrochlorides[a]

	assignments												
substituents	2	3	4	5	6	7	8	9	11	12	13	14	Me
H	146.5	125.2	141.2	126.6	126.6	141.2	125.2	146.5	135.1	135.1	128.3	128.3	
4-Me	149.1	121.2	155.7	125.5	127.2	137.9	125.1	142.3	135.1	133.1	126.7	127.4	19.0
5-Me	144.7	124.3	136.6	133.6	125.1	140.8	125.1	146.7	135.0	134.3	127.7	127.7	17.6
4,7-diMe	145.5	122.1	151.9	125.5	125.5	151.9	122.1	145.5	134.2	134.2	126.6	126.6	18.4
2,9-diMe	158.2	125.4	140.5	126.0	126.0	140.5	125.4	158.2	133.8	133.8	127.5	127.5	22.0

[a] Sample (0.25 g) dissolved in 3 mL of 2 M HCl in D_2O; δ relative to external ethylene glycol = 63.00. ^1H-decoupled spectra with a Varian XL-100-15 spectrometer with an external ^{19}F lock; probe temperature = 35 °C. Data collected on a Nicolet Model 290 computer equipped with a 36K 1080 memory and a 1010 pulse generator operating a quadrature FT mode.

Reagent grade acetonitrile (Mallinckrodt Chem. Co.) was purified by fractional distillation from calcium hydride. It was stirred with a mixture of $KMnO_4$ and Na_2CO_3, (10 g of each per liter) for 24 h and then filtered. After bulb-to-bulb distillation, it was redistilled from P_2O_5, followed by CaH_2. Acetonitrile obtained in this manner did not reduce $(phen)_3Fe(PF_6)_3$.

The iron(II) complexes were prepared by adding an equivalent amount of the appropriate ligand to an aqueous solution of ferrous sulfate. The perchlorate and hexafluorophosphate salts of the iron(II) complexes were precipitated with sodium perchlorate and ammonium hexafluorophosphates. The iron(III) complex of 1,10-phenanthroline was prepared by chlorine oxidation of an acidic aqueous solution of the sulfate salt of the corresponding iron(II) complex.[9] After complete oxidation, sodium perchlorate was added and the blue solution was subsequently cooled to allow precipitation of the blue solid. Warning: the perchlorates exploded on several occasions while drying, and the hexafluorophosphates prepared from ammonium hexafluorophosphate (Ozark-Mahoning) were thus the salts of choice. The behavior of the hexafluorophosphates was the same as the perchlorate insofar as the electrochemical reduction potentials and the absorption spectra were concerned.

Reduction of $Fe^{III}(phen)_3{}^{3+}$ by Organic Radicals. The pulse radiolysis studies were carried out with solutions which were freshly prepared before each experiment and were kept in the dark until the time of measurement. $Fe^{II}(phen)_3{}^{2+}$ was dissolved in 5 N H_2SO_4 and PbO_2 was added in excess (3–4 equiv) in order to oxidize the complex to $Fe^{III}(phen)_3{}^{3+}$. Full oxidation was achieved in 10–15 min and was evident from the color change from purple to blue. In some experiments the precipitate PbO_2 and $PbSO_4$ were removed by filtration or by decantation. $Fe^{III}(phen)_3{}^{3+}$ was precipitated as perchlorate by adding $NaClO_4$. However, in most pulse radiolysis experiments the complex was used as the sulfate salt, the solution was diluted to 1 N H_2SO_4, the required reagents were added, and the solution was deoxygenated by bubbling with pure N_2 ("oxygen free" grade from Linde). The solution was then withdrawn from above the percipitate and passed through the irradiation cell in a flow system.

Kinetic spectrophotometric experiments were carried out by the computer-controlled pulse radiolysis apparatus described previously.[11] The linear accelerator supplied 10-ns, 8-MeV electron pulses which deposited energy in the solution to produce 3–4 μM total radical concentration (determined by thiocyanate dosimetry).

Steady-state radiolysis was carried out in a Gammacell 220 ^{60}Co source with a dose rate of 2.4×10^{17} eV g^{-1} min^{-1}. Spectra were recorded on a Cary 219 spectrophotometer.

Typical Procedures for Product Analysis and Isolation. A small aliquot (10 mL) of the irradiated reaction mixture was concentrated in vacuo to remove most of the water and/or acetonitrile. A small amount of acetonitrile was added to redissolve the precipitated solids. The iron(II) complex was precipitated by the addition of ether. The ^1H NMR spectrum of the dried complex showed no methyl singlet resonance (δ 2.9 in CD_3CN), characteristic of the iron(II) phenanthroline complex. The complex was decomposed with aqueous NaOH, and the phenanthroline fraction extracted with CH_2Cl_2 repeatedly. The combined extracts were dried with $MgSO_4$ and evaporated to dryness in vacuo: yield, 95% of recovered phenanthroline, in which the ^1H NMR and ^{13}C spectra did not show the presence of a methyl singlet (δ 2.59 and 19.0 in $CDCl_3$) slightly shifted upfield from that in the iron(II) complex. From these analyses we estimate that <5% of methylphenanthroline was present.

The same procedure was used to examine the products of inner-sphere reduction of $Fe^{III}(phen)_3{}^{3+}$ with the organic radicals derived from acetonitrile, *tert*-butyl alcohol, isopropyl alcohol, acetic acid, and isobutyric acid. In each case, the analysis of the free ligand subsequent to hydrolytic cleavage of the recovered $Fe^{II}(phen)_3{}^{2+}$ indicated the presence of only 1,10-phenanthroline.

Results and Discussion

Radicals from Water. The radiolysis of water produces H, OH, and e_{aq}^-. In acid solutions e_{aq}^- is converted into H ($e_{aq}^- + H^+ \rightarrow H$, $k = 2 \times 10$ M^{-1} s^{-1}). Experiments were carried out only at >0.1 N H_2SO_4 because of the instability of the complex at lower acidities.[12] H atoms have been shown previously to reduce $Fe^{III}(phen)_3$ with a rate constant of 2.9×10^9 M^{-1} s^{-1}.[13]

$$Fe^{III}(phen)_3 + H \rightarrow Fe^{II}(phen)_3 + H^+ \qquad (3)$$

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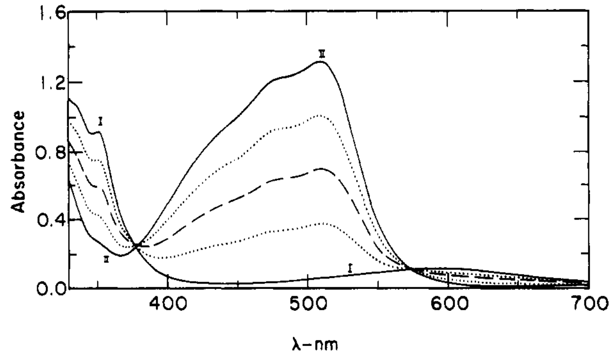

Figure 1. γ Radiolysis reduction of $Fe^{III}(phen)_3$ (I) to $Fe^{II}(phen)_3$ (II). Aqueous solutions containing 2×10^{-4} M $Fe^{III}(phen)_3$ and 0.2 M *t*-BuOH, 0.5 M H_2SO_4, N_2 bubbled, were irradiated with doses of 3.80×10^3, 7.60×10^3, 1.14×10^4, 1.52×10^4 rad.

Reduction by outer-sphere electron transfer is not likely to occur with H atoms.[14] The mechanism of reaction 3 may involve addition of H to a phenanthroline, followed by intramolecular electron transfer and release of H^+, as suggested for reaction of methyl radicals.[3] Hydroxyl radicals also react by this mechanism[15] and result in overall reduction of $Fe^{III}(phen)_3$ to a substituted $Fe^{II}(phen)_2(phen\text{–}OH)$.

$$Fe^{III}(phen)_3 + OH \rightarrow Fe^{III}(phen)_2(phen\text{–}OH)\cdot \quad (4)$$

$$Fe^{III}(phen)_2(phen\text{–}OH)\cdot \rightarrow Fe^{II}(phen)_2(phen\text{–}OH) + H^+ \quad (5)$$

γ Radiolysis of deoxygenated acid solutions of $Fe^{III}(phen)_3$ resulted in reduction of this compound to the Fe^{II} complex with an initial yield of $G \sim 6.8$ (using $\Delta\epsilon$ at 490 nm of 10 100 M^{-1} cm^{-1}),[13] indicating that both H and OH cause reduction of the iron. Pulse radiolysis experiments also showed reduction with a yield approaching $G = 6$. The kinetics of reduction as followed at 490 nm consisted of two components: a fast step corresponding to $k = 5 \times 10^9$ M^{-1} s^{-1} and G = 5–6 depending on concentration, followed by a slower step corresponding to $k = 2 \times 10^8$ M^{-1} s^{-1}. Clearly, the first step is assigned to reduction of the iron by addition of H and OH. The slower reaction cannot be ascribed to $\dot{S}O_4^-$ radicals, produced by partial reaction of OH with HSO_4^- ($k = 1.6 \times 10^6$ M^{-1} s^{-1}), since experiments with added $S_2O_8^{2-}$ to produce $\dot{S}O_4^-$ in high yield showed no appreciable reaction with this radical. As the contribution of the slower reduction step was dependent on time and temperature, it could result from the presence of free phenanthroline. This was confirmed by adding greater concentrations of phenanthroline and indeed finding increasing contributions of the slower step. Apparently, uncomplexed phenanthroline competes for the H and OH radicals[16-18] to form adducts which transfer an electron to the complex by an outer-sphere mechanism.

Radicals from Alcohols. Methanol, ethanol, 1-propanol, and 2-propanol were used as H and OH radical scavengers, which produce the reducing α-hydroxyalkyl radicals,[19] e.g.

$$CH_3OH + H \rightarrow \dot{C}H_2OH + H_2 \quad (6)$$

$$CH_3OH + OH \rightarrow \dot{C}H_2OH + H_2O \quad (7)$$

Experiments in the presence of a large excess (0.1–1 M) of these alcohols showed reduction of $Fe^{III}(phen)_3$ in one step only.

$$Fe^{II}(phen)_3 + \dot{C}H_2OH \rightarrow Fe^{II}(phen)_3 + CH_2O + H^+ \quad (8)$$

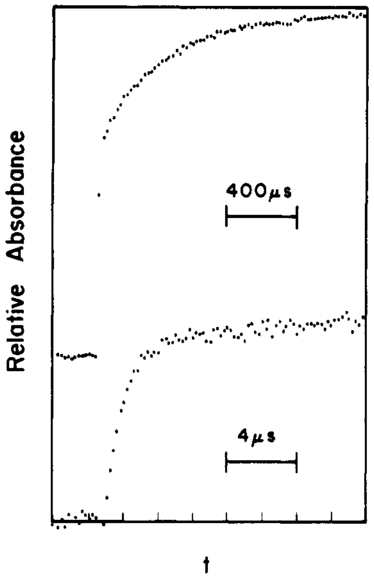

Figure 2. Kinetic traces (at 490 nm) showing the rapid reduction of $Fe^{III}(phen)_3$ by H atoms and the slower reduction by $\dot{C}H_2C(CH_3)_2OH$ radicals.

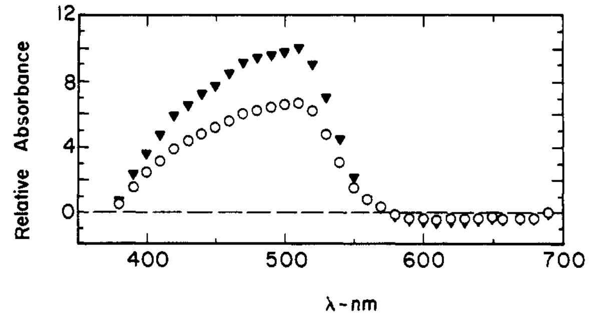

Figure 3. Differential absorption spectra monitored upon pulse radiolytic reduction of $Fe^{III}(phen)_3$. The solution contained 2×10^{-4} M $Fe^{III}(phen)_3$, 0.2 M *t*-BuOH, 0.5 M H_2SO_4, N_2 bubbled. Spectra recorded 20 μs (○) and 800 μs (▲) after the pulse. Each unit on the relative absorbance scale corresponds to ϵ = 1000 M^{-1} cm^{-1} for species produced with $G = 6$, determined by thiocyanate dosimetry.

The mechanism of reaction 8 must be an outer-sphere electron transfer as suggested for somewhat similar reactions.[5] The rate constants determined for several concentrations of $Fe^{III}(phen)_3$ in the range of $(0.4\text{–}1.0) \times 10^{-4}$ M were 5×10^9 for $\dot{C}H_2OH$ and $CH_3\dot{C}HOH$, 3.2×10^9 for $CH_3CH_2\dot{C}HOH$, and 4.1×10^9 M^{-1} s^{-1} for $(CH_3)_2\dot{C}OH$. These rate constants are near the diffusion-controlled limit, which is not surprising since the driving force for these reactions is greater than 2 V. In the case of *n*-propyl alcohol a slower reaction with $k \approx 7 \times 10^8$ M^{-1} s^{-1} and 5–10% contribution to the total yield was observed which is probably owing to the $CH_3\dot{C}HCH_2OH$ radical partially produced by the OH reaction with this alcohol.

t-BuOH is a good scavenger for OH radicals ($k = 5 \times 10^8$ M^{-1} s^{-1})[15] but not for H atoms ($k = 9 \times 10^4$ M^{-1} s^{-1}).[14] Therefore, the reactions in the presence of this alcohol are expected to be reactions 9, 10, and 3. Steady-state radiolysis shows quantitative

$$(CH_3)_3COH + OH \rightarrow \dot{C}H_2C(CH_3)_2OH + H_2O \quad (9)$$

$$Fe^{III}(phen)_3 + \dot{C}H_2C(CH_3)_2OH \rightarrow Fe^{II}\ \text{complex} \quad (10)$$

reduction of the Fe^{III} to an Fe^{II} complex (see spectra in Figure 1) with an initial yield of $G = 7.5$, indicating reduction by both H and $\dot{C}H_2C(CH_3)_2OH$. The kinetics of reactions 3 and 10, however, are different as demonstrated in Figure 2. The fast step, with a yield of $G = 3.4$, gives $k = (4.0 \pm 0.5) \times 10^9$ M^{-1} s^{-1}. This rate constant corresponds to the reaction of H atoms (reaction 1) with no contribution from OH radicals. Therefore, from the value of 5×10^9 M^{-1} s^{-1} determined above for overlapping H and OH reaction, we can estimate a rate constant of 7×10^9 M^{-1} s^{-1}

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for the reaction of OH with $Fe^{III}(phen)_3$. The slower step observed with *t*-BuOH (Figure 2, top) can be assigned to reaction 10 and occurs with a rate constant of $k_{10} = (1.5 \pm 0.2) \times 10^7$ M^{-1} s^{-1}. This rate constant is much lower than those found for the α-hydroxyalkyl radicals and reflects the low reducing power of the $\dot{C}H_2C(CH_3)_2OH$ radical. It also suggests a different mechanism for this reduction other than outer-sphere electron transfer.

The differential spectra monitored upon pulse radiolysis in the presence of *t*-BuOH are shown in Figure 3. They are found to correspond to reduction of Fe^{III} to Fe^{II} in two steps as described above. The total yield in this case is $G = 6.0$ (i.e., part of the slowly reacting $\dot{C}H_2C(CH_3)_2OH$ radicals is lost to radical–radical reactions due to the high radical concentration).

Experiments were carried out also with *tert*-amyl alcohol, $CH_3CH_2C(CH_3)_2OH$, and 2,3-dimethyl-2-butanol, $(CH_3)_2CH$-$C(CH_3)_2OH$. These compounds are expected to be reactive toward both OH and H and to undergo hydrogen abstraction mainly at the CH_2 and CH sites. The results in fact show that the initial step of the rapid reaction 3 had a very small contribution. Most of the reduction of $Fe^{III}(phen)_3$ took place by one process with $k = 1.3 \times 10^9$ and 2.4×10^9 M^{-1} s^{-1} for the two alcohols, respectively. These rates are too high to be assignable to reactions with $CH_3\dot{C}HC(CH_3)_2OH$ and $(CH_3)_2\dot{C}C(CH_3)_2OH$, respectively, since these are β-hydroxyalkyl radicals and should behave like the radical from *t*-BuOH. The high rate constants observed must be due to the acid-catalyzed conversion of the β-hydroxyalkyl radicals into more reactive species (e.g., by water elimination or 1,2-OH shift, which are faster for the above radicals than for the radical from *t*-BuOH).[20]

Similar experiments were carried out with ethylene glycol. The reactions of H and OH with this alcohol produce $HOCH_2\dot{C}HOH$ which undergoes acid-catalyzed water elimination to form $\dot{C}H_2CHO$.[21] The experimental results indicated only a low yield ($G \sim 1$) of rapid reduction by $HOCH_2\dot{C}HOH$, probably occurring in competition with the water elimination process. The $\dot{C}H_2CHO$ is known to be an oxidizing species and does not appear to react with the complex in the pulse radiolysis time scale ($k < 10^6$ M^{-1} s^{-1}). A very slow addition reaction may be possible.

Radicals from Carboxylic Acids. Acetic acid reacts somewhat rapidly with OH ($k = 3 \times 10^7$ M^{-1} s^{-1})[15]

$$CH_3CO_2H + OH \rightarrow \dot{C}H_2CO_2H + H_2O \qquad (11)$$

but not with H ($k = 8 \times 10^4$ M^{-1} s^{-1}).[14] At the concentrations used (1.5–4.0 M acetic acid with $(2–6) \times 10^{-4}$ M $Fe^{III}(phen)_3$) >90% of the OH radicals and <15% of the H atoms react with CH_3CO_2H. The kinetic traces show an initial rapid reaction 3 with $G \approx 3$ as expected, followed by a slow reaction attributed to

$$Fe^{III}(phen)_3 + \dot{C}H_2CO_2H \rightarrow Fe^{II}\ \text{complex} \qquad (12)$$

Reaction 12 did not take place quantitatively; an overall yield of only $G \sim 4.5$ was observed in the pulse radiolysis, indicating partial disappearance of $\dot{C}H_2CO_2H$ via radical–radical reactions. The observed rate constant for the slow step was 2.3×10^6 M^{-1} s^{-1}, but because the yield of reaction 12 was only $G \sim 1.5$, i.e., ~50% of that expected, k_{12} is estimated to be $\sim 1.2 \times 10^6$ M^{-1} s^{-1}.

Pivalic acid behaved in a manner similar to *t*-BuOH. It reacts with OH to produce $\dot{C}H_2C(CH_3)_2CO_2H$, but only very slowly with H. Therefore, initial reduction of $Fe^{III}(phen)_3$ by H was observed, again with $k = 4.0 \times 10^9$ M^{-1} s^{-1}, and was followed by a slower step due to reaction of the complex with $\dot{C}H_2C(CH_3)_2CO_2H$. The rate constant for the latter step was 7.2×10^7 M^{-1} s^{-1} and the overall yield was $G \sim 6$.

Isobutyric acid reacts with OH and partially with H as well. The initial rapid reaction 3 was found to occur with $G = 1.0–1.5$ depending on the relative concentrations of $Fe^{III}(phen)_3$ and isobutyric acid. The slower reduction step gave $k = 6.3 \times 10^7$ M^{-1} s^{-1} and the overall yield in the pulse radiolysis reached $G = 5.2$. The rate constant cannot be assigned to a single radical since isobutyric acid is known[22] to produce both $(CH_3)_2\dot{C}CO_2H$ and $\dot{C}H_2CH(CH_3)CO_2H$ (1:1) upon reaction with OH (the reaction with H probably favors the former).

Radicals from Hydrocarbons and Alkyls Bromides. In an attempt to measure the rate constants for reaction of alkyl radicals with $Fe^{III}(phen)_3$, solutions of the latter were saturated with either a hydrocarbon or an alkyl bromide. Saturation with methane was found to have a negligible effect on the kinetics and yields as compared with those observed under N_2 bubbling. Apparently, the solubility and reactivity of CH_4 are too low to lead to any appreciable formation of $\dot{C}H_3$ under our experimental conditions. On the other hand, CH_3Br is more soluble and much more reactive toward H

$$CH_3Br + H \rightarrow \dot{C}H_3 + HBr \qquad (13)$$

($k_{13} \sim 10^8$ M^{-1} s^{-1}) to yield predominantly $\dot{C}H_3$ radicals. It is also expected to react with OH, but to form a different radical.

$$CH_3Br + OH \rightarrow \dot{C}H_2Br + H_2O \qquad (14)$$

Experiments in the presence of CH_3Br showed only one reduction step with a yield of $G \sim 3$ and $k \sim 3 \times 10^8$ M^{-1} s^{-1}. Since this result was not affected by the presence of 1 M *t*-BuOH, which would favorably compete with reaction 14 but not 13, we conclude that the radical reacting with the complex was produced by the H atom reaction (13), i.e., $\dot{C}H_3$. The $\dot{C}H_2Br$ radical produced by reaction 14 thus appears to reach much more slowly and its reaction was not observed in the pulse radiolysis.

Experiments with ethane showed reduction of $Fe^{III}(phen)_3$ with nearly a full yield ($G \sim 5.4–5.8$) and $k \sim 1 \times 10^9$ M^{-1} s^{-1}. This process is assigned to the reaction of $CH_3\dot{C}H_2$ (produced from C_2H_6 + OH and C_2H_6 + H) with the complex. This assignment is confirmed by experiments with ethylene. In this case the reactions of H and OH (both very rapid)[14,15] produce $CH_3\dot{C}H_2$ and $\dot{C}H_2CH_2OH$, respectively. Two reduction steps were observed in the presence of ethylene, with $k \sim 1 \times 10^9$ and $k \sim 1 \times 10^8$ M^{-1} s^{-1}. The first is again assigned to reaction of $CH_3\dot{C}H_2$ while the latter must be due to $\dot{C}H_2CH_2OH$. This was further confirmed by the addition of 1 M *t*-BuOH which competes efficiently for OH but not H. Thus, the reduction by the ethyl radical with $k = 1 \times 10^9$ M^{-1} s^{-1} was still present but the slower step was replaced by the reaction of the $\dot{C}H_2C(CH_3)_2OH$ radical from *t*-BuOH with $k = 1.5 \times 10^7$ M^{-1} s^{-1} (as found above). Further confirmation was obtained from experiments with ethyl bromide. As described in reactions 13 and 14, CH_3CH_2Br should yield predominantly $CH_3\dot{C}H_2$ by reaction with H ($k = 1.7 \times 10^8$ M^{-1} s^{-1}) and $CH_3\dot{C}HBr$ + $\dot{C}H_2CH_2Br$ by reaction with OH. All of these radicals were found to reduce $Fe^{III}(phen)_3$ with $k \sim (1–2) \times 10^9$ M^{-1} s^{-1}. In order to distinguish between them we added 1 M *t*-BuOH as an OH scavenger which will prevent the formation of $CH_3\dot{C}HBr$ and $\dot{C}H_2CH_2Br$. In this case we observed the reduction by $CH_3\dot{C}H_2$ ($G \sim 3$ and $k \sim 1 \times 10^9$ M^{-1} s^{-1}) followed by the slow reduction with $\dot{C}H_2C(CH_3)_2OH$ ($k \sim 1 \times 10^7$ M^{-1} s^{-1}).

From all the above experiments it may be concluded that the rate constants for reduction of $Fe^{III}(phen)_3$ by $\dot{C}H_3$ and $CH_3\dot{C}H_2$ radicals are $\sim 3 \times 10^8$ and $(1.0 \pm 0.3) \times 10^9$ M^{-1} s^{-1}, respectively.

Aromatic Adduct Radicals. Benzene and benzoic acid react very rapidly with both OH and H to form the cyclohexadienyl type radicals.[23] All these radicals were found to react quantitatively with $Fe^{III}(phen)_3$ with rate constants of 2.4×10^9 and 2.0×10^9 M^{-1} s^{-1} for the cases of benzene and benzoic acid, respectively. As mentioned above, the phenanthroline adducts reduce $Fe^{III}(phen)_3$ about an order of magnitude more slowly.

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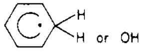
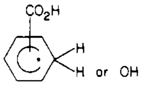
TABLE III: Rate Constants for Reaction of $Fe^{III}(phen)_3$ with Various Radicals in Aqueous Solutions

radical	k, M^{-1} s^{-1}
H	$(4.0 \pm 0.5) \times 10^9$
OH	$\sim 7 \times 10^9$
$\dot{C}H_2OH$	$(5 \pm 1) \times 10^9$
$CH_3\dot{C}HOH$	$(5 \pm 1) \times 10^9$
$CH_3CH_2\dot{C}HOH$	$(3.2 \pm 0.4) \times 10^9$
$(CH_3)_2\dot{C}OH$	$(4.1 \pm 0.5) \times 10^9$
$\dot{C}H_2C(CH_3)_2OH$	$(1.5 \pm 0.2) \times 10^7$
$\dot{C}H_2CHO$	$<1 \times 10^6$
$\dot{C}H_2CO_2H$	$(1.2 \pm 0.2) \times 10^6$
$\dot{C}H_2C(CH_3)_2CO_2H$	$(7.2 \pm 1.0) \times 10^7$
$(CH_3)_2\dot{C}CO_2H$ $\dot{C}H_2CH(CH_3)CO_2H$	$(6.3 \pm 0.9) \times 10^7$
$\dot{C}H_3$	$\sim 3 \times 10^8$
$CH_3\dot{C}H_2$	$(1.0 \pm 0.3) \times 10^9$
$\dot{C}H_2CH_2OH$	$(1.5 \pm 0.5) \times 10^8$
$\dot{C}H_2Br$	$\leqslant 10^7$
$(CH_3\dot{C}HBr + \dot{C}H_2CH_2Br)$	$\sim 1 \times 10^9$
	$(2.4 \pm 0.4) \times 10^9$
	$(2.0 \pm 0.4) \times 10^9$
$S\dot{O}_4^-$	$<10^7$
Cl_2^-	$<10^7$

Kinetics of Reduction in Aqueous Solutions. The rate constants discussed above are summarized in Table III. They indicate that the strong oxidant $Fe^{III}(phen)_3$ is reduced by a wide variety of radicals by different mechanisms. Not only is it reduced by the typically reducing α-hydroxyalkyl radicals with nearly diffusion-controlled rate constants, but also by a typical oxidizing radical—the OH. Obviously, the latter adds rapidly to phenanthroline and the adduct radical reduces the metal center within a very short time ($\ll 1$ μs). That the latter reaction is favorable and rapid is demonstrated by the bimolecular reduction of $Fe^{III}(phen)_3$ with OH and H adducts of phenanthroline and other aromatics ($k \sim 10^9$ M^{-1} s^{-1}). Other oxidizing radicals that do not add rapidly, $S\dot{O}_4^-$, Cl_2^-, and $\dot{C}H_2CHO$, were not found to react with the $Fe^{III}(phen)_3$ in the pulse radiolysis experiments.

While α-hydroxyalkyl reduce $Fe^{III}(phen)_3$ rapidly ($(3\text{–}5) \times 10^9$ M^{-1} s^{-1}) by outer-sphere electron transfer, β-hydroxyalkyl and β-carboxylalkyl radicals react more slowly ($10^7\text{–}10^8$ M^{-1} s^{-1}) and probably via an inner-sphere reaction. The carboxymethyl radical reacts more slowly (1.2×10^6 M^{-1} s^{-1}) and the formylmethyl even more so ($<10^6$ M^{-1} s^{-1}). Clearly, electron withdrawing substituents on the alkyl retard the reaction quite dramatically, as expected for a reaction in which the alkyl serves as an overall electron donor, even if via an inner-sphere mechanism.

Solvent Effects. The rate constants determined for the reactions of methyl and ethyl radicals with $Fe^{III}(phen)_3$ in aqueous solutions are much higher than those found[4] in acetonitrile solutions. To confirm the existence of this large solvent effect it is necessary to carry out pulse radiolytic measurements in acetonitrile solutions. The results of these experiments are also important in view of the use of $Fe^{III}(phen)_3$ as an oxidant for alkylmetals[24] and alkyl radicals[4] in this solvent.

In spite of the importance of acetonitrile as a polar aprotic solvent only a few pulse radiolysis studies have been carried out in this system.[25-30] As initial steps in the radiolysis of CH_3CN the following reaction scheme has been proposed[27-30]

$$CH_3CN \rightarrow CH_3CN^* + CH_3CN^{+\cdot} + e^- \quad (15)$$

$$e^- + CH_3CN \rightarrow CH_3CN^{-\cdot} \quad (16)$$

$$CH_3CN^{-\cdot} + CH_3CN \rightarrow (CH_3CN)_2^{-\cdot} \quad (17)$$

$$CH_3CN^{+\cdot} + CH_3CN \rightarrow \dot{C}H_2CN + CH_3CNH^+ \quad (18)$$

The G value of oxidizing species from experiments with appropriate scavengers was extrapolated to be 0.2–0.3;[28] for reducing species $G = 1.03$,[29] and for excited species $G \sim 0.1\text{–}0.3$.[26,29] γ Radiolysis of $Fe^{III}(phen)_3$ in CH_3CN manifested a clear reduction of Fe^{III} to Fe^{II} in the complex; the spectrum of the Fe^{III} complex gradually changed to the $Fe^{II}(phen)_3$ spectrum with well-defined isobestic points. The initial G value for this reduction was 5.3 in solution saturated with O_2, N_2O, or N_2. This is in line with the above findings that all types of radicals react with $Fe^{III}(phen)_3$ to bring about an overall reduction of the iron.

The observation of the kinetics of reduction in pulse radiolysis was more complicated. In the systems saturated with O_2 or N_2O, the reduction of the complex occurred in several steps, rather difficult to separate, with rate constants varying from 10^{10} to $<10^6$ M^{-1} s^{-1}. The maximum G value for reduction observed in pulse radiolysis was ~ 3.5. In the system saturated with N_2 only one fast reduction step was observed, with $k = 1 \times 10^{10}$ M^{-1} s^{-1} and a yield of $G = 2.3$. The lower yields found in the pulse radiolysis experiments are due to increased competition of radical–radical reactions. Nevertheless, the G value for Fe^{III} reduction surpassed the yield of reducing species in acetonitrile[29] by at least a factor of 2. In an attempt to study the reaction of $\dot{C}H_3$ in acetonitrile, we saturated this solvent with methyl bromide, which is expected to react with the primary reducing species and produce methyl radicals. The first fast step of reduction was found to be decreased in yield to $G \sim 0.5\text{–}0.7$ and was followed by a very slow reaction with rate constant of the order of $10^4\text{–}10^5$ M^{-1} s^{-1}, the total G value reaching $\sim 3\text{–}4$. This low rate constant, although it is in the range of the value found previously[4] for the reaction of methyl radicals in acetonitrile solution, cannot be ascribed to this reaction. Firstly, the yield exceeds that expected for methyl radicals (i.e., $G = 1$ for primary reducing species) and, secondly, methyl radicals under the pulse radiolysis conditions (initial concentrations of several micromolar) are expected to react with each other very rapidly ($k = 5 \times 10^9$ M^{-1} s^{-1})[31] and will disappear faster than the observed reduction of $Fe^{III}(phen)_3$. This slow reduction is ascribed, therefore, to other long-lived species or final products. It is important to point out, however, that reaction of $\dot{C}H_3$ with the complex is not occurring in acetonitrile on a time scale similar to that in water, and is probably very much slower.

Mechanism of Reaction. To distinguish between the outer-sphere electron transfer and an inner-sphere reaction (involving radical addition, electron transfer, and deprotonation) it is important to analyze the reduced complex for the possible presence of addition products. Solutions of $Fe^{III}(phen)_3$ in water, containing 0.1 M H_2SO_4 and various organic additives (*i*-PrOH, *t*-BuOH, or acetic acid) were γ irradiated to approximately 100% reduction and the products were analyzed as described before[4]. In all of these cases, the products did not contain any measurable amount of the alkyl substituted phenanthroline. This result is expected in the case of *i*-PrOH, since the $(CH_3)_2\dot{C}OH$ radical is known to react in most cases by an outer-sphere electron transfer. However, the lack of addition products with *t*-BuOH or acetic acid was at first somewhat surprising, since the $\dot{C}H_2C(CH_3)_2OH$ and $\dot{C}H_2CO_2H$ radicals are not typical reducing species as are the α-hydroxyalkyl radicals. On the other hand, the rate constants observed for these radicals are much higher than those found for addition reactions in acetonitrile.[4] These findings, along with the higher rate constants observed for Me and Et in water, as compared with acetonitrile solutions, point to the effect of water in promoting the electron-transfer route.[32] This overall electron

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transfer with alkyl radicals is not necessarily an outer-sphere reaction as is the case with α-hydroxyalkyl. More likely it involves intermediate coordination of the alkyl to the iron, either as a seventh coordinate or replacing one of the phenanthroline nitrogens temporarily. The latter process is more likely to occur in water under our experimental conditions, where the complex exists in equilibrium with a small amount of free phenanthroline, than in acetonitrile. This fast route predominates in water and makes the slow addition of alkyl radicals to the phenanthroline carbon an unlikely process.

This suggested mechanism for alkyl radicals does not rule out addition of other types of radicals to the phenanthroline carbon even in water. When such addition is known to take place very rapidly, it may in fact predominate. For example, the fast reduction of $Fe^{III}(phen)_3$ by OH radicals cannot occur except via addition of OH to phenanthroline followed by intramolecular electron transfer. The same mechanism may hold for the reaction of H atoms, where addition to aromatics is known also to be very rapid, although in this case the other mechanisms may be applicable as well.

Registry No. 4-Mephen, 31301-28-7; 5-Mephen, 3002-78-6; 4,7-diMephen, 3248-05-3; 2,9-diMephen, 484-11-7; phen hydrochloride, 22802-96-6; 4-Mephen hydrochloride, 97704-91-1; 5-Mephen hydrochloride, 97704-92-2; 4,7-diMephen hydrochloride, 97704-93-3; 2,9-diMephen hydrochloride, 41066-08-4; $Fe(phen)_3{}^{3+}$, 13479-49-7; CH_3CN, 75-05-8; H, 12385-13-6; OH, 3352-57-6; $\dot{C}H_2OH$, 2597-43-5; $CH_3\dot{C}HOH$, 2348-46-1; $CH_3CH_2\dot{C}HOH$, 5723-77-3; $(CH_3)_2\dot{C}OH$, 5131-95-3; $\dot{C}H_2C(CH_3)_2OH$, 5723-74-0; $\dot{C}H_2CHO$, 4400-01-5; $\dot{C}H_2CO_2H$, 2887-46-9; $\dot{C}H_2C(CH_3)_2CO_2H$, 26299-74-1; $(CH_3)_2\dot{C}CO_2H$, 2597-39-9; $\dot{C}H_2CH(CH_3)CO_2H$, 2887-38-9; $\dot{C}H_3$, 2229-07-4; $CH_3\dot{C}H_2$, 2025-56-1; $\dot{C}H_2CH_2OH$, 4422-54-2; $\dot{C}H_2Br$, 16519-97-4; $CH_3\dot{C}HBr$, 16520-14-2; $\dot{C}H_2CH_2Br$, 16520-00-6; $S\dot{O}_4{}^-$, 12143-45-2; $Cl_2{}^-$, 12595-89-0; cyclohexadienyl, 12169-67-4; 6-hydroxycyclohexadienyl, 11084-15-4; carboxycyclohexadienyl, 97731-50-5; carboxy-6-hydroxycyclohexadienyl, 97731-51-6.

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(32) For another example of the differences in the redox behavior of iron complexes in water and acetonitrile, see: Sugimoto, H.; Sawyer, D. T. *J. Am. Chem. Soc.* **1984**, *106*, 4283.

Heat Capacities of Aqueous Argon from 306 to 578 K

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Using a flow calorimeter, we have been able to measure directly the apparent molar heat capacity of aqueous argon from 306 to 578 K for the first time. The partial molar volume at infinite dilution of aqueous argon was also measured at 17.4 MPa and 298 K with a new vibrating tube densimeter and was found to be 30.5 ± 1.4 $cm^3\ mol^{-1}$. The partial molar heat capacity at infinite dilution does decrease as expected for a hydrophobic solute as the temperature is increased to approximately 430 K. Above this temperature, however, the partial molar heat capacity begins to increase and appears to be headed toward positive infinity. The surprising fact is the relatively low temperature at which the steep rise begins.

Introduction

A great interest in the thermodynamic properties of aqueous solutions of hydrophobic molecules has existed for quite some time. Frank and Evans in 1945 were some of the first to point out the striking properties of these solutions.[1] One of the observations they made was that the entropy of aqueous argon was mugh higher than expected. The large entropy was attributed to the formation of a more hydrogen-bonded structure around the solute, and the unusually large partial molar heat capacity was attributed to a decrease in the extent of the solvent hydrogen bonding with increasing temperature. This led to the expectation of decreasing heat capacities with increasing temperature for hydrophobic solutes.

Many low-temperature solubility studies have been performed on the noble gases. Partial molar heat capacities calculated from the appropriate second derivatives of the solubility data follow the general trend expected for a hydrophobic solute. In recent years solubilities at high temperatures have been measured[2,3] and the data indicate that the heat capacity continues to decrease up to 520 K. With the flow calorimeter we have been able to make direct measurements of the partial molar heat capacity of aqueous argon for the first time.

Experimental Section

The flow heat capacity calorimeter has been described elsewhere[4] and was modified only to permit filling of the sample loop under pressure. The argon used (Linde) was 99.9% pure and the water used was distilled, deionized water.

The calorimeter measures a power ratio between the solution and water, P_s/P_o, from which a heat capacity ratio may be calculated from

$$c_p/c_{p,w} = [1 + (f\Delta P/P_o)](d_o/d) \tag{1}$$

where f is a correction factor for heat loses, $\Delta P/P_o = (P_s/P_o) - 1$, d_o is the density of water at 298 K and experimental pressure, d is the density of the solution under the same conditions as d_o, and c_p and $c_{p,w}$ are the heat capacities of the solution and water, respectively. The f is obtained by using a 3.00 mol kg^{-1} NaCl solution as a standard.[5] The values of f are given in Table I. The apparent molar heat capacity, $C_{p,\phi}$, may be calculated from the heat capacity ratio by using

$$C_{p,\phi} = c_{p,w}\left[M_2\frac{c_p}{c_{p,w}} + \frac{1}{m}\left(\frac{c_p - c_{p,w}}{c_{p,w}}\right)\right] \tag{2}$$

where m is the molality and M_2 is the molecular mass of the solute. (Note that if the units for m, M_2, and $c_{p,w}$ are mol kg^{-1}, kg mol^{-1}, and J kg^{-1} K^{-1} respectively, then $c_{p,\phi}$ is in J mol^{-1} K^{-1}.) The results are given in Table I. For this instrument the average uncertainty in $\Delta P/P$ is about 0.0003.

The argon solution was prepared by bubbling argon through a 1-L autoclave filled with approximately 900 mL of water for 30 min to displace the air above the water. The autoclave was pressurized with argon and allowed to stand for 24 h and then connected to the sample injection port of the six-port HPLC sample injection valve. The sample loop was filled by using the

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