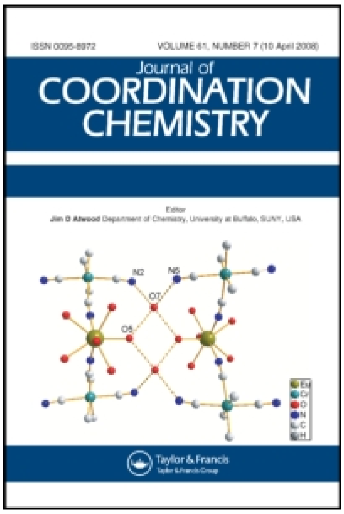

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Mechanism of oxidation of alkyl and superoxo complexes of chromium(III) by aquamanganese(III) ions

Joo-Eun Jee[a]; Oleg Pestovsky[a]; Irene Hidayat[a]; Ewa Szajna-Fuller[a]; Andreja Bakac[a]
[a] Ames Laboratory, Iowa State University, Ames, IA 50011, USA

To cite this Article Jee, Joo-Eun , Pestovsky, Oleg , Hidayat, Irene , Szajna-Fuller, Ewa and Bakac, Andreja(2010) 'Mechanism of oxidation of alkyl and superoxo complexes of chromium(III) by aquamanganese(III) ions', Journal of Coordination Chemistry, 63: 14, 2578 — 2585, First published on: 06 July 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958972.2010.498510

URL: http://dx.doi.org/10.1080/00958972.2010.498510

Journal of Coordination Chemistry
Vol. 63, Nos. 14–16, 20 July–20 August 2010, 2578–2585

Taylor & Francis
Taylor & Francis Group

Mechanism of oxidation of alkyl and superoxo complexes of chromium(III) by aquamanganese(III) ions

JOO-EUN JEE, OLEG PESTOVSKY, IRENE HIDAYAT,
EWA SZAJNA-FULLER and ANDREJA BAKAC*

Ames Laboratory, Iowa State University, 25 Spedding Hall, Ames, IA 50011, USA

(*Received 8 March 2010; in final form 6 April 2010*)

The reaction between aqueous manganese(III) ions, $Mn(H_2O)_6^{3+}$, and $(H_2O)_5CrOO^{2+}$ has a 1 : 1 stoichiometry and generates $Cr(H_2O)_6^{3+}$ and O_2 as products. The mixed second-order rate constant exhibits an $[H^+]$ dependence that identifies the hexaaquamanganese ion as the reactive form at $0.5 \le [H^+] \le 3.0\,\text{mol L}^{-1}$, $k_H = 350 \pm 10\,(\text{mol L}^{-1})^{-1}\,\text{s}^{-1}$. The reactivity of $(H_2O)_5MnOH^{2+}$ is negligible under these conditions, most likely because the much lower reduction potential of this hydrolytic form results in unfavorable thermodynamics for the overall reaction. $Mn(H_2O)_6^{3+}$ also oxidizes a benzylchromium ion, $(H_2O)_5CrCH_2Ph^{2+}$, with a rate constant $k = 273 \pm 13\,(\text{mol L}^{-1})^{-1}\,\text{s}^{-1}$ in $3.0\,\text{mol L}^{-1}$ $HClO_4$. The reaction has a 2 : 1 $[Mn(H_2O)_6^{3+}]/[(H_2O)_5CrCH_2Ph^{2+}]$ stoichiometry and generates benzyl alcohol as the sole organic product. The data are consistent with oxidative homolysis which generates benzyl radicals followed by rapid oxidation of the radicals with the second equivalent of $Mn(H_2O)_6^{3+}$. The unexpected similarity between the rate constants for the $Mn(H_2O)_6^{3+}$ oxidation of $(H_2O)_5CrOO^{2+}$ and $(H_2O)_5CrCH_2Ph^{2+}$ is discussed.

Keywords: Manganese; Oxidation; Chromium; Oxygen; Kinetics

1. Introduction

In our recent study of the kinetics and mechanism of the reactions of benzyl radicals with manganese(III) ions in aqueous and acetic acid solutions [1], we were exploring new ways to generate benzyl radicals under our experimental conditions. As part of that work, we considered the possibility of oxidizing organo-transition metal complexes, such as benzylchromium ions, $(H_2O)_5CrCH_2Ph^{2+}$, with $Mn(H_2O)_6^{3+}$ in H_2O and with Mn(III) acetate in acetic acid. Mn(III) is a powerful oxidant in both solvents. The reduction potential for $Mn(H_2O)_6^{3+/2+}$ is 1.56 V [2], which makes the oxidation of benzylchromium ions thermodynamically feasible, see section 4. We expected the $(H_2O)_5CrCH_2Ph^{2+}/Mn(H_2O)_6^{3+}$ reaction to take place by oxidative homolysis of the organochromium complex, similar to the known [3, 4] reactions of $(H_2O)_5CrCH_2Ph^{2+}$ with $Ru(bpy)_3^{3+}$, $L^1(H_2O)_2Ni^{3+}$ (L^1 = cyclam), and other strong one-electron oxidants, equations (1) and (2). As it turned out, photochemical sources of $PhCH_2^{\bullet}$ were found to

---

*Corresponding author. Email: bakac@iastate.edu

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2010 Taylor & Francis
DOI: 10.1080/00958972.2010.498510

be more convenient for our intended purpose, but the $Mn(H_2O)_6^{3+}/(H_2O)_5CrCH_2Ph^{2+}$ reaction exhibited some interesting features that are described below:

$$(H_2O)_5CrCH_2Ph^{2+} + L^1(H_2O)_2Ni^{3+} \rightarrow Cr(H_2O)_6^{3+} + PhCH_2^{\bullet} + L^1(H_2O)Ni^{2+}, \quad (1)$$

$$PhCH_2^{\bullet} + L^1(H_2O)_2Ni^{3+} \xrightarrow{H_2O} PhCH_2OH + L^1(H_2O)_2Ni^{2+} + H^+. \quad (2)$$

In addition, the reaction of $Mn(H_2O)_6^{3+}$ with a superoxochromium complex, $(H_2O)_5CrOO^{2+}$, was also investigated. This complex has been shown to react with strong oxidants by oxidative cleavage of the Cr–OO bond [5]. The combined data for the reactions of benzyl and superoxo complexes led to a consistent mechanistic picture, as described below.

2. Experimental

Manganese(II) perchlorate (G.F. Smith), manganese(II) acetate, and manganese(III) acetate (both Aldrich) were of highest purity available and used as received. Stock solutions of $Mn(H_2O)_6^{3+}$ were prepared by dissolving manganese(III) acetate (Aldrich) in 3.0 mol L^{-1} $HClO_4$ containing 0.20 mol L^{-1} Mn(II) perchlorate. High concentrations of acid and Mn(II) were necessary to stabilize $Mn(H_2O)_6^{3+}$ against disproportionation [6]. The concentration of $Mn(H_2O)_6^{3+}$ was occasionally checked by spectrophotometric titration with $Fe(H_2O)_6^{2+}$. The concentrations found were always within a few percent of those calculated on the weight basis, and were used to determine the molar absorptivity $\varepsilon = 74\,(\mathrm{mol\,L^{-1}})^{-1}\,\mathrm{cm^{-1}}$ at the 470 nm maximum in 3.0 M $HClO_4$, figure 1. This value is in reasonable agreement with the literature reports which give $\varepsilon = 80\,(\mathrm{mol\,L^{-1}})^{-1}\,\mathrm{cm^{-1}}$ in 3 mol L^{-1} $HClO_4$, $K_a = 1.0$ [2], and $\varepsilon = 60$–$92\,(\mathrm{mol\,L^{-1}})^{-1}\,\mathrm{cm^{-1}}$ at $[H^+] = 1$–6 mol L^{-1}, $K_a = 1.3$–1.7 mol L^{-1} [7].

Solutions of pentaaquabenzylchromium(III) ions, $(H_2O)_5CrCH_2Ph^{2+}$, were prepared from $Cr(H_2O)_6^{2+}$ and benzyl bromide [8], followed by ion exchange on Sephadex C25

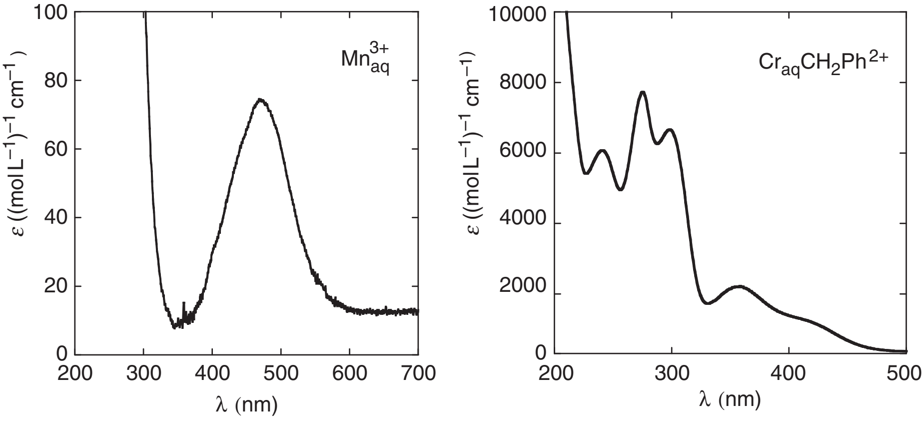

Figure 1. UV-Vis spectra of Mn_{aq}^{3+} in 3.0 mol L^{-1} $HClO_4$ containing 0.20 mol L^{-1} $Mn(H_2O)_6^{2+}$ (left) and of $(H_2O)_5CrCH_2Ph^{2+}$ in 1.0 mol L^{-1} $HClO_4$ (right).

cation exchange resin. The complex was eluted from the column with 0.50 mol L^{-1} $HClO_4$. Solutions of superoxochromium(III) ions, $(H_2O)_5CrOO^{2+}$, were prepared from $Cr(H_2O)_6^{2+}$ and excess O_2 and contained 0.10 mol L^{-1} methanol as a stabilizer [9].

All the experiments with benzylchromium ions were run under strictly air-free conditions (argon atmosphere). No attempt was made to exclude oxygen in the reactions of superoxochromium complex. All the kinetic experiments contained 0.10 mol L^{-1} $Mn(H_2O)_6^{2+}$.

UV-Vis spectral and kinetic measurements were carried out with a Shimadzu 3101 PC spectrophotometer. The kinetic data were fitted to standard kinetic equations with Kaleidagraph 4.03 software. Organic products of the $(H_2O)_5CrCH_2Ph^{2+}/Mn(H_2O)_6^{3+}$ reaction were determined by GC-MS after extraction of spent reaction solutions with CH_2Cl_2. The yields of O_2 in the reaction of $Mn(H_2O)_6^{3+}$ with superoxochromium ions were determined with a YSI oxygen electrode.

3. Results

3.1. *Oxidation of $(H_2O)_5CrCH_2Ph^{2+}$*

In the absence of added reagents, dilute solutions of $(H_2O)_5CrCH_2Ph^{2+}$ decompose by unimolecular homolysis and generate bibenzyl, equations (3) and (4) [10].

$$(H_2O)_5CrCH_2Ph^{2+} + H_2O \rightleftarrows Cr(H_2O)_6^{2+} + PhCH_2^{\bullet}, \tag{3}$$

$$2PhCH_2^{\bullet} \rightarrow PhCH_2CH_2Ph \quad \text{fast.} \tag{4}$$

Upon addition of $Mn(H_2O)_6^{3+}$, the disappearance of $(H_2O)_5CrCH_2Ph^{2+}$ was greatly accelerated, and the product changed to benzyl alcohol, see below. The stoichiometry was determined by adding a limited amount of $(H_2O)_5CrCH_2Ph^{2+}$ (0.71 mmol L^{-1}) to $Mn(H_2O)_6^{3+}$ (2.5 mmol L^{-1}) and then recording the absorbance decrease at 470 nm, where $Mn(H_2O)_6^{3+}$ has $\varepsilon = 74\,(\text{mol L}^{-1})^{-1}\,\text{cm}^{-1}$ in 3.0 mol L^{-1} $HClO_4$, and the chromium product, $Cr(H_2O)_6^{3+}$, has $\varepsilon = 3.2\,(\text{mol L}^{-1})^{-1}\,\text{cm}^{-1}$. The data yielded $\Delta[Mn(H_2O)_6^{3+}]/\Delta[(H_2O)_5CrCH_2Ph^{2+}] = 2.1$. GC-MS analysis showed that $PhCH_2OH$ was generated quantitatively as the sole benzyl-derived product under these conditions, as well as in several other experiments having $[Mn(H_2O)_6^{3+}] = 2$ mmol L^{-1} and $[(H_2O)_5CrCH_2Ph^{2+}] = (0.09\text{–}0.5)$ mmol L^{-1}. The reaction is thus fully described by equation (5):

$$(H_2O)_5CrCH_2Ph^{2+} + 2Mn^{3+} + 2H_2O \rightarrow Cr(H_2O)_6^{3+} + PhCH_2OH + 2Mn^{2+} + H^{+}. \tag{5}$$

The kinetics were monitored at the 356 nm maximum of $(H_2O)_5CrCH_2Ph^{2+}$ ($\varepsilon = 2.2 \times 10^3\,(\text{mol L}^{-1})^{-1}\,\text{cm}^{-1}$) [10], figure 1. The absorbance-time traces were exponential and yielded pseudo-first order rate constants that exhibited linear dependence on the concentration of $Mn(H_2O)_6^{3+}$, figure 2, yielding the rate law in equation (6), with $k_{ox} = 412 \pm 10\,(\text{mol L}^{-1})^{-1}\,\text{s}^{-1}$.

$$-d[CrCH_2Ph^{2+}]/dt = k_{ox}[Mn^{3+}][CrCH_2Ph^{2+}] = k_{obs}[CrCH_2Ph^{2+}]. \tag{6}$$

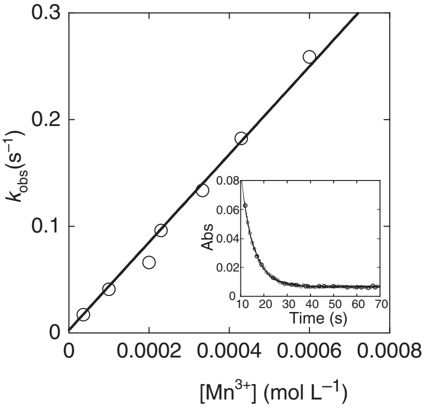

Figure 2. Plot of k_{obs} against the concentration of $Mn(H_2O)_6^{3+}$ for the reaction with $(H_2O)_5CrCH_2Ph^{2+}$ (0.01–0.06 mmol L^{-1}) in 3.0 mol L^{-1} aqueous $HClO_4$ at 0.10 mol L^{-1} $Mn(H_2O)_6^{2+}$. Inset: a typical kinetic trace and an exponential fit at $[Mn^{3+}] = 0.43$ mmol L^{-1}.

Experiments using excess $(H_2O)_5CrCH_2Ph^{2+}$ were complicated by the background homolysis of $(H_2O)_5CrCH_2Ph^{2+}$, equations (3) and (4). Even though this reaction is reasonably slow ($k = 2.6 \times 10^{-3}\,s^{-1}$) [10], the required large excess of $(H_2O)_5CrCH_2Ph^{2+}$ generated sufficient amounts of $Cr(H_2O)_6^{2+}$ and benzyl radicals to interfere with the reaction of interest.

3.2. *Oxidation of $(H_2O)_5CrOO^{2+}$*

The addition of $Mn(H_2O)_6^{3+}$ to solutions of $(H_2O)_5CrOO^{2+}$ led to the disappearance of the characteristic 290 nm band of $(H_2O)_5CrOO^{2+}$ and formation of O_2. The yield of O_2, determined with an oxygen electrode in two separate experiments, was 1.0 ± 0.1 mol per mol of $(H_2O)_5CrOO^{2+}$, as shown in equation (7):

$$Mn(H_2O)_6^{3+} + (H_2O)_5CrOO^{2+} + H_2O \rightarrow Mn(H_2O)_6^{2+} + Cr(H_2O)_6^{3+} + O_2. \qquad (7)$$

In the kinetics experiments, the concentrations of $Mn(H_2O)_6^{3+}$ were always much larger than those of the superoxo complex ($(1\text{–}3) \times 10^{-5}$ mol L^{-1}). The disappearance of $(H_2O)_5CrOO^{2+}$ was monitored at its 290-nm absorption maximum ($\varepsilon = 3000$ $(\text{mol}\,L^{-1})^{-1}\,cm^{-1}$) [9]. The traces were exponential and yielded pseudo-first order rate constants that were corrected for the independently determined self-decay of $(H_2O)_5CrOO^{2+}$ ($k_{self} = 0.0037\,s^{-1}$ in 3.0 mol L^{-1} $HClO_4$ at 0.10 mol L^{-1} $Mn(H_2O)_6^{2+}$) and were plotted against the concentration of $Mn(H_2O)_6^{3+}$ in figure 3. The slope of the linear plot was $273 \pm 13\,(\text{mol}\,L^{-1})^{-1}\,s^{-1}$ in 3.0 mol L^{-1} $HClO_4$.

The dependence on $[H^+]$ was studied in the range 0.46 mol $L^{-1} \le [H^+] \le 3.0$ M at a constant 3.3 mol L^{-1} ionic strength ($HClO_4 + NaClO_4 + Mn(ClO_4)_2$). The reaction was mildly accelerated by H^+ in a nonlinear fashion, figure 4, consistent with $Mn(H_2O)_6^{3+}$ reacting faster than $Mn(H_2O)_5OH^{2+}$. The proposed scheme is shown in equations (8)–(10) and the corresponding rate law in equation (11) [11]. Using $K_a = 1.0$ mol L^{-1} [2], the fit yielded $k_H = 333 \pm 18\,(\text{mol}\,L^{-1})^{-1}\,s^{-1}$ and

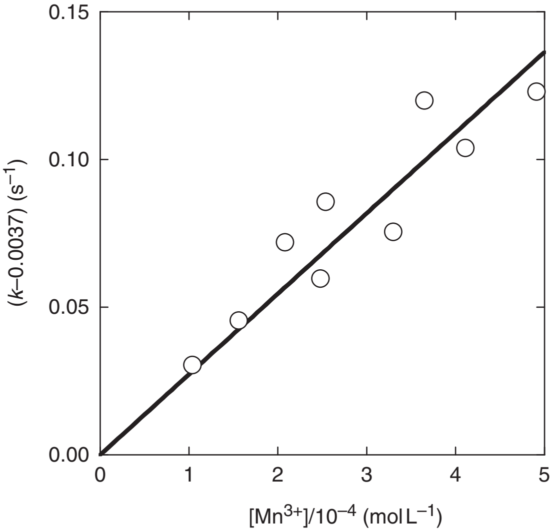

Figure 3. Plot of corrected pseudo-first order rate constants for the reaction of $Mn(H_2O)_6^{3+}$ with $(H_2O)_5CrOO^{2+}$ against $[Mn(H_2O)_6^{3+}]$ in 3.0 mol L^{-1} $HClO_4$ at 25°C in the presence of 0.10 mol L^{-1} $Mn(H_2O)_6^{2+}$.

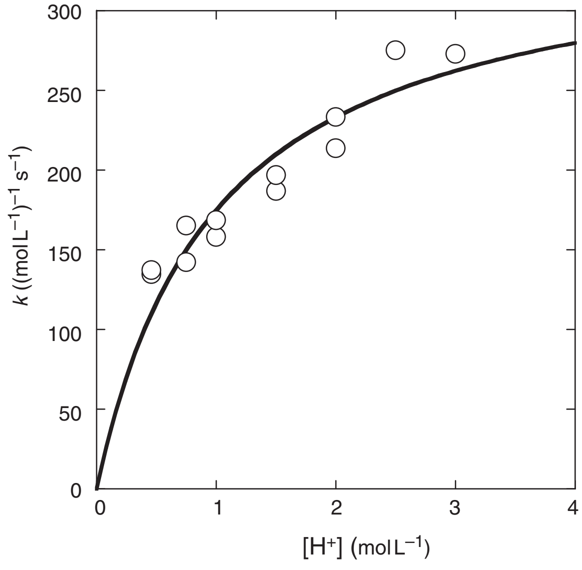

Figure 4. Plot of the second-order rate constant against [H$^+$] for the reaction of $Mn(H_2O)_6^{3+}$ with $(H_2O)_5CrOO^{2+}$. The line is a fit to equation (11) with $k_{OH} = 0$ and $K_a = 1.0$ mol L^{-1}.

$k_{OH} = 23 \pm 21\,(\text{mol L}^{-1})^{-1}\,\text{s}^{-1}$. When the small and highly uncertain k_{OH} term was set to zero, the fit yielded $k_H = 350 \pm 10\,(\text{mol L}^{-1})^{-1}\,\text{s}^{-1}$, figure 4.

$$Mn(H_2O)_6^{3+} \rightleftarrows Mn(H_2O)_5OH^{2+} + H^+ \quad K_a, \tag{8}$$

$$Mn(H_2O)_6^{3+} + (H_2O)_5CrOO^{2+} \rightarrow \text{products} \quad k_H, \tag{9}$$

$$Mn(H_2O)_5OH^{2+} + (H_2O)_5CrOO^{2+} \rightarrow \text{products} \quad k_{OH}, \tag{10}$$

$$\text{Rate} = \frac{k_H[H^+] + K_a k_{OH}}{K_a + [H^+]}[Mn(III)]_{tot}[(H_2O)_5CrOO^{2+}] = k_{obs}[Cr(H_2O)_5OO^{2+}]. \tag{11}$$

Independent experiments in 1.0 and 3.0 mol L^{-1} $HClO_4$ confirmed that the kinetics were independent of $[O_2]$ in the range 0.34–1.11 mmol L^{-1}. The values measured in 3.0 mol L^{-1} H^+ were 303 and 338 (mol L^{-1})$^{-1}$ s^{-1} at the two respective O_2 concentrations. In 1.0 mol L^{-1} $HClO_4$, the values were 168 and 163 (mol L^{-1})$^{-1}$ s^{-1}, respectively.

4. Discussion

The overall 2 : 1 $Mn(H_2O)_6^{3+}/(H_2O)_5CrCH_2Ph^{2+}$ stoichiometry and quantitative formation of benzyl alcohol as the sole product strongly support the mechanism in equations (12) and (13), whereby one-electron oxidation of the organochromium cation results in the cleavage of the Cr–C bond and the formation of benzyl radicals. This is followed by rapid [1] oxidation of benzyl radicals by the second equivalent of $Mn(H_2O)_6^{3+}$, equation (13), to yield the observed products.

$$(H_2O)_5CrCH_2Ph^{2+} + Mn(H_2O)_6^{3+} + H_2O \rightarrow Cr(H_2O)_6^{3+} + {}^{\bullet}CH_2Ph + Mn(H_2O)_6^{2+}, \tag{12}$$

$$PhCH_2^{\bullet} + Mn(H_2O)_6^{3+} + H_2O \rightarrow PhCH_2OH + Mn(H_2O)_6^{2+} + H^+ \quad k_{Mn}. \tag{13}$$

The rate constant k_{Mn} is large enough (10^7 (mol L^{-1})$^{-1}$ s^{-1}) [1] to prevent radical dimerization under the experimental conditions despite the large rate constant for equation (4), $k_{dim} = 1.5 \times 10^9$ (mol L^{-1})$^{-1}$ s^{-1} [12].

The 1 : 1 stoichiometry of the $Mn(H_2O)_6^{3+}/(H_2O)_5CrOO^{2+}$ reaction and the formation of one equivalent of O_2 per mole of $(H_2O)_5CrOO^{2+}$ is also consistent with oxidative homolysis, as shown in equation (14):

$$(H_2O)_5CrOO^{2+} + Mn(H_2O)_6^{3+} + H_2O \rightarrow Cr(H_2O)_6^{3+} + O_2 + Mn(H_2O)_6^{2+}. \tag{14}$$

In the reactions of both $(H_2O)_5CrCH_2Ph^{2+}$ and $(H_2O)_5CrOO^{2+}$, one could envisage an alternative route initiated by homolysis, equation (15), followed by rapid oxidation of the homolysis fragments, equations (13) and (16). This path is clearly ruled out by the observation that the reactions of both chromium complexes are much faster than the independently known homolytic cleavages, and that both exhibit a mixed second-order rate law. The mechanism of equations (15) and (16) would yield first-order kinetics independent of the concentration of $Mn(H_2O)_6^{3+}$.

$$(H_2O)_5CrCH_2Ph^{2+} \text{ (or } (H_2O)_5CrOO^{2+}) \xrightarrow{H_2O} Cr(H_2O)_6^{2+} + {}^{\bullet}CH_2Ph \text{ (or } O_2), \tag{15}$$

$$Cr(H_2O)_6^{2+} + Mn(H_2O)_6^{3+} \rightarrow Cr(H_2O)_6^{3+} + Mn(H_2O)_6^{2+}. \tag{16}$$

The effect of H^+ on the kinetics of the oxidation of the superoxo complex in figure 4 shows that $Mn(H_2O)_6^{3+}$ is the major reactive form of Mn(III). The contribution from the deprotonated form $Mn(H_2O)_5OH^{2+}$ is either minor or negligible. This reactivity pattern is indicative of an outer-sphere process which benefits from the greater oxidizing power of the hexaaqua species, E^0 $((Mn(H_2O)_6^{3+}/Mn(H_2O)_6^{2+}) = 1.56\,V)$ [2, 13]. Similar behavior was observed earlier in the reactions of aquamanganese(III) ions with polypyridine complexes of iron, ruthenium and osmium which cannot react by an inner-sphere mechanism [2]. Macrocyclic nickel complexes and $Fe(H_2O)_6^{2+}$, on the other hand, react at least in part *via* an OH-bridged, inner-sphere path as shown by the presence of a major $1/[H^+]$ term in the rate law.

It is interesting that $(H_2O)_5CrOO^{2+}$ and, by implication, $(H_2O)_5CrCH_2Ph^{2+}$ should react by an outer-sphere mechanism despite the availability of labile positions *trans* to the superoxo and benzyl groups. An OH-bridged transition state is clearly feasible in both cases. The fact that an inner-sphere path does not seem to operate is probably a result of the much lower reduction potential of $Mn(H_2O)_5OH^{2+}$, estimated at about 0.95 V [2], that is, 0.1–0.4 V lower than the estimated potential for $(H_2O)_5CrOO^{3+}/(H_2O)_5CrOO^{2+}$ [14]. The reaction with $Mn(H_2O)_6^{3+}$, on the other hand, has a positive driving force of $\geq 0.15\,V$.

Electrochemical data are not available for $(H_2O)_5CrCH_2Ph^{2+}$, but the facility with which it reacts with $Ni(cyclam)^{3+}$ ($E^0 = 1.0\,V$) [15], $k = 1.9 \times 10^4\,(mol\,L^{-1})^{-1}\,s^{-1}$ [4], shows that it is more easily oxidized than $(H_2O)_5CrOO^{2+}$. Similarly, $Ru(bpy)_3^{3+}$ and ^2E excited state of $Cr(bpy)_3^{3+}$ oxidize $(H_2O)_5CrCH_2Ph^{2+}$ with rate constants in the neighborhood of $10^9\,(mol\,L^{-1})^{-1}\,s^{-1}$, whereas the $Ru(bpy)_3^{3+}/(H_2O)_5CrOO^{2+}$ reaction has a rate constant of only $2.6 \times 10^3\,(mol\,L^{-1})^{-1}\,s^{-1}$. It is not clear whether the reactivity difference between $(H_2O)_5CrCH_2Ph^{2+}$ and $(H_2O)_5CrOO^{2+}$ is the result of kinetics or thermodynamics, but it is surprising that two chromium complexes exhibit almost identical rate constants for their reactions with Mn(III) in $3\,mol\,L^{-1}$ $HClO_4$. Admittedly, the $[H^+]$ dependence was not examined for the benzyl complex, and a change in mechanism cannot be entirely ruled out, but a potential contribution from an inner-sphere process would have the opposite effect and would make the rate constant greater than expected for a purely outer-sphere reaction. $Mn(H_2O)_6^{3+}$ is by far the strongest oxidant [6] used so far in the reactions with these two chromium complexes. Its self-exchange rate constant for electron transfer [2] is not only small, but the values calculated from the Marcus cross-reaction cover a large range, from 10^{-9} to $4 \times 10^{-3}\,(mol\,L^{-1})^{-1}\,s^{-1}$ [2]. The smaller derived values are typically associated with the reactions having a greater driving force. In that respect, our observations follow the same pattern, but more work will be required to fully understand the mechanistic detail.

Acknowledgments

This manuscript has been authored under Contract No. DE-AC02-07CH11358 with the US Department of Energy.

References

[1] J.-E. Jee, A. Bakac. *J. Phys. Chem. A*, **114**, 2136 (2010).
[2] D.H. Macartney, N. Sutin. *Inorg. Chem.*, **24**, 3403 (1985).

[3] A. Bakac, J.H. Espenson. *J. Am. Chem. Soc.*, **110**, 3453 (1988).
[4] T. Katsuyama, A. Bakac, J.H. Espenson. *Inorg. Chem.*, **28**, 339 (1989).
[5] A. Bakac, J.H. Espenson, J.A. Janni. *J. Chem. Soc., Chem. Commun.*, 315 (1994).
[6] D. Richens. *Perspectives Bioinorg. Chem.*, **2**, 245 (1993).
[7] J.P. Fackler, I.D. Chawla. *Inorg. Chem.*, **3**, 1130 (1964).
[8] J.K. Kochi, D.D. Davis. *J. Am. Chem. Soc.*, **86**, 5264 (1964).
[9] A. Bakac. *J. Am. Chem. Soc.*, **122**, 1092 (2000).
[10] R.J. Blau, J.H. Espenson, A. Bakac. *Inorg. Chem.*, **23**, 3526 (1984).
[11] The rate law in equation (11) was derived with the assumption of a fast acid-base pre-equilibrium in equation (8), and the rate-controlling steps in equations (9) and (10). In such a case, $Mn(H_2O)_6^{3+} = [H^+]/(K_a + [H^+])\ [Mn(III)]_{tot}$, and $Mn(H_2O)_5OH^{2+} = K_a/(K_a + [H^+])\ [Mn(III)]_{tot}$.
[12] A.M. Mayouf, H. Lemmetyinen, J. Koskikallio. *J. Photochem. Photobiol. A*, **70**, 215 (1993).
[13] H. Diebler, N. Sutin. *J. Phys. Chem.*, **68**, 174 (1964).
[14] C. Kang, F.C. Anson. *Inorg. Chem.*, **33**, 2624 (1994).
[15] R.I. Haines, A. McAuley. *Coord. Chem. Rev.*, **39**, 77 (1981).