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Evidence for a Tetraoxo Intermediate in a Reaction Between a Superoxometal Complex and Acylperoxyl Radicals

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The superoxo complex $\mathrm{Cr_{aq}(^{18}O^{18}O)^{2+}}$ reacts with $\mathrm{(CH_3)_3C(O)^{16}O^{16}O^\bullet}$ to generate quantitative yields of mixed-label dioxygen, $\mathrm{^{18}O^{16}O}$, demonstrating that this cross-reaction involves head-to-head interaction between the metal-activated and alkyl-activated dioxygen.

Introduction

Alkylperoxyl radicals $\mathrm{ROO^\bullet}$ (R = alkyl or substituted alkyl) are crucial intermediates in stoichiometric and catalytic oxidations of hydrocarbons with molecular oxygen. The most prevalent reactions of these oxygen-centered radicals are hydrogen atom abstraction from substrates, unimolecular rearrangements and/or dissociation, and bimolecular termination.[1] For the latter, detailed investigations,[1] including ^{18}O[2,3] and deuterium[4,5] labeling experiments and detection of singlet oxygen,[6] have led to the widely accepted mechanistic picture according to which tetraoxo intermediates are generated in head-to-head dimerization, followed by dissociation of $\mathrm{O_2}$ and formation of organic fragments and/or products ($\mathrm{RO^\bullet}$, ROOR, or disproportionation products, depending on the nature of R).[1,7]

$$\mathrm{2R_2CHOO^\bullet \rightarrow [R_2CHOOOOCHR_2] \rightarrow (O_2 + R_2CHOOCHR_2) + (R_2C{=}O + R_2CHOH + O_2) + (2R_2C{=}O + H_2O_2) + (2R_2CHO^\bullet + O_2)} \quad (1)$$

Superoxometal complexes, LMOO^n (L = ligands, M = metal) are inorganic analogues of alkylperoxyl radicals. These species are typically much more persistent than $\mathrm{ROO^\bullet}$ radicals, and show little tendency to decompose in second-order self-reactions.[8] We have, however, observed and reported a fast reaction between one such complex, $\mathrm{Cr_{aq}OO^{2+}}$, and acylperoxyl radicals that were generated either by hydrogen atom abstraction from the aldehyde by $\mathrm{Cr_{aq}OO^{2+}}$ or $\mathrm{Cr_{aq}O^{2+}}$ or photochemically from an organocobalt precursor in the presence of molecular oxygen.[9,10] With acetylperoxyl radicals, $\mathrm{CH_3C(O)OO^\bullet}$, the reaction has $k = 1.49 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$ and yields chromate and $\mathrm{Cr_{aq}}^{3+}$.[9]

A mechanism, eqs 2−4, was proposed to involve head-to-head collision of $\mathrm{Cr_{aq}OO^{2+}}$ and $\mathrm{RC(O)OO^\bullet}$, eq 2, analogous to the self-reactions of acetylperoxyl radicals (eq 3, R = $\mathrm{CH_3}$) followed by dissociation of molecular oxygen, formation of chromium(V) and acetate, and disproportionation of Cr(V). The formation of molecular oxygen has not been confirmed in these experiments, which were carried out in oxygen-saturated solutions to minimize side reactions.[9,10]

$$\mathrm{RC(O)OO^\bullet + Cr_{aq}OO^{2+} \rightarrow [Cr_{aq}OOOOC(O)R^{2+}] \xrightarrow{H^+} OCr(V) + O_2 + RCOOH} \quad (2)$$

$$\mathrm{2RC(O)OO^\bullet \rightarrow RC(O)OOOO(O)CR \rightarrow O_2 + RC(O)OO(O)CR} \quad (3)$$

$$\mathrm{3Cr(V) \rightarrow 2Cr(VI) + Cr(III)} \quad (4)$$

A somewhat more complex scheme, involving a branching intermediate, was proposed for the reaction of $\mathrm{Cr_{aq}OO^{2+}}$ and pivaloylperoxyl radicals, $\mathrm{(CH_3)_3C(O)OO^\bullet}$, but the head-to-head collision and dissociation of molecular oxygen were again the essential steps.[9]

With neither aldehyde, however, could we definitely rule out the alternative head-to-tail attack and elimination of the molecule of $\mathrm{O_2}$ that was initially present as the Cr-bound superoxo group, eq 5. Such a mechanism appears feasible because the position trans to coordinated superoxide is labile and because the head-to-tail attack appears to take place in the bimolecular (albeit slow) self-reaction of $\mathrm{Cr_{aq}OO^{2+}}$, eq 6.[11]

$$\mathrm{RC(O)OO^\bullet + Cr_{aq}OO^{2+} \rightarrow [RC(O)OOCr_{aq}OO]^{2+} \xrightarrow{H^+} RC(O)OH + OCr(V) + O_2} \quad (5)$$

$$\mathrm{2Cr_{aq}OO^{2+} \rightarrow [Cr_{aq}OOCr_{aq}OO]^{4+} \xrightarrow{-O_2} Cr_{aq}OOCr_{aq}{}^{4+} \rightarrow 2Cr^{IV}{}_{aq}O^{2+}} \quad (6)$$

The sources of $\mathrm{O_2}$ eliminated in eq 3 are the two central oxygen atoms in RC(O)OOOO(O)CR,[1−4] that is, each $\mathrm{RC(O)OO^\bullet}$ contributes one (terminal) oxygen atom to the product $\mathrm{O_2}$. The same should be true for the reaction in eq 2 if a tetraoxo intermediate is involved. The reaction in eq 5, on the other hand, regenerates a molecule of oxygen that was initially coordinated to chromium.

We have now carried out oxygen labeling experiments to establish (1) whether molecular oxygen is produced in the $\mathrm{Cr_{aq}OO^{2+}/C(CH_3)_3C(O)OO^\bullet}$ reaction and (2) to identify its origin. These experiments were facilitated by the slow kinetics

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of O_2 exchange between $Cr_{aq}OO^{2+}$ and dissolved O_2, $k = 2.5 \times 10^{-4}$ s^{-1} at 25 °C,[8] which made it possible to generate $RC(O)^{16}O^{16}O^{\bullet}$ in situ in the presence of $Cr_{aq}(^{18}O^{18}O)^{2+}$ and to monitor the fate of the two labels.

Experimental Section

A solution of $Cr_{aq}(^{18}O^{18}O)^{2+}$ was prepared by degassing 0.10 M $HClO_4$ (15.5 mL) in four freeze−pump−thaw cycles and saturating the solution with $^{18}O_2$ by vigorous stirring under 1 atm of $^{18}O_2$ (Cambridge Isotope Laboratories, $[^{18}O_2]/[^{18}O^{16}O] = 17.2$ by GC MS) at 0 °C for 15 min. This was followed by addition of 1.44 mL of a solution containing 5.0 mM Cr_{aq}^{2+}, 0.10 M $HClO_4$, and 0.040 M EtOH, which resulted in instantaneous formation of $Cr_{aq}{}^{18}O^{18}O^{2+}$ (0.29 mM by UV). The role of ethanol is to improve the yield and purity of the superoxo complex.[9] Typically, methanol is used for this purpose, but it was avoided here because its molecular weight coincides with that of $^{16}O_2$.

The unreacted $^{18}O_2$ was removed from the solution of $Cr_{aq}(^{18}O^{18}O)^{2+}$ by vigorous bubbling with $^{16}O_2$ for 10 min at 0 °C. The solution was then quickly warmed up to room temperature and shaken vigorously while releasing excess oxygen pressure to avoid oversaturation of oxygen in solution.

At this point, the reaction between $Cr_{aq}(^{18}O^{18}O)^{2+}$ and aldehyde was initiated by injecting 0.25 mL of 0.10 M $Mn_{aq}{}^{2+}$ (as a scavenger for traces of $Cr_{aq}O^{2+}$)[9] followed by 1.1 mL of air-free 0.92 M Me_3CCHO in CH_3CN. Twelve milliliters of this solution, now containing 0.27 mM $Cr_{aq}(^{18}O^{18}O)^{2+}$, was withdrawn immediately with a syringe and placed into an evacuated 12 mL vial so that only a minimal head space remained. The reaction was allowed to proceed at room temperature for 7 min (ca. nine half-lives), at which point 0.5 mL of argon was injected, displacing an equal volume of the reaction solution through the outlet needle and creating a 0.5 mL head space. The gases dissolved in the remaining solution were allowed to equilibrate in the newly created gas space by vigorous shaking for 30 s before a sample was withdrawn for GC MS analysis. GC/MS spectra were obtained with a Thermo-Finnigan (San Jose, CA) TSQ700 mass spectrometer in the Q1MS EI mode. The tuning and calibration were performed using the air leak peaks at *m/z* 28 and 32. Gas samples (10 μL) were injected directly through the GC equipped with a DB-5 ms column. The column temperature was kept at 100 °C isothermally. Several scans were averaged across the GC peak, and the background was subtracted. The$^{18}O/^{16}O$ ratios were measured directly.

Simulations were performed with the Chemical Kinetics Simulator (IBM).

Results and Discussion

The reaction of 0.27 mM $Cr_{aq}(^{18}O^{18}O)^{2+}$ and an excess of Me_3CCHO yielded a ratio of $^{16}(O_2)/(^{16}O^{18}O) = 7.5$ (i. e., 11.8% of total O_2 was present as $^{16}O^{18}O$). In a control experiment that utilized identical concentrations and conditions in every detail, except that $^{16}O_2$ was used throughout, including the preparation of $Cr_{aq}OO^{2+}$, the ratio $(^{16}O_2)/(^{16}O^{18}O)$ appeared as 28 (i.e., 3.4% $^{16}O^{18}O$). This background value represents a GC-MS response to the combination of gaseous organics from the sample (major contribution) and a small trail from a strong *m/z* = 32 peak (minor) and was used to correct the measured $^{16}(O_2)/(^{16}O^{18}O)$ determined above.

Taking the solubility of O_2 in H_2O at room temperature as 1.26 mM, the measured $^{16}(O_2)/(^{16}O^{18}O)$ ratio (corrected for the background) translates to 0.11 mM $^{16}O^{18}O$ produced in the $Cr_{aq}(^{18}O^{18}O)^{2+}/RC(O)^{16}O^{16}O^{\bullet}$ reaction. This is 81% based on the initial concentration of superoxochromium (0.27 mM) and the 2:1 stoichiometry derived from eqs 7 and 8 followed by eq 2. Additional minor adjustments were necessary to account for the isotopic composition of $^{18}O_2$ used in the preparation of the superoxochromium ($[^{18}O_2]/[^{16}O^{18}O] = 17.2$; see Experimental Section) and the slow background $^{16}O_2/Cr_{aq}(^{18}O^{18}O)^{2+}$ exchange. All of the information is included in the Supporting Information, along with the simulation of the complete reaction scheme,[9] which yielded $[^{16}O^{18}O]_{calc} = 0.12$ mM, in excellent agreement with the experiment, 0.11 mM.

$$Cr_{aq}{}^{18}O^{18}O^{2+} + RCHO \rightarrow Cr_{aq}{}^{18}O^{18}OH^{2+} + RC^{\bullet}O \quad (7)$$

$$RC^{\bullet}O + {}^{16}O^{16}O \xrightarrow{\text{fast}} RC(O)^{16}O^{16}O^{\bullet} \quad (8)$$

The hydroperoxochromium, $Cr_{aq}OOH^{2+}$, generated in eq 7 also reacts with pivaldehyde.[9] Preliminary data are consistent with heterolytic cleavage of the hydroperoxide to yield Cr(V), followed by oxidation of the substrate, although other mechanisms, such as direct hydrogen abstraction,[12] cannot be totally ruled out. Nonetheless, it is highly unlikely that mixed-label oxygen could be generated by either mechanism, and this reaction was ignored in our simulations of $^{16}O^{18}O$.

The fact that $^{18}O^{16}O$ was formed in the $RC(O)OO^{\bullet}/Cr_{aq}OO^{2+}$ reaction in nearly quantitative yield confirms that the reaction in eq 2 produces O_2 in head-to-head collision and that a tetraoxo intermediate of finite lifetime is involved. To the best of our knowledge, this is the first example of such a reaction involving an inorganic superoxo complex. As it turns out, the initial steps in the $RC(O)OO^{\bullet}/Cr_{aq}OO^{2+}$ cross-reaction are mechanistically analogous and kinetically similar to the bimolecular self-reaction of $RC(O)OO^{\bullet}$, as already implied by eqs 2 and 3. This result becomes even more remarkable when one considers the bimolecular self-reaction of $Cr_{aq}OO^{2+}$ ($k \leq 6$ M^{-1} s^{-1}),[11] which is at least 10^7-fold slower than the $Cr_{aq}OO^{2+}/RC(O)OO^{\bullet}$ cross-reaction,[9] and head-to-head dimerization is much slower still. This conclusion is based on the results of ^{18}O labeling experiments,[11] which provided no evidence for mixed-labeled O_2 in the reaction between $Cr_{aq}(^{18}O^{18}O)^{2+}$ and $Cr_{aq(}(^{16}O^{16}O)^{2+}$, thus placing a limit of $\ll 6$ M^{-1} s^{-1} for that pathway.

In the likely possibility that other superoxometal complexes behave similarly to $Cr_{aq}OO^{2+}$, such chemistry is an important part of metal-catalyzed oxidations of organic substrates, which, by definition, involve both organic and metal-based radicals. The slow self-termination and great reactivity toward organic-based peroxyl radicals makes superoxometal complexes excellent candidates to exhibit a persistent radical effect[13,14] and divert the reaction in directions not expected for substrate-derived radicals alone, especially when their steady-state concentrations are small.

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Supporting Information Available: Complete reaction scheme with simulations details. This material is available free of charge via the Internet at http://pubs.acs.org.

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