# Reactions of Mn(II) and Mn(III) with Alkyl, Peroxyalkyl, and Peroxyacyl Radicals in Water and Acetic Acid

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The kinetics of oxidation of Mn(II) with acylperoxyl and alkylperoxyl radicals were determined by laser flash photolysis utilizing a macrocyclic nickel complex as a kinetic probe. Radicals were generated photochemically from the appropriate ketones in the presence of molecular oxygen. In both acidic aqueous solutions and in 95% acetic acid, Mn(II) reacts with acylperoxyl radicals with  $k = (0.5-1.6) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and somewhat more slowly with alkylperoxyl radicals,  $k = (0.5-5) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ . Mn(III) rapidly oxidizes benzyl radicals,  $k = 2.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  (glacial acetic acid) and  $3.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  (95% acetic acid). The value in 3.0 M aqueous perchloric acid is much smaller,  $1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ . The decarbonylation of benzoyl radicals in H<sub>2</sub>O has  $k = 1.2 \times 10^6 \text{ s}^{-1}$ .

### Introduction

The interaction of transition metal complexes with free radicals is one of the most widespread occurrences in biology, environment, and laboratory.<sup>1–12</sup> Among the common reactivity modes are metal—element bond formation; oxidation and reduction of the metal center; and metal-catalyzed dimerization, disproportionation, fragmentation, or rearrangement of free or coordinated radicals. Most prevalent are reactions with carbon<sup>13</sup> and oxygen<sup>14</sup> radicals owing to the central role that these two elements hold in chemistry and biology, but sulfur, halogen, nitrogen, and several other types of radicals have also been exhaustively studied.<sup>1–4,7,15,16</sup>

Carbon and oxygen radicals are crucial intermediates in metalcatalyzed oxidations of organic substrates with molecular oxygen and peroxides. One such reaction is the industrially important oxidation of para-xylene to terephthalic acid with O2, catalyzed by cobalt and manganese salts and HBr in acetic acid. The mechanistic picture is far from understood, but some key features have been resolved.<sup>17-23</sup> It is now widely accepted that the reaction generates HBr<sub>2</sub>, which abstracts hydrogen atoms from C-H bonds to generate carbon radicals. In the oxygen atmosphere of the Mid Century (MC) process, carbon radicals are captured by oxygen and are converted to alkylperoxyl and acylperoxyl radicals. Even though these radicals almost certainly react with the cobalt and manganese catalysts, and are crucial in determining the course, selectivity, and rates of the remainder of the oxidation process, the kinetic data for such reactions are scarce. This is in contrast to the wealth of information on the corresponding reactions with well-defined macrocyclic complexes, especially those of cobalt.<sup>13</sup>

Here we report the results of our kinetic and mechanistic study of the reactions of several oxygen and carbon radicals with Mn(II) and Mn(III) acetates in aqueous and acetic acid solutions.

# **Experimental Section**

Glacial acetic acid, manganese(II) acetate, manganese(III) acetate (all Aldrich), phenyl-*tert*-butyl ketone (**K1**), di-*tert*-butyl

ketone (K3) (both Aldrich), phenyl-2-propylphenyl ketone (K2, Ryan Scientific), and dibenzyl ketone (K4, Acros) were used as received. Stock solutions of  ${Mn_{aq}}^{3+}$  were prepared by dissolving manganese(III) acetate (Aldrich) in 3.0 M HClO<sub>4</sub> containing 0.20 M Mn(II) perchlorate. High concentrations of acid and Mn(II) were necessary to stabilize Mn<sub>aq</sub><sup>3+</sup> against disproportionation. Solutions of Mn(III) acetate in acetic acid did not require stabilization by Mn((II). Alkylcobaloximes were prepared by literature procedures.<sup>24,25</sup> Alkylperoxyl and acylperoxyl radicals  $(1-3 \mu M)$  were generated in oxygen-saturated aqueous or mixed acetic acid/water solvents (95:5, v/v) by laser flash photolysis of the appropriate ketones K1-K4 (0.05-0.2 mM) or alkylcobalt precursors (0.05 mM), Chart 1. The concentration of metal complexes in all of the kinetic experiments was always much greater ( $\geq 0.05 \text{ mM}$ ) than the concentration of the radicals generated in the flash. When required, the ionic strength was adjusted with NaClO<sub>4</sub>.

Laser-flash photolysis experiments utilized a laser system based on a Lambda Physik Excimer Pro 2 xenon chloride excimer laser and an Applied Photophysics monitoring system. The 308-nm laser beam (pulse width 10 ns) was set up perpendicular to the monitoring beam provided by a pulsed xenon lamp. The monitoring beam passed through the cell and grating monochromator to a five-stage photomultiplier tube. The output signal was digitized with an Agilent Infinium digital oscilloscope interfaced to an Acorn computer. The kinetic data were fitted to standard kinetic equations with Kaleidagraph 4.03 software.

Organic products of the PhCH<sub>2</sub>'/Mn<sub>aq</sub><sup>3+</sup> reaction were determined by GC-MS after extraction of spent reaction solutions (3 mL) with 3 mL of CH<sub>2</sub>Cl<sub>2</sub>. The concentration of benzyl alcohol was determined from GC peak areas and a calibration curve which was constructed from the data that were also obtained by extraction of 3 mL of known concentration of PhCH<sub>2</sub>OH in 3 M HClO<sub>4</sub> with 3 mL of CH<sub>2</sub>Cl<sub>2</sub>.

# Results

Reaction of  $Mn_{aq}^{2+}$  with Alkylperoxyl and Acylperoxyl Radicals. The chemistry involved in the photochemical generation of alkylperoxyl radicals from ketones, taking K1 as an

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CHART 1: Structures of the Ketones K1-K4 and an Organocobalt Complex Used As Radical Sources in This Work









example, is summarized in Scheme 1. The short-lived  $n\pi^*$ excited state dissociates to benzoyl and tert-butyl radicals with a first-order rate constant of ca.  $10^7 \text{ s}^{-1.26}$  Both carbon radicals are rapidly  $(k \ge 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})^{27}$  intercepted by molecular oxygen and converted to peroxyl radicals, PhC(O)OO' and (CH<sub>3</sub>)<sub>3</sub>COO<sup>•</sup>. Except for partial decarbonylation of PhCH<sub>2</sub>C(O)<sup>•</sup>, which loses CO in several microseconds in both nonaqueous<sup>28,29</sup> and aqueous (see below) solutions, none of the acyl radicals in this work undergo measurable decarbonylation on the time scale of the radical/O<sub>2</sub> reaction.<sup>28,29</sup> Potential partial decarbonylation of PhCH<sub>2</sub>C(O)<sup>•</sup> would diminish the yield of the desired acylperoxyl radicals, but would not interfere with the measurement of the metal/PhCH<sub>2</sub>C(O)OO<sup>•</sup> kinetics since the resulting alkylperoxyl radicals react with metal complexes much more slowly, see below.

Other radicals were generated in similar reactions, as summarized in Table 1. In some cases, several different sources were used to generate the same radical to check the reliability of the method and to confirm that no other chemistry interfered under the experimental conditions. Owing to the strong absorbance of the ketones K1-K3 and the organocobalt complexes in the UV, it was not feasible to directly monitor the growth of Mn(III), which absorbs strongly only below 300 nm. Instead,  $L^{1}Ni^{2+}$  ( $L^{1} = 1,4,8,11$ -tetraazacyclotetradecane) was used as a radical probe, and the formation of the Ni(III) product in reaction 1 was monitored at 370 nm.

$$L^{1}Ni^{2+} + ROO \xrightarrow{k_{Ni}} L^{1}Ni^{III}OOR^{2+}$$
(1)

As shown in the examples of the kinetic traces in Figure 1, there was an initial bleach followed by exponential absorbance increase. The bleach was unexpected because kinetic solutions did not absorb measurably at 370 nm prior to laser-flash experiments. Additional tests showed that small amounts of a new radical source, presumably L<sup>1</sup>NiOO(O)CR<sup>2+</sup> and L<sup>1</sup>NiOOR<sup>2+</sup>, were generated photochemically prior to the laser shot. Most likely, the photolysis of ketones with the analyzing beam during the short time (about 100 ms) between the opening of the shutter and the flash was responsible for initiating (prematurely) the photochemistry of Scheme 1 and capture of the radicals by

 $L^1Ni^{2+}$ . The use of UV filters (absorbance >2 below 360 nm) eliminated the bleach, leaving only the expected exponential absorbance increase following the flash. The rate constants obtained with and without the filters were the same, but the signal was larger in the absence of optical filters. The rest of the experiments were therefore carried out without the filters.

The rate constants for reaction 1 were determined from experiments at several different concentrations of LNi<sup>2+</sup>, typically in the range  $(0.5-8.0) \times 10^{-4}$  M. Under these conditions, and taking PhC(O)OO' as an example, the reaction followed the rate law of eq 2, where  $k_0$  represents the sum of all of the first and pseudofirst order rate constants for the loss of radicals in reactions not involving  $L^1Ni^{2+}$ , and  $k_{Ni}$  is the desired secondorder rate constant for the L<sup>1</sup>Ni<sup>2+</sup>/radical reaction. The slope of the linear plot of  $k_{obs}$  against [L<sup>1</sup>Ni<sup>2+</sup>] for the reaction with PhC(O)OO' in aqueous solutions, Figure 2, yielded the rate constant  $k_{\text{Ni}} = (1.0 \pm 0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

$$-d[PhC(O)OO']/dt = (k_0 + k_{Ni}[L^1Ni^{2+}])[PhC(O)OO']$$
(2)

In the next series of experiments, both Mn<sub>aq</sub><sup>2+</sup> and LNi<sup>2+</sup> were present and competing for the radical. The concentration of  $Mn_{aq}^{2+}$  was varied as much as was experimentally feasible while keeping [L<sup>1</sup>Ni<sup>2+</sup>] constant. Under such conditions, an additional term appears in the rate law, eq 3:

$$-d[PhC(O)OO']/dt = (k_0 + k_{Ni}[L^1Ni^{2+}] + k_{Mn}[Mn^{2+}])[PhC(O)OO'] \quad (3)$$

A plot of  $k_{obs}$  against  $[Mn_{aq}^{2+}]$  yielded a straight line that, for the reaction with PhC(O)OO<sup>•</sup>, had a slope  $k_{\rm Mn} = (1.0 \pm$ 0.1) × 10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup>, Figure 3.

In view of the large and variable concentrations of Mn<sub>aq</sub><sup>2+</sup> in kinetic runs, the effect of ionic strength on the kinetics was explored in several experiments. For the reaction between PhC(O)OO<sup>•</sup> (generated from K1) and  $Mn_{aq}^{2+}$ , the variation of ionic strength in the range 0.10-0.50 M had a minimal effect (<10%) on the rate constant, as expected for a reaction with an uncharged reactant. Subsequent experiments were run at variable ionic strength determined by the concentration of H<sup>+</sup> and reactants.

Experimental observations in 95% acetic acid were similar to those in 0.10 M aqueous HClO<sub>4</sub>, except that the intercepts in the plots of  $k_{obs}$  versus [L<sup>1</sup>Ni<sup>2+</sup>] for acylperoxyl radicals were significantly larger than for aqueous solutions, Figure S1. Under such conditions, an additional pathway, perhaps oxidation of

TABLE 1: Summary of Rate Constants for Reactions<sup>a</sup> of Peroxyl Radicals with L<sup>1</sup>Ni<sup>2+b</sup> and Mn(II)

radical source	radical	$k_{\rm Ni}~(10^8~{ m M}^{-1}~{ m s}^{-1})^c$	$k_{\rm Mn} \left(10^6 \ {\rm M}^{-1} \ {\rm s}^{-1}\right)^c$	solvent
<b>K1</b> and <b>K2</b>	PhC(O)OO*	10	1.0	water, pH 1.0
K3	<sup>t</sup> BuC(O)OO•	10	1.1	water, pH 1.0
$L^1CoC(O)CH_3^{2+b,d}$	$CH_3C(O)OO^{\bullet}$	9.7		water, pH 1.0
K4	PhCH <sub>2</sub> C(O)OO <sup>•</sup>	9.1	0.55	water, pH 1.0
K3	<sup>t</sup> BuC(O)OO•	2.2	1.5	95% AcOH
K1	PhC(O)OO•	2.1	1.6	95% AcOH
(dmgH) <sub>2</sub> (H <sub>2</sub> O)CoCH <sub>3</sub>	CH <sub>3</sub> OO <sup>•</sup>	0.40		95% AcOH
$L^1CoCH_3^{2+b,d}$	CH <sub>3</sub> OO <sup>•</sup>	0.27		water, pH 1.0
(dmgH) <sub>2</sub> (H <sub>2</sub> O)CoCH <sub>2</sub> Ph	PhCH <sub>2</sub> OO <sup>•</sup>	0.37		95% AcOH
K3	'BuOO'	0.14	0.45	95% AcOH
K2	PhCMe <sub>2</sub> OO <sup>•</sup>	0.13	0.18	95% AcOH
<b>K1</b> and <b>K3</b>	'BuOO'	0.025	0.049	water, pH 1.0

<sup>*a*</sup> At 25 °C,  $\lambda_{irr} = 308$  nm,  $\lambda_{det} = 370$  nm, O<sub>2</sub>-saturated. <sup>*b*</sup> L<sup>1</sup> = 1,4,8,11-tetraazacyclotetradecane. <sup>*c*</sup> Estimated standard deviation is 10%. <sup>*d*</sup> Reference 31.



**Figure 1.** Kinetic traces for the reaction of benzoylperoxyl radical from K1 with  $L^1Ni^{2+}$  (left) and with Mn(OAc)<sub>2</sub> (right). Conditions: **[K1]** = 1.6 × 10<sup>-4</sup> M, 95% acetic acid, O<sub>2</sub>-saturated,  $\lambda_{irr}$  = 308 nm,  $\lambda_{det}$  = 370 nm. Experiment in the right-hand panel had 0.16 mM  $L^1Ni^{2+}$  as a kinetic probe.



**Figure 2.** Plot of  $k_{obs}$  against the concentration of  $L^1Ni^{2+}$  for the reaction with PhC(O)OO<sup>•</sup> generated by laser flash photolysis of **K1** (open circles) and **K2** (filled circles) in aqueous 0.10 M HClO<sub>4</sub>.

the solvent, appears to contribute to the disappearance of RC(O)OO<sup>•</sup> radicals. The slopes yielded  $k_{\rm Ni} = (2.1 \pm 0.2) \times 10^8 \, {\rm M}^{-1} \, {\rm s}^{-1}$  (Figure S1) and  $k_{\rm Mn} = (1.6 \pm 0.2) \times 10^6 \, {\rm M}^{-1} \, {\rm s}^{-1}$  (Figure S2). Several other radicals were also examined in both solvents. All the kinetic data are summarized in Table 1.

As expected on the basis of Scheme 1, two successive reactions were observed for each metal complex with each ketone precursor. The faster step, described above, was assigned to the reactions with acylperoxyl radicals, and the slower to alkylperoxyl radicals, consistent with the greater reduction potential<sup>30</sup> of RC(O)OO<sup>•</sup> and also with our earlier observations in the reactions of CH<sub>3</sub>OO<sup>•</sup> and CH<sub>3</sub>C(O)OO<sup>•</sup> with L<sup>1</sup>Ni<sup>2+,31</sup> In every case, the two reactions were sufficiently separated in time to allow the use of simple first-order kinetic treatment for each step. The rate constants for the reactions of alkylperoxyl radicals required the use of higher concentrations of metal complexes,



**Figure 3.** Plot of  $k_{obs}$  against the concentration of  $Mn_{aq}^{2+}$  for the reaction with PhC(O)OO<sup>•</sup> generated by laser flash photolysis of **K1** (open circles) and **K2** (filled circles) in the presence of 0.080 mM  $L^1Ni^{2+}$  as a radical probe in aqueous 0.10 M HClO<sub>4</sub>.

typically  $1-3 \text{ mM } \text{L}^1\text{Ni}^{2+}$  and 0.02-0.10 M Mn(II). Under these conditions, the reactions of acylperoxyl radicals were complete in the first few microseconds, and the slower observed reactions were those of alkylperoxyl radicals.

**Decarbonylation of PhCH<sub>2</sub>CO'.** The rate constant for this reaction was determined by observing the growth of benzyl radicals at 317 nm ( $\epsilon = 5500 \text{ M}^{-1} \text{ cm}^{-1}$ )<sup>32</sup> upon laser flash photolysis of the ketone **K4**. At the monitoring wavelength of 317 nm, the signal-to-noise ratio was less than optimal, and the precision of the data in our estimate was no better than about  $\pm 30\%$ . The more intense maximum at 258 nm ( $\epsilon = 14000 \text{ M}^{-1} \text{ cm}^{-1}$ ) was not useful because of the interfering background absorbance by **K4**.

The sudden absorbance increase during the flash, corresponding to the instantaneous formation of  $PhCH_2^{\bullet}$  in the photochemical step of eq 4 was followed by an exponential growth in absorbance that we associate with reaction 5, in agreement with previous studies in nonaqueous solutions.<sup>28,29,33</sup> At longer times, the bimolecular self-decay of benzyl radicals caused the absorbance to decrease again.

$$PhCH_2COCH_2Ph \xrightarrow{h\nu} PhCH_2CO' + PhCH_2' \qquad (4)$$

$$PhCH_2CO' \rightarrow PhCH_2 + CO$$
 (5)

The experiments were carried out in three solvent systems and yielded the following rate constants for reaction 5: 1.2 ×  $10^6 \text{ s}^{-1}$  (H<sub>2</sub>O), 2.0 ×  $10^6$  (3.0 M aqueous HClO<sub>4</sub>), and 2.3 ×  $10^6$  (glacial acetic acid). The latter value is in good agreement with the reported 2.0 ×  $10^6 \text{ s}^{-1}$  in this solvent.<sup>34</sup>

**Oxidation of Benzyl Radicals with Mn(III).** The kinetic data were obtained by laser flash photolysis of **K4** under airfree conditions (argon) in the presence of  $Mn_{aq}^{3+}$  by monitoring the disappearance of benzyl radicals at 317 nm. The signal-tonoise ratio was again small for reasons mentioned above, so that the precision on these rate constants is also no better than  $\pm 30\%$ .

The spectrum of  $Mn_{aq}^{3+}$  in 3.0 M HClO<sub>4</sub> is shown in Figure S3. The high [H<sup>+</sup>] and  $Mn_{aq}^{2+}$  in these solutions were necessary to stabilize  $Mn_{aq}^{3+}$  against disproportionation, see the Experimental Section. The use of L<sup>1</sup>Ni<sup>2+</sup> as a kinetic probe in reactions of  $Mn_{aq}^{3+}$  with radicals is ruled out by the rapid oxidation of L<sup>1</sup>Ni<sup>2+</sup> by  $Mn_{aq}^{3+}$ . Initial concentrations of the radicals were calculated from the maximum absorbance at 317 nm, reached after the chemistry in eqs 4–5 was completed (2–3 microseconds after the flash).

Under the reaction conditions ([PhCH<sub>2</sub><sup>•</sup>]<sub>0</sub> = 1-3  $\mu$ M, [Mn<sub>aq</sub><sup>3+</sup>] = 0.2-0.9 mM), radical dimerization, eq 6, competes with the PhCH<sub>2</sub><sup>•</sup>/Mn<sub>aq</sub><sup>3+</sup> reaction of eq 7.

$$2PhCH_2 \rightarrow PhCH_2CH_2Ph \quad k_{self} \tag{6}$$

$$PhCH_{2} + Mn_{aq}^{3+} \xrightarrow{H_{2}O, -H^{+}} PhCH_{2}OH + Mn_{aq}^{2+} k_{Mn}$$
(7)

The data were fitted to an expression for mixed first and second order kinetics, eq 8, where Abs<sub>0</sub>, Abs<sub>t</sub>, and Abs<sub>inf</sub> represent absorbances at times zero, *t*, and after completion of the reaction;  $k_{\psi}$  is the pseudo-first-order rate constant  $k_{\rm Mn}$ [Mn<sub>aq</sub><sup>3+</sup>] for reaction 7; and  $k_{\rm self}$  is the rate constant for radical self-reaction. The value of the latter was determined in the absence of added Mn<sup>3+</sup>,  $k_{\rm self} = 2.0 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>, in good agreement with literature values which range from  $1.2 \times 10^9$  to  $3.2 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>.<sup>13</sup>

$$Abs_{t} = Abs_{inf} + \frac{k_{\psi}e^{-k_{\psi}t}(Abs_{0} - Abs_{\infty})}{k_{\psi} + 2k_{self}[PhCH_{2}^{\bullet}]_{0}(1 - e^{-k_{\psi}t})}$$
(8)

Representative traces for benzyl radical self-reaction and the reaction with  $Mn_{aq}^{3+}$  are shown in Figure S4. A plot of  $k_{\psi}$  against the concentration of  $Mn_{aq}^{3+}$ , Figure S5, yielded  $k_{Mn} = (1.0 \pm 0.3) \times 10^7$  M<sup>-1</sup> s<sup>-1</sup>.



**Figure 4.** Kinetic traces at 317 nm for the self-reaction of 9.0  $\mu$ M PhCH<sub>2</sub><sup>•</sup> radicals (left) and oxidation of PhCH<sub>2</sub><sup>•</sup> with 9.6 × 10<sup>-5</sup> M Mn(III) (right) in glacial acetic acid. Conditions: [**K4**] = 0.16 mM, 25 °C,  $\lambda_{exc} = 308$  nm,  $\lambda_{det} = 317$  nm.

Similar experiments in glacial acetic acid yielded traces such as those illustrated in Figure 4 from which we obtained  $k_{self} =$  $(4.3 \pm 0.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . The plot of  $k_{obs}$  against [Mn(III)], shown in Figure S6, yielded  $k_{Mn} = (2.3 \pm 0.3) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . In 95% acetic acid, the values are  $k_{self}$  (4.1 ± 0.3) × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> and  $k_{Mn}$  (3.7 ± 0.4) × 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>.

Organic products were analyzed by GC-MS and NMR. For this purpose, benzyl radicals were generated by steady-state photolysis of **K4** with the 313 nm light. In aqueous solutions (3.0 M HClO<sub>4</sub>) in the absence of Mn(III), bibenzyl was the exclusive product. When the radicals were generated in the presence of 2 mM Mn(III), benzyl alcohol and benzaldehyde were produced, as shown in Figure S7. No bibenzyl was found, as expected from the large rate constants for the Mn(III)/PhCH<sub>2</sub><sup>•</sup> reaction.

In 95% acetic acid, the results were similar to those in aqueous solution, but somewhat unexpectedly, small amounts of bibenzyl were observed even in the presence of Mn(III), Figure S8. This result can be rationalized by the greater steady state concentrations of  $PhCH_2^{\bullet}$  in acetic acid, as judged by the much stronger signals in this solvent in the kinetic experiments and by the known inefficiency of radical formation by ketone photolysis in water.

### Discussion

The data in Table 1 follow a clear pattern. Acylperoxyl radicals react much faster than alkylperoxyl radicals with Mn(II) and L<sup>1</sup>Ni<sup>2+</sup> in both water and 95% acetic acid. This result is consistent with the greater reduction potential of acylperoxyl radicals.<sup>30</sup> Of the two metal complexes, L<sup>1</sup>Ni<sup>2+</sup> is oxidized more rapidly, again in agreement with the reduction potentials,  $E(L^1Ni^{3+/2+}) = 1.0 V^{35}$  in acidic aqueous solutions,  $E(Mn^{III/I}) \sim 1.5 V$  in aqueous solutions,<sup>36</sup> and 1.77 V in acetic acid.<sup>37</sup> The great reactivity of L<sup>1</sup>Ni<sup>2+</sup> toward free radicals has been already demonstrated in earlier studies.<sup>31,38–41</sup>

Overall, the solvent effect on the rate constants in Table 1 is quite modest. This might be surprising in view of the chemical differences between the species involved, and different polarity of the two solvents. In aqueous solutions, manganese ions are present as cationic aqua complexes, but in 95% acetic acid, acetato and/or mixed acetato-aqua species are involved. On the other hand, the reduction potential of Mn(III)/Mn(II) is only moderately higher in acetic acid  $(1.77 \text{ V})^{37}$  than in water (~1.5 V),<sup>36</sup> which accounts for similar kinetics. Also, the lack of major effect of solvent polarity agrees with a kinetic step that involves a metal—radical bond formation, as opposed to an outer-sphere electron transfer that would be facilitated in the more polar solvent. The rate constants obtained for the reaction of Mn(II) with alkylperoxyl radicals in 95% acetic acid,  $(2-4) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , are close to the (extrapolated) value of  $3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  that was reported for the analogous reaction of cyanoisopropylperoxyl radicals, (CN)(CH<sub>3</sub>)<sub>2</sub>COO<sup>•</sup>, at 70 °C.<sup>22,42</sup> That study of a thermal reaction initiated by homolysis of azo-bis-isobutyronitrile (AIBN) in the presence of oxygen and manganese ions employed spectrophotometric product analysis and chemiluminescence to derive the rate constant. The agreement between that work and ours lends credence to both approaches, one based on small, steady-state concentrations of the radicals,<sup>22,42</sup> and the other, reported here, utilizing bursts of radicals generated by laser flash photolysis and L<sup>1</sup>Ni<sup>2+</sup> as a kinetic probe. The latter method does offer an advantage in that it can generate a variety of radicals from appropriate precursors for kinetic studies.

The proposed scheme<sup>22,42</sup> for the ROO'/Mn(II) reaction is shown in eqs 9 and 10.

$$\text{ROO'} + \text{Mn}(\text{II}) \rightleftharpoons \text{ROOMn}(\text{III})$$
 (9)

$$\text{ROOMn(III)} \xrightarrow{\text{H}^+} \text{ROOH} + \text{Mn(III)}$$
(10)

In the previous work it was noticed,<sup>22,42</sup> however, that the kinetics of formation of Mn(III) and ROOH depended inversely on the concentration of Mn(II) in the 0.1–1 mM range. The reported value of  $3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  was obtained by extrapolation to [Mn(II)] = 0. The dependence on [Mn(II)] was explained by an additional "deactivation" step, eq 11, whereby Mn(II) catalyzes the dissociation of ROOMn(III) back to ROO<sup>•</sup> and Mn(II). Our data show that the initial formation of ROOMn(III) is first order in each reactant, which supports the proposal that later steps, such as that in eq 11, are responsible for the inverse dependence on [Mn(II)] in the earlier work.<sup>22,42</sup>

$$ROOMn(III) + Mn(II) \rightarrow ROO' + 2Mn(II) \quad (11)$$

The reaction of benzyl radicals with Mn(III) is fast in aqueous solutions  $(1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1})$  and even faster in acetic acid where the observed rate constant was  $2.3 \times 10^8 \, M^{-1} \, s^{-1}$  (glacial acetic acid) or  $3.7 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup> (95% acetic acid). Our study<sup>43</sup> of the reaction between Mn(III) and bromide in acetic acid yielded biexponential kinetics that led to the conclusion that commercial Mn(III) acetate exists in at least two forms in an approximate 1:1 ratio. The same source of Mn(III) was used in the present study, and we must assume that the manganese reactant is again a mixture of two forms. The kinetic traces were exponential because Mn(III) was used in large excess over the concentration of the radicals but we cannot be certain whether only one or both forms of Mn(III) reacted. If the former is true, then the actual second-order rate constant for that form is up to a factor of 2 greater than the values listed above, which are based on the total (analytical) concentrations of Mn(III). We presume that in aqueous solutions all of the Mn(III) is present as  $Mn(H_2O)_6^{3+}$ and that the observed rate constant applies to the reaction of this ion with PhCH<sub>2</sub>.

The large rate constant for the Mn(III)/PhCH<sub>2</sub><sup>•</sup> reaction in acetic acid suggests that the reactions of Mn(III) with carbon radicals could be involved in the catalytic oxidations of hydrocarbons if the concentrations of Mn(III) approach or exceed those of molecular oxygen. The latter reacts with benzyl and related radicals with diffusion controlled kinetics, but at

higher temperatures, where the solubility of  $O_2$  is significantly reduced, Mn(III)-radical reactions may become competitive.

The kinetics of decarbonylation of benzoyl radicals have been studied earlier by other groups in several solvents,<sup>28,29,33</sup> but no data were available for aqueous solutions. Our value in water,  $1.2 \times 10^6 \text{ s}^{-1}$ , is smaller than any of the values in other solvents. Admittedly, the range is quite narrow, but there is a clear trend of increasing rate constants with decreasing polarity of the solvent.

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**Supporting Information Available:** Figures S1–S8. This information is available free of charge via the Internet at http:// pubs.acs.org.

#### **References and Notes**

(1) Nitroxide Radicals and Nitroxide Based High-Spin Systems; Landolt-Boernstein: Numerical Data and Functional Relationships in Science and Technology-New Series, Group 2; Molecules and Radicals, Magnetics Properties of Free Radicals, Subvolume D.; Alberti, A., Editor; 2005.

- (2) N-Centered Radicals; Alfassi, Z. B. Ed.; 1998.
- (3) S-Centered Radicals; Alfassi, Z. B. Ed.; 1999.
- (4) Chatgilialoglu, C. Organosilanes in Radical Chemistry; 2004.

(5) Gansaeuer, E., Ed.; In Radicals in Synthesis I: Methods and Mechanisms; Top. Curr. Chem. 2006, 263.

(6) Hallwell, B.; Gutteridge, J. M. C. Free Radicals Biol. Med. 1988.
(7) Ingold, K. U.; Roberts, B. P. Landolt-Boernstein Numerical Data

and Functional Relationships in Science and Technology, Group II: Atomic and Molecular Physics, Vol. 13: Radical Reaction Rates in Liquids. Pt. C:

Radicals Centered in N, S, P and Other Heteroatoms. Nitroxyls; 1983.

(8) Free Radicals; Kochi, J. K. Ed.; 1973; Vol. 2.

- (9) Free Radicals in Biology; Pryor, W. A. Ed.; 1980; Vol. 4.
- (10) Togo, H. Advanced Free Radical Reactions for Organic Synthesis; 2003.

(11) Focused Issue. Oxygen/Nitrogen Radicals: Cell Injury and Disease. (Proceedings of a Conference held in 2001.) In *Mol. Cell. Biochem.* 

Vallyathan, V.; Castranova, V.; Shi, X. Eds.; 2002; Vol. 234/235, (1&2). (12) Free Radicals in Chemistry, Biology and Medicine; Yoshikawa, T., Toyokuni, S., Yamamoto, Y., Naito, Y. Eds.; 2000.

(13) Neta, P.; Grodkowski, J.; Ross, A. B. J. Phys. Chem. Ref. Data 1996, 25, 709–1050.

(14) Alfassi, Z. B. Peroxyl Radicals, Wiley: Chichester, 1997.

(15) Neta, P.; Huie, R. E.; Ross, A. B. J. Phys. Chem. Ref. Data 1988, 17, 1027–1284.

(16) Symons, M. C. Phil. Trans. Royal Soc. London, Series B, Biological sciences 1985, 311, 451–472.

(17) Ishii, Y.; Sakaguchi, S.; Iwahama, T. Adv. Synth. Cat. 2001, 343, 393–427.

(18) Jones, G. H. J. Chem. Res. (S) 1981, 207.

- (19) Metelski, P. D.; Espenson, J. H. J. Phys. Chem. A 2001, 105, 5881-5884.
  - (20) Partenheimer, W. Catal. Today 1995, 23, 69-158.
- (21) Partenheimer, W.; Gipe, R. K. ACS Symp. Ser 1993, 523, 81-88.
- (22) Zakharov, I. V. Kinet. Cat. 1998, 39, 485-492.

(23) Zakharov, I. V.; Kumpan, Y. V. Kinetika i Kataliz 1993, 34, 1026–1031.

(24) Schrauzer, G. N. Inorg. Synth. 1968, 11, 61-70.

(25) Yamazaki, N.; Hohokabe, Y. Bull. Chem. Soc. Jpn. 1971, 44, 63–69.

(26) Turro, N. J. Modern Molecular Photochemistry; Benjamin/Cummings Publishing Co.: Menlo Park, 1978; Ch 13.

(27) Marchaj, A.; Kelley, D. G.; Bakac, A.; Esenson, J. H. J. Phys. Chem. 1991, 95, 4440–4441.

(28) Fischer, H.; Paul, H. Acc. Chem. Res. 1987, 20, 200-206.

(29) Tsentalovich, Y. P.; Fischer, H. J. Chem. Soc., Perkin Trans. 1994, 2, 729–733.

(30) Merenyi, G.; Lind, J.; Engman, L. J. Chem. Soc., Perkin Trans. 1994, 2, 2551–2553.

(31) Bakac, A. J. Am. Chem. Soc. 2002, 124, 9136-9144.

(32) Christensen, H. C.; Sehested, K.; Hart, E. J. J. Phys. Chem. 1973, 77, 983–987.

(33) Tsentalovich, Y. P.; Kurnysheva, O. A.; Gritsan, N. P. Russ. Chem. Bull., Int. Ed. 2001, 50, 237–240.

(34) Kurnysheva, O. A.; Gritsan, N. P.; Tsentalovich, Y. P. Phys. Chem. Chem. Phys. 2001, 3, 3677–3682.

(35) Haines, R. I.; McAuley, A. Coord. Chem. Rev. 1981, 39, 77–119.
(36) Bard, A. J.; Parsons, R.; Jordan, J. Standard Potentials in Aqueous

Solution; Marcel Dekker: New York and Basel, 1985; p 430.(37) Jiao, X.-D.; Espenson, J. H. Inorg. Chem. 2000, 39, 1549–1554.

(38) Sauer, A.; Cohen, H.; Meyerstein, D. Inorg. Chem. 1988, 27, 4578–4581.

(39) Kelley, D. G.; Marchaj, A.; Bakac, A.; Espenson, J. H. J. Am. Chem. Soc. **1991**, *113*, 7583–7587.

(40) Kelly, C. A.; Mulazzani, Q. G.; Venturi, M.; Blinn, E. L.; Rodgers, M. A. J. J. Am. Chem. Soc. **1995**, 117, 4911–4919.

- (41) Zilbermann, I.; Maimon, E.; Cohen, H.; Meyerstein, D. Chem. Rev. 2005, 105, 2609–2625.
- (42) Adamyan, V. A.; Geletii, Y. V.; Popova, O. G.; Zakharov, I. V. Kinet. Catal. 1991, 31, 1307–1310.

(43) Jee, J.-E.; Pestovsky, O.; Bakac A., manuscript in preparation.

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