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Rapid Cross-Disproportionation between Superoxometal Ions and Acylperoxyl Radicals

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Alkylperoxyl radicals, $ROO^\bullet$, and the formally analogous superoxometal complexes, $LMOO^\bullet$ (M = metal, L = ligand system), are often generated simultaneously as intermediates in biological and catalytic oxidations of organic materials by molecular oxygen. The rates of hydrogen atom abstraction by at least one superoxometal complex, $Cr_{aq}OO^{2+}$, are not much lower than the rates of hydrogen abstraction by alkylperoxyl radicals.[1] Despite the similar reactivity toward external reagents, the lifetimes of the two species in the absence of added substrates are very different, $Cr_{aq}OO^{2+}$ being the longer lived. Bimolecular self-reactions of alkylperoxyl radicals are typically fast, and even the "slow" ones have rate constants in the thousands.[2,3] Dilute aqueous solutions of $Cr_{aq}OO^{2+}$, on the other hand, can survive for hours at room temperature.

We have now found that a cross reaction between $Cr_{aq}OO^{2+}$ and $ROO^\bullet$ radicals is fast and comparable to self-reactions of alkylperoxyl radicals, eqs 1 and 2.

$$ROO^\bullet + R'OO^\bullet \rightarrow \text{nonradical products} \tag{1}$$

$$ROO^\bullet + Cr_{aq}OO^{2+} \rightarrow \text{nonradical products} \tag{2}$$

To the best of our knowledge, there are no literature data on the mixed cross reactions of the type described in eq 2, although we have proposed such a reaction as a step in the oxidation of trimethylacetaldehyde ($R = C(CH_3)_3CO$) by $Cr_{aq}OO^{2+}$.[1] The need to generate $Cr_{aq}OO^{2+}$ and $ROO^\bullet$ in the same solution and to find a kinetic probe that is compatible with $Cr_{aq}OO^{2+}$ but very reactive toward $ROO^\bullet$ presented a challenge, but we now have direct evidence and kinetic data for the reaction between $Cr_{aq}OO^{2+}$ and acetylperoxyl radicals, $CH_3C(O)OO^\bullet$.

The kinetics of reaction 3 were determined by laser flash

$$CH_3C(O)OO^\bullet + Cr_{aq}OO^{2+} \rightarrow \text{products} \tag{3}$$

photolysis of an organocobalt precursor, $L^1CoC(O)CH_3^{2+}$ (eq 4 ,

$$L^1CoC(O)CH_3^{2+} \xrightarrow[-L^1Co^{2+}]{h\nu} CH_3C^\bullet(O) \xrightarrow[\text{fast}]{O_2} CH_3C(O)OO^\bullet \tag{4}$$

L^1 = [14]aneN_4), in 0.1 M $HClO_4$ in the presence of O_2, $Cr_{aq}OO^{2+}$, and $ABTS^{\bullet-}$ as a kinetic probe (eq 5). This probe was

$$CH_3C(O)OO^\bullet + ABTS^{\bullet-} \xrightarrow{H^+} CH_3C(O)OOH + ABTS^0 \tag{5}$$

selected on the basis of the reduction potentials of the relevant couples, $ABTS^0/ABTS^{\bullet-}$ (1.09 V),[4] $Cr_{aq}OO^{2+}/Cr_{aq}OOH^{2+}$ (~0.97 V at 0.1 M H^+),[5] and $CH_3C(O)OO^\bullet/CH_3C(O)OOH$ (1.53 V at 0.1 M H^+),[6] which favor the oxidation of $ABTS^{\bullet-}$ by $CH_3C(O)OO^\bullet$, but not by $Cr_{aq}OO^{2+}$. In agreement with the thermodynamics, $ABTS^{\bullet-}$ and $Cr_{aq}OO^{2+}$ proved unreactive toward each other, while $CH_3C(O)OO^\bullet$ oxidized $ABTS^{\bullet-}$ rapidly in a successful probe reaction of eq 5.

Typically, a small amount of $ABTS^{2-}$ was injected into an O_2-saturated solution of freshly prepared $Cr_{aq}OO^{2+}$ [1] (0.045−0.40 mM) and $L^1CoC(O)CH_3^{2+}$ (0.10 mM). The oxidation of $ABTS^{2-}$ (0.026 μM) to $ABTS^{\bullet-}$ by $Cr_{aq}OO^{2+}$ was complete in a few seconds, after which time several laser shots were taken in less than 30 s.[7,8]

The absorbance increase at 518 nm followed first-order kinetics. The plot of the pseudo-first-order rate constants against the concentration of excess $Cr_{aq}OO^{2+}$, Figure 1 and eq 6, yielded $k_3 = (1.49 \pm 0.14) \times 10^8$ M^{-1} s^{-1}. The intercept is the sum of all the pseudo-first-order rate constants for the disappearance of $CH_3C(O)OO^\bullet$, including the probe reaction, for which $k_5 = (1.22 \pm 0.04) \times 10^9$ M^{-1} s^{-1}.[9]

$$\begin{aligned}-d[CH_3C(O)OO^\bullet]/dt = (k_3[Cr_{aq}OO^{2+}] + k_5[ABTS^{\bullet-}] + \\ k_{self}[CH_3C(O)OO^\bullet])\,[CH_3C(O)OO^\bullet]\end{aligned} \tag{6}$$

The rate constant for reaction 3 exceeds by several orders of magnitude the geometric mean of the individual rate constants for self-reactions, 6 M^{-1} s^{-1} for $Cr_{aq}OO^{2+}$ [10] and probably >10^8 M^{-1} s^{-1} for $CH_3C(O)OO^\bullet$.[11] The geometric mean rule is used routinely to estimate rate constants for the cross-combination reactions in the gas phase.[12,13] Obviously, this simple rule does not apply to the exergonic $Cr_{aq}OO^{2+}/CH_3C(O)OO^\bullet$ reaction. Our data agree much better with another study which concluded that all cross reactions of $CH_3C(O)OO^\bullet$ are fast.[14]

We utilized the large difference in reactivity between alkylperoxyl and acylperoxyl radicals toward L^1Ni^{2+} [15] to rule out the intermediate formation of $CH_3OO^\bullet$ (and thus $CH_3^\bullet$) in the $CH_3C(O)OO^\bullet/Cr_{aq}OO^{2+}$ reaction. An O_2-saturated solution containing 0.35 mM $Cr_{aq}OO^{2+}$, 0.027 mM L^1Ni^{2+}, and 0.16 mM $L^1CoC(O)CH_3^{2+}$ was flashed (λ_{irr}490 nm), and the absorbance was monitored at 360 nm. At these concentrations, approximately 65% of $CH_3C(O)OO^\bullet$ should react with $Cr_{aq}OO^{2+}$ (eq 3), and the rest with L^1Ni^{2+} as in eq 7 ($R = CH_3C(O)$, $k = 9.7 \times 10^8$ M^{-1} s^{-1}).

$$L^1Ni^{2+} + ROO^\bullet \rightarrow L^1NiOOR^{2+} \tag{7}$$

Had $CH_3OO^\bullet$ been produced, then the $CH_3OO^\bullet/L^1Ni^{2+}$ reaction (eq 7, $R = CH_3$, $k = 2.7 \times 10^7$ M^{-1} s^{-1})[15] should have been observed well after completion of reaction 3 and the $CH_3C(O)OO^\bullet/L^1Ni^{2+}$ reaction. No significant increase in $CH_3OO^\bullet$ above the background level was observed.[16]

For the purpose of product analysis, $CH_3C(O)OO^\bullet$ was generated from CH_3CHO and $Cr_{aq}OO^{2+}$ in O_2 saturated solutions, eqs 8 and

$$CH_3CHO + Cr_{aq}OO^{2+} \xrightarrow{O_2} Cr_{aq}OOH^{2+} + CH_3C(O)OO^\bullet \tag{8}$$

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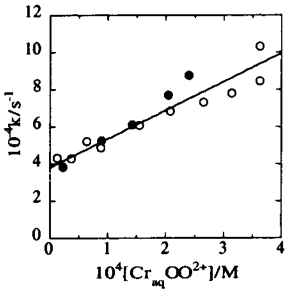

Figure 1. Plot of k_{obs} against $[Cr_{aq}OO^{2+}]$ for the reaction between $Cr_{aq}OO^{2+}$ and $CH_3C(O)OO^{\bullet}$ in the presence of 0.026 mM $ABTS^{\bullet-}$ as a kinetic probe at 0.1 M $HClO_4$ and 25 °C, $\lambda_{irr} = 490$ (dye laser, filled circles) and 355 nm (Nd:YAG laser, open circles).

3.[17] The reaction between 0.23 mM $Cr_{aq}OO^{2+}$ and 0.5 M CH_3CHO in the presence of 5 mM Mn^{2+} produced 0.08 mM $HCrO_4^-$ (35% of initial $Cr_{aq}OO^{2+}$). In the absence of Mn^{2+}, the yield was 0.10 mM (43%) $HCrO_4^-$. The rest of the chromium is believed to be present as the weakly absorbing Cr_{aq}^{3+}. No CO_2 or CH_2O were detected.[18]

The proposed mechanism for reaction 3, Scheme 1, begins with a radical coupling step, similar to the reactions of $Cr_{aq}OO^{2+}$ with N-centered radicals,[19] which have comparable rate constants (10^8–10^9 M^{-1} s^{-1}) despite the great difference in reduction potentials.

Scheme 1

$$CH_3C(O)OO^{\bullet} + Cr_{aq}OO^{2+} \rightarrow [Cr_{aq}OOOOC(O)CH_3^{2+}] \xrightarrow{H^+} O_2 + Cr_{aq}O^{3+} + CH_3COOH \quad (S1)$$

$$2Cr_{aq}O^{3+} \rightarrow Cr_{aq}O^{2+} + HCrO_4^- + 5\,H^+ \quad (S2)$$

$$Cr_{aq}O^{2+} + CH_3CHO \xrightarrow{O_2,H^+} CH_3C(O)OO^{\bullet} + Cr_{aq}^{3+} \quad (S3)$$

$$Cr_{aq}O^{2+} + Cr_{aq}O^{3+} \rightarrow HCrO_4^- + Cr_{aq}^{3+} + 3H^+ \quad (S4)$$

The extrusion of O_2 from the tetraoxo intermediate may initially yield a μ-peroxide,[2] $Cr_{aq}OOC(O)CH_3^{2+}$. If so, the peroxide is short-lived, as judged by the comparable kinetics for the disappearance of $Cr_{aq}OO^{2+}$ and build-up of the final product, $HCrO_4^-$. An intramolecular electron transfer in concert with hydrolysis would readily transform the μ-peroxide to $Cr_{aq}O^{3+}$ and CH_3COOH. Another possibility, the homolytic cleavage to $Cr_{aq}O^{2+}$ and $CH_3C(O)O^{\bullet}$, is ruled out by the absence of CO_2 and $CH_3^{\bullet}$, the decarboxylation products of $CH_3C(O)O^{\bullet}$.

The evidence for $Cr_{aq}O^{3+}$ is indirect and based on the decrease in chromate yields when the $Cr_{aq}OO^{2+}/CH_3C(O)OO^{\bullet}$ reaction was conducted in the presence of Mn^{2+} (a scavenger for $Cr_{aq}O^{2+}$), and an increase in $[HCrO_4^-]$ in the presence of externally added $Cr_{aq}O^{2+}$,[20] a species believed to oxidize Cr(V) to $HCrO_4^-$.[21] In the absence of $Cr_{aq}O^{2+}$, reaction S4 is eliminated, and the disproportionation of eq S2 is the only source of chromate.

The novel reactions of the type uncovered in this work need to be considered as mechanistic steps and a potential source of reactive peroxo and high-valent metal intermediates in both biological systems and metal-catalyzed autoxidation reactions.

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(7) λ_{irr} was either 490 (Phase-R Model DL-1100 dye laser, LD 490 dye) or 355 nm (Nd: YAG laser, Applied Photophysics). λ_{mon} was 518 nm, where ΔAbs was the greatest and where $ABTS^0$ exhibits a maximum with $\epsilon = 3.6 \times 10^4$ M^{-1} cm^{-1}.[4] The traces were averaged and fitted to a first-order rate law.
(8) Solutions containing $Cr_{aq}OO^{2+}$ and $ABTS^{\bullet-}$ were stable for the short periods of time necessary to mix the reagents and carry out laser experiments (~1 min). At longer times, both $Cr_{aq}OO^{2+}$ and $ABTS^{\bullet-}$ decreased measurably.
(9) The kinetics of reaction 5 were determined by laser flash photolysis of $L^1CoC(O)CH_3^{2+}$ in the presence of O_2 and $ABTS^{\bullet-}$, which was in turn generated by oxidation of $ABTS^{2-}$ with stoichiometric amounts of Ce(IV).
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(15) Kinetics of the capture of $CH_3C(O)OO^{\bullet}$ and $CH_3OO^{\bullet}$ by L^1Ni^{2+} were determined by laser flash photolysis of the appropriate organocobalt precursors in O_2-saturated solutions in the presence of L^1Ni^{2+}. The plots of k_{obs} against $[L^1Ni^{2+}]$ yielded $k_7 = (9.7 \pm 0.8) \times 10^8$ M^{-1} s^{-1} for $CH_3C(O)OO^{\bullet}$ and $(2.7 \pm 0.2) \times 10^7$ M^{-1} s^{-1} for $CH_3OO^{\bullet}$.
(16) A small absorbance change on the expected time scale ($k = 600 \pm 300$ s^{-1}, ΔAbs ~0.01) was comparable in size to that in a control experiment having no $Cr_{aq}OO^{2+}$. The amount of $CH_3OO^{\bullet}$ should have been at least three times as large as the observed background if reaction 3 produced a stoichiometric amount of methyl radicals. The background $CH_3^{\bullet}$ was traced to direct photolysis of $L^1CoCH_3^{2+}$, which is the starting material for, and an unavoidable impurity in our samples of $L^1CoCOCH_3^{2+}$.
(17) (a) Hydrogen abstraction from aldehydes by $Cr_{aq}OO^{2+}$ to generate acyl radicals has been studied in detail earlier,[1] although the kinetics of the $CH_3CHO/Cr_{aq}OO^{2+}$ reaction have not been determined. We have now measured $k = 3.5 \times 10^{-3}$ s^{-1} in 0.1 M $HClO_4$ at 0.5 M CH_3CHO and 25° C. At this stage, we are ignoring the possibility that hydrated radicals $CH_3C^{\bullet}(OH)_2$ also may be involved. The amounts must be small, because CH_3CHO is favored over $CH_3C(OH)_2$ in H-abstraction reactions,[17b] and the hydration of $CH_3C^{\bullet}O$ ($k \sim 10^4$ s^{-1})[17b] is too slow to compete with the capture of $CH_3C^{\bullet}O$ by O_2 in O_2-saturated solutions. (b) Schuchmann, M. N.; von Sonntag, C. J. *Am. Chem. Soc.* **1988**, *110*, 5698–5701.
(18) The test for CO_2 was carried out by passing a stream of argon through a spent reaction solution (initial concentrations 0.4 mM $Cr_{aq}OO^{2+}$, 0.5 M CH_3CHO, 5 mM Mn^{2+}, 0.05 M CH_3OH, ~1 mM O_2, 0.1 M $HClO_4$) into slightly alkaline $Ba(ClO_4)_2$. No cloudiness was observed in 30 min. A control solution of 0.1 mM CO_2 yielded a strongly positive test in less than 10 min. The test for CH_2O was based on chromotropic acid.
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(20) A solution of 61 μM $Cr_{aq}O^{2+}$, 42 μM $Cr_{aq}OO^{2+}$, 1.2 mM O_2, and 3 mM CH_3CHO produced 25 μM $HCrO_4^-$. Under these conditions, the $Cr_{aq}O^{2+}/CH_3CHO$ reaction generates acylperoxyl radicals which are captured by $Cr_{aq}OO^{2+}$, eq 3. If Scheme 1 applies, then ~50% of $Cr_{aq}O^{2+}$ will be used to generate $CH_3C(O)OO^{\bullet}$, and the rest will oxidize Cr(V), yielding a total of ~30 μM Cr(VI), close to the observed amount.
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