

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

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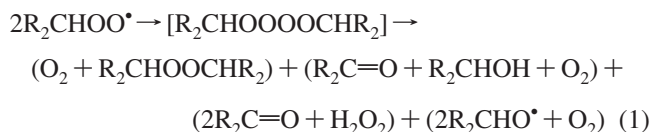
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The superoxo complex $\text{Cr}_{\text{aq}}(^{18}\text{O}^{18}\text{O})^{2+}$ reacts with $(\text{CH}_3)_3\text{C}(\text{O})^{16}\text{O}^{16}\text{O}^\bullet$ to generate quantitative yields of mixed-label dioxygen, $^{18}\text{O}^{16}\text{O}$, demonstrating that this cross-reaction involves head-to-head interaction between the metal-activated and alkyl-activated dioxygen.

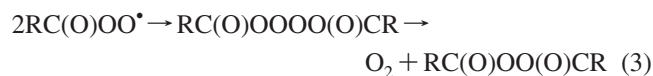
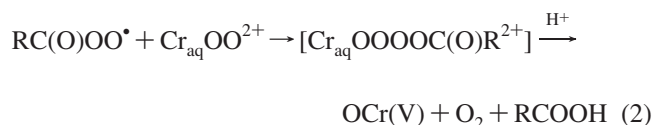
Introduction

Alkylperoxy radicals 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 O_2 and formation of organic fragments and/or products (RO^\bullet , ROOR , or disproportionation products, depending on the nature of R).^{1,7}



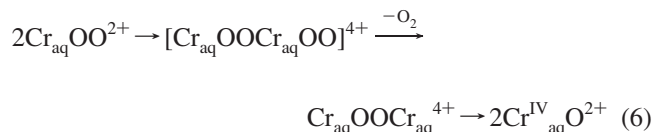
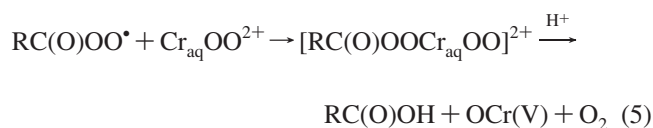
Superoxometal complexes, LMOO^n (L = ligands, M = metal) are inorganic analogues of alkylperoxy radicals. These species are typically much more persistent than ROO^\bullet radicals, and show little tendency to decompose in second-order self-reactions.⁸ We have, however, observed and reported a fast reaction between one such complex, $\text{Cr}_{\text{aq}}\text{OO}^{2+}$, and acylperoxy radicals that were generated either by hydrogen atom abstraction from the aldehyde by $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ or $\text{Cr}_{\text{aq}}\text{O}^{2+}$ or photochemically from an organocobalt precursor in the presence of molecular oxygen.^{9,10} With acetylperoxy radicals, $\text{CH}_3\text{C}(\text{O})\text{OO}^\bullet$, the reaction has $k = 1.49 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and yields chromate and $\text{Cr}_{\text{aq}}^{3+}$.⁹

A mechanism, eqs 2–4, was proposed to involve head-to-head collision of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ and $\text{RC}(\text{O})\text{OO}^\bullet$, eq 2, analogous to the self-reactions of acetylperoxy radicals (eq 3, R = 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}



A somewhat more complex scheme, involving a branching intermediate, was proposed for the reaction of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ and pivaloylperoxy radicals, $(\text{CH}_3)_3\text{C}(\text{O})\text{OO}^\bullet$, 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 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 $\text{Cr}_{\text{aq}}\text{OO}^{2+}$, eq 6.¹¹



The sources of O_2 eliminated in eq 3 are the two central oxygen atoms in $\text{RC}(\text{O})\text{OOOO}(\text{O})\text{CR}$,^{1–4} that is, each $\text{RC}(\text{O})\text{OO}^\bullet$ contributes one (terminal) oxygen atom to the product 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 $\text{Cr}_{\text{aq}}\text{OO}^{2+}/\text{C}(\text{CH}_3)_3\text{C}(\text{O})\text{OO}^\bullet$ reaction and (2) to identify its origin. These experiments were facilitated by the slow kinetics

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of O₂ exchange between Cr_{aq}OO²⁺ and dissolved O₂, $k = 2.5 \times 10^{-4} \text{ s}^{-1}$ at 25 °C,⁸ which made it possible to generate RC(O)¹⁶O¹⁶O[•] in situ in the presence of Cr_{aq}(¹⁸O¹⁸O)²⁺ and to monitor the fate of the two labels.

Experimental Section

A solution of Cr_{aq}(¹⁸O¹⁸O)²⁺ was prepared by degassing 0.10 M HClO₄ (15.5 mL) in four freeze–pump–thaw cycles and saturating the solution with ¹⁸O₂ by vigorous stirring under 1 atm of ¹⁸O₂ (Cambridge Isotope Laboratories, [¹⁸O₂]/[¹⁸O¹⁶O]) = 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 HClO₄, and 0.040 M EtOH, which resulted in instantaneous formation of Cr_{aq}¹⁸O¹⁸O²⁺ (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 ¹⁶O₂.

The unreacted ¹⁸O₂ was removed from the solution of Cr_{aq}(¹⁸O¹⁸O)²⁺ by vigorous bubbling with ¹⁶O₂ 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}(¹⁸O¹⁸O)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}O²⁺)⁹ followed by 1.1 mL of air-free 0.92 M Me₃CCHO in CH₃CN. Twelve milliliters of this solution, now containing 0.27 mM Cr_{aq}(¹⁸O¹⁸O)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 ¹⁸O/¹⁶O ratios were measured directly.

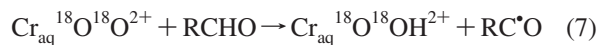
Simulations were performed with the Chemical Kinetics Simulator (IBM).

Results and Discussion

The reaction of 0.27 mM Cr_{aq}(¹⁸O¹⁸O)²⁺ and an excess of Me₃CCHO yielded a ratio of ¹⁶(O₂)/(¹⁶O¹⁸O) = 7.5 (i. e., 11.8% of total O₂ was present as ¹⁶O¹⁸O). In a control experiment that utilized identical concentrations and conditions in every detail, except that ¹⁶O₂ was used throughout, including the preparation of Cr_{aq}OO²⁺, the ratio (¹⁶O₂)/(¹⁶O¹⁸O) appeared as 28 (i. e., 3.4% ¹⁶O¹⁸O). 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(O₂)/(¹⁶O¹⁸O) determined above.

Taking the solubility of O₂ in H₂O at room temperature as 1.26 mM, the measured ¹⁶(O₂)/(¹⁶O¹⁸O) ratio (corrected for the background) translates to 0.11 mM ¹⁶O¹⁸O produced in the Cr_{aq}(¹⁸O¹⁸O)²⁺/RC(O)¹⁶O¹⁶O[•] 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 ¹⁸O₂ used in the preparation of the superoxochromium ([¹⁸O₂]/[¹⁶O¹⁸O]) = 17.2; see Experimental Section) and the slow background ¹⁶O₂/Cr_{aq}(¹⁸O¹⁸O)²⁺ exchange. All of the information is included in the Supporting Information, along with the simulation of the complete reaction scheme,⁹ which yielded [¹⁶O¹⁸O]_{calc} = 0.12 mM, in excellent agreement with the experiment, 0.11 mM.



The hydroperoxochromium, Cr_{aq}OOH²⁺, 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 ¹⁶O¹⁸O.

The fact that ¹⁸O¹⁶O was formed in the RC(O)OO[•]/Cr_{aq}OO²⁺ reaction in nearly quantitative yield confirms that the reaction in eq 2 produces O₂ 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[•]/Cr_{aq}OO²⁺ cross-reaction are mechanistically analogous and kinetically similar to the bimolecular self-reaction of RC(O)OO[•], as already implied by eqs 2 and 3. This result becomes even more remarkable when one considers the bimolecular self-reaction of Cr_{aq}OO²⁺ ($k \leq 6 \text{ M}^{-1} \text{ s}^{-1}$),¹¹ which is at least 10⁷-fold slower than the Cr_{aq}OO²⁺/RC(O)OO[•] cross-reaction,⁹ and head-to-head dimerization is much slower still. This conclusion is based on the results of ¹⁸O labeling experiments,¹¹ which provided no evidence for mixed-labeled O₂ in the reaction between Cr_{aq}(¹⁸O¹⁸O)²⁺ and Cr_{aq}(¹⁶O¹⁶O)²⁺, thus placing a limit of $\ll 6 \text{ M}^{-1} \text{ s}^{-1}$ for that pathway.

In the likely possibility that other superoxometal complexes behave similarly to Cr_{aq}OO²⁺, 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 peroxy 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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