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Effects of Halide Ions and Carbon Monoxide on the Reactions of Iron(III) with Alkyl Radicals*

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In aqueous solutions in the presence of carbon monoxide, the Fenton-like reactions between $Fe(H_2O)_6^{2+}$ and alkyl hydroperoxides ($RC(CH_3)_2OOH$, R = CH_3, C_2H_5) readily produce acyl radicals, $R\dot{C}O$. For R = CH_3, the resulting acetyl radicals reduce $Fe(H_2O)_6^{3+}$, $k = 6 \times 10^5$ mol^{-1} dm^3 s^{-1}. The reaction of $Fe(H_2O)_6^{3+}$ with $^{\bullet}CH_3$ is much slower, $k \approx 4 \times 10^3$ mol^{-1} dm^3 s^{-1}. Halide ions have an accelerating effect and lead to the formation of halomethanes. The rate constant for the reaction $Fe(H_2O)_5Br^{2+} + {}^{\bullet}CH_3 \rightarrow CH_3Br + Fe(H_2O)_6^{2+}$ is greater than 10^8 mol^{-1} dm^3 s^{-1}.

Key words: carbon monoxide, Fenton reaction, alkyl hydroperoxide, iron, alkyl radicals.

INTRODUCTION

Transition metal complexes react with alkyl radicals by a variety of mechanisms, including electron transfer, atom transfer, and metal-carbon bond formation. Because of the transient nature of most radicals, which typically disappear in self-reactions at close to diffusion-controlled rates, only fast reactions with chosen substrates can compete.

Despite the reasonably high reduction potential for the couple $Fe(H_2O)_6^{3+}$ / $Fe(H_2O)_6^{2+}$, the ion $Fe(H_2O)_6^{3+}$ does not react readily with alkyl radicals, presumably because of the lack of a suitable mechanism. The Fenton-like reactions between $Fe(H_2O)_6^{2+}$ and alkyl hydroperoxides of the type $RC(CH_3)_2OOH$

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* Dedicated to Professor Smiljko Ašperger on the occasion of his 80th birthday.

thus proceed with an overall 1:1 stoichiometry as shown for *tert*-butylhydroperoxide ($(CH_3)_3COOH$ or *t*-BuOOH) in Eqs. (1) to (3).

$$Fe^{2+} + (CH_3)_3COOH \rightarrow FeOH^{2+} + (CH_3)_3CO^{\bullet} \qquad (k_{Fe} = 18.7\ mol^{-1}\ dm^3\ s^{-1})^1 \quad (1)$$

$$(CH_3)_3CO^{\bullet} \rightarrow {}^{\bullet}CH_3 + (CH_3)_2CO \qquad (k_{\beta} = 1.4 \times 10^6\ s^{-1})^2 \quad (2)$$

$$2\ {}^{\bullet}CH_3 \rightarrow C_2H_6 \qquad (k \approx 10^9\ mol^{-1}\ dm^3\ s^{-1})^3 \quad (3)$$

In this paper we explore the effect of two types of reagents – halide ions and carbon monoxide – on the mechanism and stoichiometry of the reactions of $Fe(H_2O)_6{}^{2+}$ with $(CH_3)_3COOH$ and $C_2H_5C(CH_3)_2OOH$. The role of added reagents is to modify either the metal (by complex formation with halide ions) or the alkyl radicals (by addition of CO) to facilitate the Fe^{III}-radical reaction and make it competitive with the self-reaction of Eq. (3).

EXPERIMENTAL

tert-Butylhydroperoxide (Aldrich) and carbon monoxide (Air Products) were used as received. $C_2H_5C(CH_3)_2OOH$ was synthesized according to a literature procedure.[4] Solutions of $Fe(H_2O)_6{}^{2+}$ were prepared by the reduction of $Fe(H_2O)_6{}^{3+}$ with zinc amalgam.

Organic products (hydrocarbons, biacetyl, and alkyl halides) were analyzed by use of a Hewlett-Packard 5790 A gas chromatograph equipped with a FID detector and packed VZ-10, OV-101, and Porapak-Q columns (Alltech). In most of the experiments the samples were withdrawn from the head space in the spectrophotometric cell after the completion of the reaction. Biacetyl was determined quantitatively by injecting 1–2 microliters of liquid samples onto the column of Porapak-Q. Despite a serious effort, we were not successful in detecting acetic acid, the presumed product of the reaction between $Fe(H_2O)_6{}^{3+}$ and acetyl radicals. Standards, including some with much higher concentrations of CH_3COOH than those expected in the samples, also produced no observable peaks in gas chromatograms.

Kinetic measurements were conducted at 240 nm, where $Fe(H_2O)_6{}^{3+}$ has an absorption maximum, $\varepsilon = 4160\ mol^{-1}\ dm^3\ cm^{-1}$. The amount of $Fe(H_2O)_6{}^{3+}$ produced in each kinetic run was calculated from the absorbance change and related to the initial concentration of the hydroperoxide. These data, combined with a reasonable estimate for the rate constant for radical self-reactions, were used to calculate the rate constant for the reaction of $Fe(H_2O)_6{}^{3+}$ with $CH_3\dot{C}O/CH_3\dot{C}(OH)_2$.

RESULTS AND DISCUSSION

Under typical conditions ($[Fe^{2+}] = (0.5–5) \times 10^{-3}\ mol\ dm^{-3}$, $[t\text{-BuOOH}] = (0.5–1) \times 10^{-4}\ mol\ dm^{-3}$, $0.1\ mol\ dm^{-3}\ HClO_4$, argon atmosphere, 25 °C), $Fe(H_2O)_6{}^{2+}$ reacts with *t*-BuOOH as in Eqs. (1) to (3). Less than 3% of ${}^{\bullet}CH_3$

produced in reaction (2) engages in hydrogen atom abstraction from the hydroperoxide, Eq. (4).[1]

$$^{\bullet}CH_3 + (CH_3)_3COOH \rightarrow CH_4 + (CH_3)_3COO^{\bullet} \tag{4}$$

The 1:1 stoichiometry, required by Eqs. (1–3), is obeyed closely, as shown by the measured yields of $Fe(H_2O)_6^{3+}$ in Table I. The yields get smaller when large concentrations of $Fe(H_2O)_6^{3+}$ are present initially. This situation will be discussed later.

Effect of CO

When the argon atmosphere was replaced by CO, the yields of hydrocarbons ($CH_4 + C_2H_6$) and $Fe(H_2O)_6^{3+}$ decreased, and the apparent rate constant increased, Table I. A new peak, corresponding to biacetyl, appeared in gas chromatograms. These observations are consistent with the formation of acetyl radicals and their subsequent self-reactions and oxidation by $Fe(H_2O)_6^{3+}$, Eqs. (5) to (8). Using $k_{CO} = 2.0 \times 10^6$ mol^{-1} dm^3 s^{-1},[5] we calculate that >95% of $^{\bullet}CH_3$, produced in reactions (1–2), reacts with CO in CO-saturated solutions (0.96 mmol dm^{-3} at 1 atm and 25 °C).[6] The reaction with $Fe(H_2O)_6^{3+}$ may involve either $CH_3\dot{C}O$ or the hydrated form, $CH_3\dot{C}(OH)_2$, produced rapidly in aqueous solutions ($k_6 \approx 10^4$ s^{-1}).[5,7]

$$^{\bullet}CH_3 + CO \rightarrow CH_3\dot{C}O \qquad k_{CO} \tag{5}$$

$$CH_3\dot{C}O + H_2O \rightleftharpoons CH_3\dot{C}(OH)_2 \qquad K \approx 1^{7} \tag{6}$$

$$CH_3\dot{C}O/CH_3\dot{C}(OH)_2 + Fe^{3+} \rightarrow CH_3COOH + Fe^{2+} \tag{7}$$

$$CH_3\dot{C}O/CH_3\dot{C}(OH)_2 \rightarrow \{CH_3COCOCH_3 + CH_3CHO + CH_3COOH\} \tag{8}$$

The oxidation by $Fe(H_2O)_6^{3+}$ and self-reactions of acetyl radicals are competitive processes in the absence of significant amounts of externally added $Fe(H_2O)_6^{3+}$. The kinetic effect of CO on $Fe(H_2O)_6^{2+}$/*t*-BuOOH reaction, monitored at an absorption maximum for $Fe(H_2O)_6^{3+}$ at 240 nm, Table I, is thus caused by gradual decrease in $[CH_3\dot{C}O]_{ss}$ (and increased importance of reaction (7) relative to reaction (8)) as the reaction proceeds. In the later stages the greater fraction of the radicals reacts with $Fe(H_2O)_6^{3+}$, leading to a decrease in the rate of growth of $Fe(H_2O)_6^{3+}$ and producing unrealistically high values of k_1. Because of the subtle interplay between reactions (1), (7) and (8), the kinetic curves do not deviate significantly from those expected

TABLE I

Effect of CO on the kinetics and products of the reaction between $Fe(H_2O)_6^{2+}$ and *t*-BuOOH [a]

conc. / mmol dm^{-3}			Atmosphere	$\Delta[Fe^{3+}]^b$ / mmol dm^{-3}		k / s^{-1}	
$[Fe^{2+}]_0$	$[t\text{-BuOOH}]_0$	$[Fe^{3+}]_0^c$		obs.	calc.[d]	obs.	calc.[d]
1.0	0.10	0.01	Ar	0.107	0.10	0.0182	0.0178
			CO	0.053	0.052	0.0291	0.0296
1.0	0.10	0.089	CO	0.040	0.030	0.031	0.033
1.0	0.10	1.0	Ar	0.089		0.0188	0.0178
			CO	v. small			
0.50	0.10	0.006	Ar	0.103	0.10	0.00855	0.00842
			CO	0.045	0.049	0.0161	0.0162
0.50	0.10	0.053	Ar	0.099	0.10	0.00856	0.00842
			CO	0.033	0.030	0.0158	0.0162
0.50	0.0467	0.014	CO	0.021	0.020	0.0171	0.0158

[a] Conditions: 0.10 mol dm^{-3} $HClO_4$, 25 °C, solutions saturated with either Ar or CO (0.96 mmol dm^{-3}).

[b] Concentration of $Fe(H_2O)_6^{3+}$ produced during the reaction, calculated from the absorbance change at 240 nm.

[c] Introduced with $Fe(H_2O)_6^{2+}$ solution or added deliberately.

[d] Obtained from the traces simulated with k_1 = 18.7 mol^{-1} dm^3 s^{-1}, $k_7 = 6 \times 10^5$ mol^{-1} dm^3 s^{-1}, and $k_8 = 1 \times 10^9$ mol^{-1} dm^3 s^{-1}.

for a first order product build-up, but the calculated rate constant is no longer the pure k_1, as shown in the kinetic simulations described below.

Consistent with the proposed mechanism, the build-up of $Fe(H_2O)_6{}^{3+}$ is diminished when small amounts of $Fe(H_2O)_6{}^{3+}$ are initially present in the reaction mixtures. In an experiment having $[Fe(H_2O)_6{}^{3+}]_0 = [Fe(H_2O)_6{}^{2+}]_0 = 1$ mmol dm^{-3} and $[t\text{-BuOOH}]_0 = 0.10$ mmol dm^{-3}, there was no absorbance change at 270 nm ($\varepsilon_{Fe^{3+}} = 1960$ mol^{-1} dm^3 cm^{-1}), the shortest wavelength that had an acceptably low background absorbance caused by added $Fe(H_2O)_6{}^{3+}$. This result shows that the reaction has become purely catalytic such that the formation of $Fe(H_2O)_6{}^{3+}$, Eq. (1), and the consumption, Eq. (7), cancel each other out.

Experiments with large amounts of added $Fe(H_2O)_6{}^{3+}$ provide convincing support for the proposed mechanism, but are not useful for the determination of k_7. This determination relies on the competition between reactions (7) and (8) and had to be carried out at low $[Fe(H_2O)_6{}^{3+}]$. As a result, $[Fe(H_2O)_6{}^{3+}]$ varied during each experiment that was designed for kinetic purposes. For each run the calculations, Eq. (9), used the observed increase in $[Fe(H_2O)_6{}^{3+}]$, denoted as $\Delta[Fe^{3+}]$, as a measure of $[CH_3\dot{C}O]$ that disappeared in self-reactions, and an average concentration of $Fe(H_2O)_6{}^{3+}$ ($[Fe^{3+}]_{av}$) to convert the approximate pseudo-first order rate constants into second order rate constants. The concentration of acetyl radicals was calculated by use of a steady state approximation and taking $k_8 = 1 \times 10^9$ mol^{-1} dm^3 s^{-1}, a value typical for aliphatic radicals. These calculations yielded an estimate for k_7 of $\approx 10^6$ mol^{-1} dm^3 s^{-1}.

$$k_7 = \frac{2k_8\,[CH_3\dot{C}O]_{SS}\,\dfrac{[t\text{-BuOOH}]_0 - \Delta[Fe^{3+}]}{\Delta[Fe^{3+}]}}{[Fe^{3+}]_{av}} \tag{9}$$

Kinetic simulations were carried out using the program Chemical Kinetics Simulator (IBM). The initial concentrations of all the reactants and the rate constants k_1 (18.7 mol^{-1} dm^3 s^{-1}) and k_8 (1×10^9 mol^{-1} dm^3 s^{-1}) were fixed, and k_7 was floated until the calculated rate constants and absorbance changes matched the observed values. The best agreement was obtained with $k_7 = 6 \times 10^5$ mol^{-1} dm^3 s^{-1}, reasonably close to the value of $\approx 10^6$, estimated by use of Eq. (9). Table I lists the agreement between the measured and calculated values for k_{obs} and $\Delta[Fe^{3+}]$.

From the reduced yield of $Fe(H_2O)_6{}^{3+}$ in a single experiment under argon in the presence of added $Fe(H_2O)_6{}^{3+}$ (1 mmol dm^{-3}), we calculate $k \approx 4 \times 10^3$ mol^{-1} dm^3 s^{-1} for the reaction between $^\bullet CH_3$ and $Fe(H_2O)_6{}^{3+}$. The keto form of acetyl radicals, $CH_3\dot{C}O$, is probably not much more reactive than $^\bullet CH_3$ toward $Fe(H_2O)_6{}^{3+}$, which leads us to suggest that the reduction of $Fe(H_2O)_6{}^{3+}$ in the $Fe(H_2O)_6^{2+}$/*t*-BuOOH/CO reaction is carried out by $CH_3\dot{C}(OH)_2$. The great increase in the reducing power of acetyl radicals upon hydration has been demonstrated previously.[5,7]

In the reaction between $C_2H_5C(CH_3)_2OOH$ and $Fe(H_2O)_6^{2+}$, which generates ethyl radicals in a scheme analogous to Eqs. (1–2), the combined yields of hydrocarbons produced in the self-reactions (ethane, ethene and butane) are significantly lower under CO than under argon. An experiment having 1.5 mmol dm^{-3} $Fe(H_2O)_6^{2+}$ and 0.6 mmol dm^{-3} $C_2H_5C(CH_3)_2OOH$ in 0.2 mol dm^{-3} $HClO_4$ was run at 0 °C to increase the solubility of CO to 1.6 mmol dm^{-3}.[6] The total yield of hydrocarbons was only 10% of the yield obtained in an otherwise identical experiment that was run under argon. These results are comparable to those observed with *t*-BuOOH, suggesting that the rate constants for the capture of CO by $^\bullet CH_3$ and $^\bullet C_2H_5$ are comparable. Similar observations were made earlier in the gas phase, where the two rate constants differ by only a factor of two, even though the absolute values are several orders of magnitude smaller than in solution.[8]

Effect of Halide Ions

When the reaction between *t*-BuOOH and $Fe(H_2O)_6^{2+}$ was conducted in the presence of 0.10 mol dm^{-3} NaBr, the combined yield of CH_4 and C_2H_6 decreased dramatically compared to the experiments under argon. Only one new peak, corresponding to CH_3Br, appeared in gas chromatograms, suggesting that bromide ions facilitate only one major new pathway. Because of the different solubilities and volatilities of alkanes and alkyl halides in water, the peak areas for the two types of compounds are not a direct measure of solution concentrations. Instead, a decrease in $[CH_4 + C_2H_6]$ was taken to represent the amount of CH_3Br produced. Similar experiments were conducted in the presence of chloride ions.

The large effect of halides on the yield and chemical identity of products, Table II, strongly suggests that $Fe(H_2O)_5Br^{2+}$ and $Fe(H_2O)_5Cl^{2+}$ react rapidly with methyl radicals as in Eq. (10).

$$FeX^{2+} + {}^\bullet CH_3 \rightarrow Fe^{2+} + CH_3X \qquad X = Br,\ Cl \tag{10}$$

Solutions of Fe^{III} containing halide ions absorb strongly in the UV, which prevented us from using an excess of Fe^{III}. This and the lack of precise spectral data for various Fe^{III} species involved made it impossible to determine the relevant concentrations needed to calculate the rate constants for reaction (10). A limit of $>10^8$ mol^{-1} dm^3 s^{-1} can be, however, safely placed on the reaction of $Fe(H_2O)_5Br^{2+}$, given that 0.1 mol dm^{-3} Br^- reduces the yield of $[CH_4 + C_2H_6]$ to only ≈5% of that observed in the absence of Br^-. Less than

TABLE II

Effect of Br^- and Cl^- on the yields of hydrocarbons in the reaction of Fe^{III} with $^{\bullet}CH_3$ [a]

Halide (conc. / mol dm^{-3})	$[CH_4 + C_2H_6]$[b]
–	1.3×10^5
NaBr (0.10)	6×10^3
HCl (0.20)	4×10^4
HCl (0.20)	9×10^3 [c]

[a] Fe^{III} and $^{\bullet}CH_3$ were generated in the reaction between 10 mmol dm^{-3} Fe^{2+} and 1 mmol dm^{-3} *t*-BuOOH in 0.20 mol dm^{-3} $HClO_4$ at 25 °C.

[b] Integrated GC areas, arbitrary units.

[c] $[Fe(H_2O)_6^{3+}]_0$ = 4.5 mmol dm^{-3}.

10% of Fe^{III} is present as $Fe(H_2O)_5Br^{2+}$ under our conditions.[9] Similar arguments applied to the data in chloride solutions lead to $k_{10} > (5 \times 10^6)$ mol^{-1} dm^3 s^{-1} for $Fe(H_2O)_5Cl^{2+}$.

We rule out another mechanistic option whereby the accelerating effect of halide ions would be caused by the formation of $(CH_3X)^{\bullet -}$ and its rapid reaction with $Fe(H_2O)_6^{3+}$. Alkyl halide radical anions are extremely short-lived to the point of being practically non-existent, as demonstrated by the fact that the reduction of aliphatic halides takes place by dissociative electron transfer to produce $R^{\bullet}$ and X^- directly without the involvement of observable $(RX)^{\bullet -}$ intermediates.[10]

CONCLUSIONS

Both carbon monoxide and halide ions change the outcome of $Fe(H_2O)_6^{2+}$-hydroperoxide reactions. In the presence of CO, alkyl radicals are converted to acyl radicals which either undergo self-reactions or reduce $Fe(H_2O)_6^{3+}$. The latter reaction prevails in the presence of externally added $Fe(H_2O)_6^{3+}$ so that the $Fe(H_2O)_6^{2+}$/hydroperoxide/CO reaction becomes catalytic, much like the classical Fenton reaction involving $Fe(H_2O)_6^{2+}$, H_2O_2 and oxidizable substrates.

Halide ions greatly accelerate the reaction between iron(III) and alkyl radicals. The reaction yields alkyl halides, most likely by halogen atom transfer between $Fe(H_2O)_5X^{2+}$ and the radicals.

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SAŽETAK

Efekt halogenidnih iona i ugljikova monoksida na reakciju željeza(III) s alkilnim radikalima

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U modificiranoj Fentonovoj reakciji između $Fe(H_2O)_6^{2+}$ i alkilhidroperoksida ($RC(CH_3)_2OOH$, R = CH_3, C_2H_5), u vodenoj otopini u prisutnosti ugljikova monoksida pretežito nastaju acilni radikali, $R\dot{C}O$. Za R = CH_3, nastali acetilni radikali reduciraju $Fe(H_2O)_6^{3+}$, $k = 6 \times 10^5$ dm^3 mol^{-1} s^{-1}. Reakcija $Fe(H_2O)_6^{3+}$ s $^\bullet CH_3$ mnogo je polaganija: $k \approx 4 \times 10^3$ dm^3 mol^{-1} s^{-1}. Halogenidni ioni djeluju ubrzavajuće, što dovodi do nastajanja halogenmetana. Konstanta brzine reakcije $Fe(H_2O)_5Br^{2+} + {}^\bullet CH_3 \rightarrow CH_3Br + Fe(H_2O)_6^{2+}$ veća je od 10^8 dm^3 mol^{-1} s^{-1}.