Reactions of Superoxo and Oxo Metal Complexes with Aldehydes. Radical-Specific Pathways for Cross-Disproportionation of Superoxometal Ions and Acylperoxyl Radicals

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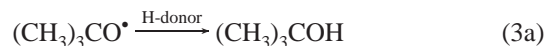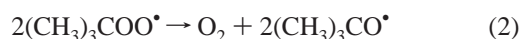
Received March 29, 2002

Abstract: The aquachromyl(IV) ion, $Cr_{aq}O^{2+}$, reacts with acetaldehyde and pivaldehyde by hydrogen atom abstraction and, in the presence of O_2, produces acylperoxyl radicals, $RC(O)OO^•$. In the next step, the radicals react with $Cr_{aq}OO^{2+}$, a species accompanying $Cr_{aq}O^{2+}$ in our preparations. The rate constant for the $Cr_{aq}OO^{2+}/CH_3C(O)OO^•$ cross reaction, $k_{Cr} = 1.5 \times 10^8$ M^{-1} s^{-1}, was determined by laser flash photolysis. The evidence points to radical coupling at the remote oxygen of $Cr_{aq}OO^{2+}$, followed by elimination of O_2 and formation of CH_3COOH and $Cr^V_{aq}O^{3+}$. The latter disproportionates and ultimately yields Cr_{aq}^{3+} and $HCrO_4^-$. No CO_2 was detected. The $Cr_{aq}OO^{2+}/C(CH_3)_3C(O)OO^•$ reaction yielded isobutene, CO_2, and Cr_{aq}^{3+}, in addition to chromate. In the suggested mechanism, the transient $Cr_{aq}OOOO(O)CC(CH_3)_3^{2+}$ branches into two sets of products. The path leading to chromate resembles the $CH_3C(O)OO^•$ reaction. The other products arise from an unprecedented intramolecular hydrogen transfer from the *tert*-butyl group to the CrO entity and elimination of CO_2 and O_2. A portion of $C(CH_3)_3C(O)OO^•$ was captured by $(CH_3)_3COO^•$, which was in turn generated by decarbonylation of acyl radicals and oxygenation of *tert*-butyl radicals so formed.

Introduction

Our recent efforts in oxygen activation have dealt with hydrogen atom abstraction by superoxochromium(III) and aquachromium(IV) ions, $Cr_{aq}OO^{2+}$ and $Cr_{aq}O^{2+}$, respectively.[1-4] We have concentrated on both absolute and relative reactivities of these species and of their organic counterparts, $RO^•$ and $ROO^•$ radicals (R = *t*-Bu). The thermodynamics seem to play a dominant role, such that the formation of strong RO–H bonds in the reactions of $RO^•$ translates into close to diffusion-controlled kinetics. At the other extreme are the sluggish reactions producing weak CrOO–H and ROO–H bonds.

Even though $ROO^•$ radicals are only modestly more reactive than $Cr_{aq}OO^{2+}$ in hydrogen atom abstractions, the intrinsic lifetimes of the two species differ greatly, $Cr_{aq}OO^{2+}$ being the longer-lived. Alkylperoxyl radicals disappear in bimolecular self-reactions having rate constants greater than 10^3 M^{-1} s^{-1}, and often as high as 10^8–10^9 M^{-1} s^{-1}. These self-reactions either produce nonradical species, as shown in eq 1 for $CH_3OO^•$ ($k_1 = 2 \times 10^8$ M^{-1} s^{-1} in hydrocarbon solvents),[5] or generate other carbon- and oxygen-centered radicals which complicate mechanistic studies, as shown in eqs 2 and 3 for *tert*-butylperoxyl radicals ($k_2 = 700$ M^{-1} s^{-1} in hydrocarbon solvents,[5] and 5×10^3 M^{-1} s^{-1} in aqueous[6] solution). Work at low, steady-state concentrations will eliminate self-reactions, but such conditions are often not useful in direct kinetic studies of substrate–radical reactions.

$$2CH_3OO^• \rightarrow O_2 + CH_3OH + CH_2O \qquad (1)$$

$$2(CH_3)_3COO^• \rightarrow O_2 + 2(CH_3)_3CO^• \qquad (2)$$

$$(CH_3)_3CO^• \xrightarrow{\text{H-donor}} (CH_3)_3COH \qquad (3a)$$

$$(CH_3)_3CO^• \xrightarrow{-(CH_3)_2CO} CH_3^• \xrightarrow{O_2} CH_3OO^• \qquad (3b)$$

Superoxochromium(III) ions, and presumably other superoxometal complexes, react in bimolecular self-reactions only slowly[7] or not at all, which makes it possible to carry out direct kinetic studies with these species, even when reactions with substrates are slow.

In many systems involving metal-catalyzed oxidation of hydrocarbons, and certainly in every case of hydrogen atom abstraction from C–H bonds by superoxometal complexes in the presence of molecular oxygen, both alkylperoxyl radicals and superoxometal complexes will be present, yet no data are available for cross reactions between these two forms of activated oxygen. In the absence of kinetic data, or even a direct

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qualitative evidence for the cross reactions, it is impossible to establish the role of such reactions in catalytic systems.

A study of almost any LMOO/ROO$^\bullet$ (LM = metal complex) reaction will be challenging. To begin with, controlled amounts of the two reactants need to be generated in the same solution. LMOO and ROO$^\bullet$ are typically produced from O$_2$ and the respective radicals, LM and R$^\bullet$. To generate LMOO and ROO$^\bullet$ simultaneously, or one in the presence of the other, requires various degrees of reagent compatibility and selective excitation by, for instance, photolysis.
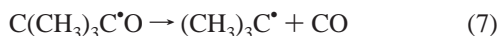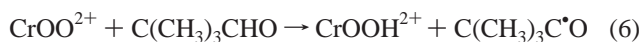
The stability of LMOO has to be substantial to avoid the formation of additional species that could interfere in the measurements. In the example below, LMOO is in rapid equilibrium with O$_2$ and LM, such that reactions 4 and possibly 5 become part of the kinetic picture, which is already complicated by having the self-reactions of ROO$^\bullet$ compete with the desired cross reactions.

$$LMOO \underset{k_{off}}{\overset{k_{on}}{\rightleftharpoons}} LM + O_2 \quad (4)$$

$$LM + ROO^\bullet \rightarrow LMOOR \quad (5)$$
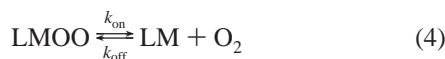
Even if ROO$^\bullet$ and reasonably stable LMOO can be produced at known concentrations, it is unlikely that kinetic measurements could be carried out without the use of kinetic probes. In the most likely scenario, LMOO and the kinetic probe will be present in solution at the moment when ROO$^\bullet$ is generated by, for instance, flash photolysis. Thus, the kinetic probe has to be compatible with LMOO but very reactive toward ROO$^\bullet$, a difficult requirement in view of the expected similarity in the chemistry and oxidation potentials of LMOO and ROO$^\bullet$.

Earlier[1,2] we proposed the mechanism shown in Scheme 1 for the reaction of Cr$_{aq}$OO^{2+} with trimethylacetaldehyde (pivaldehyde), C(CH$_3$)$_3$CHO.

Scheme 1

$$CrOO^{2+} + C(CH_3)_3CHO \rightarrow CrOOH^{2+} + C(CH_3)_3C^\bullet O \quad (6)$$

$$C(CH_3)_3C^\bullet O \rightarrow (CH_3)_3C^\bullet + CO \quad (7)$$

$$C(CH_3)_3C^\bullet O + O_2 \rightarrow C(CH_3)_3C(O)OO^\bullet \quad (8)$$

$$C(CH_3)_3C(O)OO^\bullet + CrOO^{2+} \rightarrow \rightarrow CrO^{2+} \quad (9)$$
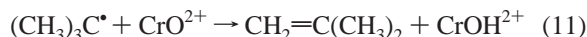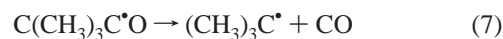
According to this scheme, the hydrogen abstraction step is followed by known reactions of acyl radicals, including decarbonylation and capture by molecular oxygen. The resulting acylperoxyl radicals were proposed to react with Cr$_{aq}$OO^{2+}, possibly by a modified Russell mechanism[8,9] to produce Cr$_{aq}$O^{2+}. The overall behavior of the system under various conditions—O$_2$ vs Ar atmosphere, the presence or absence of scavengers for Cr$_{aq}$$^{2+}$ and Cr$_{aq}$O^{2+}—provided convincing arguments but no direct evidence for the occurrence of reaction 9.

The reaction of oxochromium(IV) ion, Cr$_{aq}$O^{2+}, with C(CH$_3$)$_3$-CHO was suggested to take place as in Scheme 2,[3,10] featuring hydrogen atom abstraction, decarbonylation of acyl radicals, and rapid oxidation of *tert*-butyl radicals by Cr$_{aq}$O^{2+} to generate isobutene under conditions of limiting [O$_2$].[3,10]

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Scheme 2

$$CrO^{2+} + C(CH_3)_3CHO \rightarrow CrOH^{2+} + C(CH_3)_3C^\bullet O \quad (10)$$

$$C(CH_3)_3C^\bullet O \rightarrow (CH_3)_3C^\bullet + CO \quad (7)$$

$$(CH_3)_3C^\bullet + CrO^{2+} \rightarrow CH_2{=}C(CH_3)_2 + CrOH^{2+} \quad (11)$$

The goal of the present study was to provide direct evidence for some of the intermediates and steps in Schemes 1 and 2, especially the novel cross reaction 9. In the process, we also discovered that the chemistry in Scheme 2 is more complex than earlier thought, in part because our solutions of Cr$_{aq}$O^{2+} always contain large amounts (up to 30%) of Cr$_{aq}$OO^{2+}. Solutions of Cr$_{aq}$OO^{2+}, on the other hand, are free of Cr$_{aq}$O^{2+} in the presence of low concentrations of methanol ($\leq$0.05 M).[11]

The formulas CH$_3$C$^\bullet$O and (CH$_3$)$_3$C$^\bullet$O for the radicals derived from the two aldehydes will be used throughout, despite the possibility that the hydrated forms, CH$_3$C$^\bullet$(OH)$_2$ and (CH$_3$)$_3$C$^\bullet$-(OH)$_2$, are involved as well. The amounts should be small, however, because RCHO is preferred over RCH(OH)$_2$ in hydrogen abstraction reactions,[12] and the hydration of RC$^\bullet$O radicals, although fast,[12] is still more than an order of magnitude slower than the reaction with O$_2$ to generate RC(O)OO$^\bullet$ under our conditions.

A preliminary report on some of the findings in this work has appeared.[13]

Experimental Section

Reagents. Solutions of Cr$_{aq}$O^{2+} were generated in spectrophotometric cells immediately before use by injecting dilute Cr$_{aq}$$^{2+}$ (typically 90 μL of a 5 mM solution) into 2.8 mL of air-saturated, aqueous 0.10 M HClO$_4$. The concentration of Cr$_{aq}$O^{2+} was determined by converting it to Cr$_{aq}$OO^{2+} with O$_2$-saturated methanol,[14] as will be described in more detail later. When prepared in this way, chromyl solutions contained $\sim$45 μM Cr$_{aq}$O^{2+} and $\sim$20 μM Cr$_{aq}$OO^{2+}. In some experiments it was necessary to vary relative amounts of the two species. This was achieved by changing the concentration of either O$_2$ or Cr$_{aq}$$^{2+}$. An increase in [O$_2$] and/or a decrease in [Cr$_{aq}$$^{2+}$] resulted in a greater [Cr$_{aq}$OO^{2+}]/[Cr$_{aq}$O^{2+}] ratio.

Solutions of Cr$_{aq}$OO^{2+} were prepared from Cr$_{aq}$$^{2+}$ and a large excess of O$_2$ in the presence of 0.05−0.1 M methanol. A quick, in situ reduction of such solutions with stoichiometric amounts of Ru(NH$_3$)$_6$$^{2+}$ yielded Cr$_{aq}$OOH^{2+} for kinetic purposes.

Solid samples of [L^{1}CoC(O)CH$_3$](ClO$_4$)$_2$ and [L^{1}CoCH$_3$](ClO$_4$)$_2$ (L^1 = 1,4,8,11-tetraazacyclotetradecane) were available from our previous work,[15] and [L^{1}Ni](ClO$_4$)$_2$ was prepared by a literature procedure.[16]

Products. Gaseous products were analyzed by gas chromatography, which utilized a HP 5730A instrument and a packed OV 101 column. Before analysis, the solutions were frozen in an ice/salt bath, and samples were withdrawn from the headspace. The freezing step was required to decrease the amount of isobutane and isobutene produced by decomposition of gaseous C(CH$_3$)$_3$CHO inside the injector. Retention times for isobutane and isobutene were calibrated with use of commercial gases. Product analysis for the C(CH$_3$)$_3$CHO/Cr$_{aq}$O^{2+} reaction was carried out on solutions that were initially saturated with either air or O$_2$. After the addition of Cr$_{aq}$$^{2+}$ (final concentration 0.15

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mM), the concentrations of unused O_2 in the two solutions were estimated to be $\sim$0.2 and 1.2 mM, respectively. These calculations took into account the yields of three major chromium products ($Cr_{aq}OO^{2+}$, $Cr_{aq}O^{2+}$, and Cr_{aq}^{3+}) and the appropriate $[Cr_{aq}^{2+}]$:$[O_2]$ stoichiometry for the formation of each.

A qualitative test for CO_2 in the reactions of $Cr_{aq}OO^{2+}$ with aldehydes utilized 7 mL of a slightly alkaline, aqueous solution of $BaClO_4$ in a tall, narrow test tube. Argon was passed slowly through 40 mL of a spent reaction solution initially containing 0.4 mM $Cr_{aq}OO^{2+}$, 0.05 M $C(CH_3)_3CHO$ (or 0.3 M CH_3CHO), 5 mM Mn^{2+} (a scavenger for $Cr_{aq}O^{2+}$), 0.2 M CH_3OH, $\sim$1 mM O_2, and 0.1 M $HClO_4$. The outlet tube was inserted close to the bottom of the test tube containing $BaClO_4$. Visual observation of the white precipitate of $BaCO_3$ was taken as a positive test for CO_2. A control experiment was carried out on a solution prepared by dissolving 0.4 mM $NaHCO_3$ in 0.1 M $HClO_4$ and transferring the gas into $BaClO_4$ solution as described above.

To test for $Cr_{aq}OOH^{2+}$,[11] a small amount of Ce(IV) was injected into a spent reaction solution, and the amount of $Cr_{aq}OO^{2+}$ produced was determined from the absorbance increase at 290 nm. Chromate was determined spectrophotometrically from the absorbance at 350 nm, where $\epsilon = 1600$ M^{-1} cm^{-1} in 0.10 M $HClO_4$.

Kinetics. The reactions of $CH_3C(O)OO^\bullet$ with $ABTS^{\bullet-}$ and $Cr_{aq}OO^{2+}$ were studied by laser flash photolysis. The radicals were generated from an organocobalt precursor, $L^1CoC(O)CH_3^{2+}$,[15] in the presence of O_2 (eq 12).

$$L^1CoC(O)CH_3{}^{2+} \xrightarrow[-L^1Co^{2+}]{h\nu} CH_3C^\bullet(O) \xrightarrow{O_2} CH_3C(O)OO^\bullet \quad (12)$$

First, the rate constant was determined for the oxidation of $ABTS^{\bullet-}$ to $ABTS^0$ by $CH_3C(O)OO^\bullet$. A small amount of $ABTS^{2-}$ (15–65 μM) was mixed with an equimolar amount of Ce(IV) in a 1-cm fluorescence cell to generate the green radical anion $ABTS^{\bullet-}$. The cobalt complex was injected, the solution was exposed to a laser shot from a Phase-R model DL-1100 dye laser[17] (LD dye, emission at 490 nm), and the absorbance increase was monitored at several wavelengths in the 500–600 nm range. The maximum change was observed at 518 nm, where $ABTS^0$ exhibits a maximum with $\epsilon = 3.6 \times 10^4$ M^{-1} cm^{-1}.[18] The traces were averaged and fitted to a first-order rate law, $Abs_t = Abs_\infty + (Abs_0 - Abs_\infty) e^{-kt}$, where Abs_t, Abs_0, and Abs_∞ stand for the absorbance at time t, at time zero, and after completion of the reaction, respectively.

In the next set of experiments, the $ABTS^{\bullet-}$/$CH_3C(O)OO^\bullet$ reaction was used as a kinetic probe for the $Cr_{aq}OO^{2+}$/$CH_3C(O)OO^\bullet$ reaction. Solutions containing $Cr_{aq}OO^{2+}$ and $ABTS^{\bullet-}$ were shown to be stable for the short periods of time ($\sim$1 min at typical conditions) necessary to mix the reagents and carry out laser experiments. At longer times (several minutes), the absorbance of both $Cr_{aq}OO^{2+}$ and $ABTS^{\bullet-}$ decreased measurably.

In a typical experiment, a small volume of $ABTS^{2-}$ was injected into an O_2-saturated solution of freshly prepared $Cr_{aq}OO^{2+}$ (0.045–0.40 mM) and $L^1CoC(O)CH_3^{2+}$ (0.10 mM). The oxidation of $ABTS^{2-}$ (0.026 M) 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. The irradiating wavelength in these experiments was either 490 (dye laser)[17] or 355 nm (Nd:YAG laser, Applied Photophysics).[19]

The kinetics were again monitored at 518 nm. Two to three traces were averaged for each run, and pseudo-first-order rate constants were evaluated as described above. Under these conditions, both $ABTS^{\bullet-}$ and $Cr_{aq}OO^{2+}$ react with $CH_3C(O)OO^\bullet$, and the rate law is given by eq 13. The rate constants k_A, k_{Cr}, and k_{self} correspond to the respective reactions of the radicals with $ABTS^{\bullet-}$ and $Cr_{aq}OO^{2+}$ and the self-

$$-d[CH_3C(O)OO^\bullet]/dt = (k_A[ABTS^{\bullet-}] + k_{Cr}[Cr_{aq}OO^{2+}] + k_{self}[CH_3C(O)OO^\bullet]) [CH_3C(O)OO^\bullet] \quad (13)$$

reactions. The concentration of $CH_3C(O)OO^\bullet$ was <2 μM, which made the radical self-reaction nearly negligible in all the experiments.

The kinetics of the reactions between L^1Ni^{2+} and $ROO^\bullet$ (R = CH_3C-(O) and CH_3) used the dye laser ($\lambda_{exc} = 490$ nm) and were monitored at 360 nm, where Ni(III) products absorb substantially, $\Delta\epsilon \geq 7 \times 10^3$ M^{-1} cm^{-1}.[20,21] In experiments in which both $Cr_{aq}OO^{2+}$ and L^1Ni^{2+} (as a probe) react with $ROO^\bullet$, the two competitors were mixed immediately prior to the shot to avoid losses caused by the direct reaction between $Cr_{aq}OO^{2+}$ and L^1Ni^{2+}. Under the conditions used, less than 10% of either reagent was lost in the time required for the experiment to be completed ($\sim$25 s).
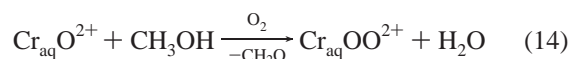
The kinetics of the CH_3CHO/$Cr_{aq}O^{2+}$ reaction and all the spectral determinations utilized a Shimadzu 3100 spectrophotometer equipped with a thermostated cell holder.

Kinetic experiments were carried out at 25.0 $\pm$ 0.2° C, and product analyses were carried out at room temperature (25 $\pm$ 2° C). All the experiments were conducted in 0.10 M aqueous $HClO_4$.

Results

UV Spectrum of $Cr_{aq}O^{2+}$. The kinetics of the $Cr_{aq}O^{2+}$/$C(CH_3)_3CHO$ reaction were determined earlier[3,10] by monitoring the absorbance decrease at 240 nm, where $Cr_{aq}O^{2+}$ was believed to absorb intensely. Our subsequent work[14] suggested, however, that the absorbing species in chromyl solutions is not $Cr_{aq}O^{2+}$ itself, but rather the inevitable coproduct, $Cr_{aq}OO^{2+}$.

We have now utilized the reaction between $Cr_{aq}O^{2+}$ and methanol in the presence of molecular oxygen (eq 14)[11] to determine precisely the UV spectrum of $Cr_{aq}O^{2+}$. The concen-

$$Cr_{aq}O^{2+} + CH_3OH \xrightarrow[-CH_2O]{O_2} Cr_{aq}OO^{2+} + H_2O \quad (14)$$

tration of $Cr_{aq}O^{2+}$ in a freshly prepared solution was determined by injecting a small volume of O_2-saturated methanol, measuring the absorbance increase at 290 nm, and taking $\Delta\epsilon = \epsilon(Cr_{aq}OO^{2+}) = 3000$ M^{-1} cm^{-1},[22–24] as described recently.[14] This determination makes a reasonable assumption that $Cr_{aq}O^{2+}$ absorbs negligibly at 290 nm. The same experiment was repeated two more times, and the absorbance changes were recorded at 245 (maximum for $Cr_{aq}OO^{2+}$) and 220 nm.

As shown in Figure 1, the three difference points (each an average of four determinations) lie close to the independently determined spectrum of $Cr_{aq}OO^{2+}$ and show that $Cr_{aq}O^{2+}$ absorbs negligibly ($\epsilon < 500$ M^{-1} cm^{-1}) throughout the UV range down to at least 220 nm.

Clearly, it was not the absorbance of $Cr_{aq}O^{2+}$ that was monitored in our earlier kinetic studies, although we are confident that the measured rate constant was assigned correctly to the reaction of $C(CH_3)_3CHO$ with $Cr_{aq}O^{2+}$ for the following reasons. First, the rate constant is more than 2 orders of magnitude larger than that determined directly[3] for $Cr_{aq}OO^{2+}$, the only other major species in solution. The absorbance of the kinetic solutions immediately upon mixing was precisely that calculated from the individual absorbancies of $Cr_{aq}O^{2+}$/$Cr_{aq}OO^{2+}$ and $C(CH_3)_3CHO$, i.e., no new absorbing species had

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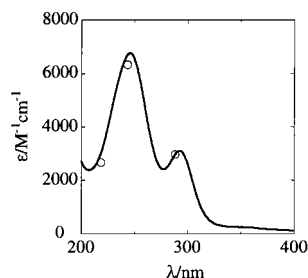(24) Ilan, Y. A.; Czapski, G.; Ardon, M. *Isr. J. Chem.* **1975**, *13*, 15–21.

Figure 1. UV spectrum of $Cr_{aq}OO^{2+}$ and difference points ($\bigcirc$) at 290, 245, and 220 nm for the conversion of $Cr_{aq}O^{2+}$ to $Cr_{aq}OO^{2+}$.

been formed, which confirms that the disappearance of $Cr_{aq}OO^{2+}$ was responsible for the absorbance decrease at 240 nm. Most importantly, we have now determined the $Cr_{aq}O^{2+}/$ $C(CH_3)_3CHO$ rate constant by the methanol method, i.e., by quenching the reaction at various times with methanol[14] and calculating the concentration of unreacted $Cr_{aq}O^{2+}$ from the absorbance increase at 290 nm. This method requires a fresh $Cr_{aq}O^{2+}$ solution for each kinetic point, which limits the number of points per run and assumes that each preparation yields the exact same initial concentration of $Cr_{aq}O^{2+}$. Nonetheless, the method was precise enough to confirm unequivocally our earlier findings. Figure S1 (Supporting Information) shows two kinetic traces obtained by the methanol method at 0.74 and 1.62 mM $C(CH_3)_3CHO$. After correction for the disproportionation of $Cr_{aq}O^{2+}$,[14] the two experiments yielded second-order rate constants of 45 and 43 M^{-1} s^{-1}, in excellent agreement with our published value of 45.2 M^{-1} s^{-1}.[3]

On the basis of these results, we conclude that an intermediate, identified below as $C(CH_3)_3C(O)OO^\bullet$, reacts rapidly with $Cr_{aq}OO^{2+}$, which thus becomes, in effect, a kinetic probe. The probe reaction consumes, however, only a fraction of the radical. Figure 2a shows a kinetic trace at 240 nm for an air-saturated solution containing 1.89 mM $C(CH_3)_3CHO$, 47 μM $Cr_{aq}O^{2+}$, and 22 μM $Cr_{aq}OO^{2+}$. The apparent $\Delta\epsilon$ for the first step, calculated as $\Delta Abs/[Cr_{aq}O^{2+}]$, was 1.3×10^3 M^{-1} cm^{-1}. After the completion of the $Cr_{aq}O^{2+}/C(CH_3)_3CHO$ reaction, some $Cr_{aq}OO^{2+}$ (7 μM) still remained and reacted with $C(CH_3)_3CHO$ in a slower step at its independently known rate. The $Cr_{aq}O^{2+}/$ $C(CH_3)_3CHO$ reaction thus consumed $\sim$0.3 mol of $Cr_{aq}OO^{2+}$ per mole of $Cr_{aq}O^{2+}$. As discussed in detail later, the total yield of $C(CH_3)_3C(O)OO^\bullet$ is $>$0.6 mol per mole of $Cr_{aq}O^{2+}$. It follows that another scavenger must be involved. This was confirmed in an experiment with a solution of $Cr_{aq}O^{2+}$ (61 μM) containing a higher proportion of $Cr_{aq}OO^{2+}$ (42 μM). As expected, the reaction consumed more $Cr_{aq}OO^{2+}$ ($\sim$0.5 mol per mole of $Cr_{aq}O^{2+}$) and exhibited a larger $\Delta\epsilon = 2.1 \times 10^3$ M^{-1} cm^{-1} (Figure 2b). The values of $\Delta\epsilon$ quoted are those recorded during the kinetic runs. The actual values are larger by $\sim$30%, the amount that escaped detection during the $\sim$5 s required to mix the reagents and initiate the reaction. The qualitative trend in $\Delta\epsilon$ is, however, real, since the two experiments had the same rate constant and the same fraction of the reaction was "lost" in the mixing time.

Kinetics of $Cr_{aq}OO^{2+}/CH_3C(O)OO^\bullet$ Reaction. In the absence of a suitable precursor of $C(CH_3)_3C(O)OO^\bullet$ for direct kinetic measurements, we studied the reaction of $Cr_{aq}OO^{2+}$ with the related acetylperoxyl radicals, $CH_3C(O)OO^\bullet$, which were generated photochemically from $L^1CoC(O)CH_3{}^{2+}$;[15] see the Experimental Section. The two acylperoxyl radicals are expected

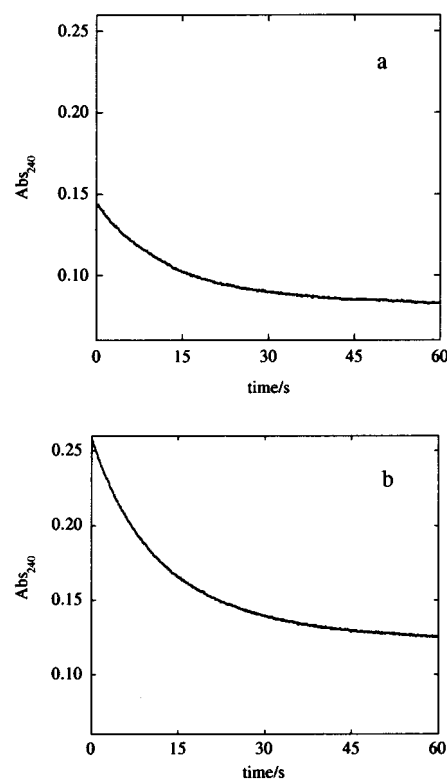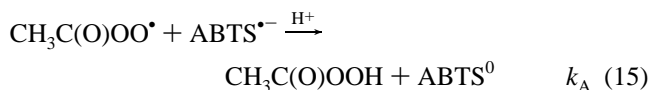**Figure 2.** Kinetic traces at 240 nm for the reaction of 1.89 mM $C(CH_3)_3$-CHO with (a) 47 μM $Cr_{aq}O^{2+}$/22 μM $Cr_{aq}OO^{2+}$ in air-saturated 0.1 M $HClO_4$ and (b) 61 μM $Cr_{aq}O^{2+}$/42 μM $Cr_{aq}OO^{2+}$ in O_2-saturated 0.1 M $HClO_4$.

to have comparable reactivities. For all practical purposes, their reduction potentials are identical,[25] and the steric bulk of the alkyl group should not affect greatly the reactivity at the peroxyl site.

The reaction produced no measurable absorbance change in the visible range and required a kinetic probe. After an extensive search, $ABTS^{\bullet-}$ was found to have the desired properties. The reduction potential for the $ABTS^0/ABTS^{\bullet-}$ couple, 1. 09 V in 1.5 M $HClO_4$,[18] is well within the reach of acylperoxyl radicals (1.54 V for $CH_3C(O)OO^\bullet/CH_3C(O)OOH$ at 0.10 M H^+)[25] but too high for $Cr_{aq}OO^{2+}$ ($E = 0.97$ V at 0.10 M H^+)[11] to oxidize $ABTS^{\bullet-}$. As shown in separate experiments, $ABTS^{\bullet-}$ can be handled in the presence of $Cr_{aq}OO^{2+}$ for brief periods of time (about 1 min).

A plot of k_{obs} vs $[ABTS^{\bullet-}]$ for the $CH_3C(O)OO^\bullet/ABTS^{\bullet-}$ reaction (eq 15 and Figure S2, Supporting Information), yielded $k_A = (1.22 \pm 0.04) \times 10^9$ M^{-1} s^{-1}.

$$CH_3C(O)OO^\bullet + ABTS^{\bullet-} \xrightarrow{H^+}$$
$$CH_3C(O)OOH + ABTS^0 \qquad k_A \quad (15)$$

When both $ABTS^{\bullet-}$ and $Cr_{aq}OO^{2+}$ were present, the signal decreased and the rate constant increased with $[Cr_{aq}OO^{2+}]$, as expected if the radical was consumed in reactions with both reagents. The data obtained at two different excitation wavelengths with two different laser systems form a single line with a slope $k_{Cr} = (1.49 \pm 0.14) \times 10^8$ M^{-1} s^{-1} (Figure 3). The intercept, $(3.9 \pm 0.3) \times 10^4$ s^{-1}, which is the sum of all the

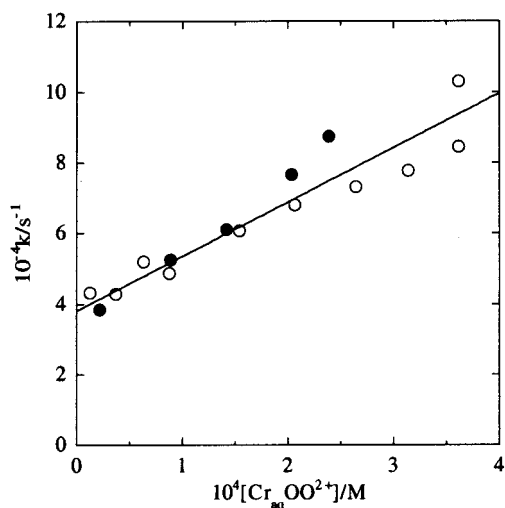(25) Merenyi, G.; Lind, J.; Engman, L. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2551−2553.

Figure 3. 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 26 μM $ABTS^{\bullet-}$ as a kinetic probe at 0.1 M $HClO_4$ and 25 °C, λ_{irr} = 490 nm (dye laser, ●) and 355 nm (Nd:YAG laser, ○).

rate constants for the disappearance of $CH_3C(O)OO^\bullet$ in the absence of $Cr_{aq}OO^{2+}$, agrees reasonably well with 3.3×10^4 s^{-1}, the value in Figure S2 (Supporting Information) at [$ABTS^{\bullet-}$] used in these experiments, 26 μM.

Kinetics of the $Cr_{aq}O^{2+}$/CH_3CHO reaction were monitored at 245 nm. Kinetic traces in air-saturated solutions appeared exponential in the early stages but ended abruptly when all the (absorbing) $Cr_{aq}OO^{2+}$ was consumed (Figure 4a). This behavior is different from that observed in the corresponding reaction with $C(CH_3)_3CHO$, which consumed only a fraction of the available $Cr_{aq}OO^{2+}$ and exhibited first-order kinetics, followed by the much slower direct reaction between the remaining $Cr_{aq}OO^{2+}$ and $C(CH_3)_3CHO$.

To check for the presence of unreacted $Cr_{aq}O^{2+}$ after the break in Figure 4a, a solution that initially contained 45 μM $Cr_{aq}O^{2+}$, 22 μM $Cr_{aq}OO^{2+}$, and 2.4 mM CH_3CHO was allowed to react until the absorbance stopped changing. At that point, a small amount of methanol was quickly injected to convert any remaining $Cr_{aq}O^{2+}$ to $Cr_{aq}OO^{2+}$. The absorbance increased by 0.026 units (~4 μM $Cr_{aq}O^{2+}$). The exact value is somewhat larger but could not be determined precisely because the $Cr_{aq}O^{2+}$/CH_3CHO reaction is fast and the exact timing of methanol injection difficult. Nonetheless, the very presence of $Cr_{aq}O^{2+}$, even after all the $Cr_{aq}OO^{2+}$ was consumed, shows that the $Cr_{aq}O^{2+}$/CH_3CHO reaction indeed consumes significantly more $Cr_{aq}OO^{2+}$ than the corresponding $C(CH_3)_3CHO$ reaction. A solution having a larger proportion of $Cr_{aq}OO^{2+}$ (see the Experimental Section) yielded a kinetic trace that was exponential throughout (Figure 4b).

For air-saturated solutions, the rate constants were obtained by fitting the initial portions of the kinetic curves to the exponential rate law and varying Abs$_\infty$. A representative fit is shown in Figure 4a. A plot of k_{obs} against the average concentration of CH_3CHO is linear and yields k = 39 ± 5 M^{-1} s^{-1}, close to the value for $C(CH_3)_3CHO$ (45.2 M^{-1} s^{-1}).[3]

Products of $Cr_{aq}O^{2+}$/Aldehyde Reactions. The isobutene found earlier in the $C(CH_3)_3CHO$ reaction[3,10] was believed to have been produced by the oxidation of *tert*-butyl radicals (from reaction 7) with $Cr_{aq}O^{2+}$. The concentration of O_2 in those experiments, ~0.1 mM, seemed low enough to allow $Cr_{aq}O^{2+}$ to compete for carbon radicals.

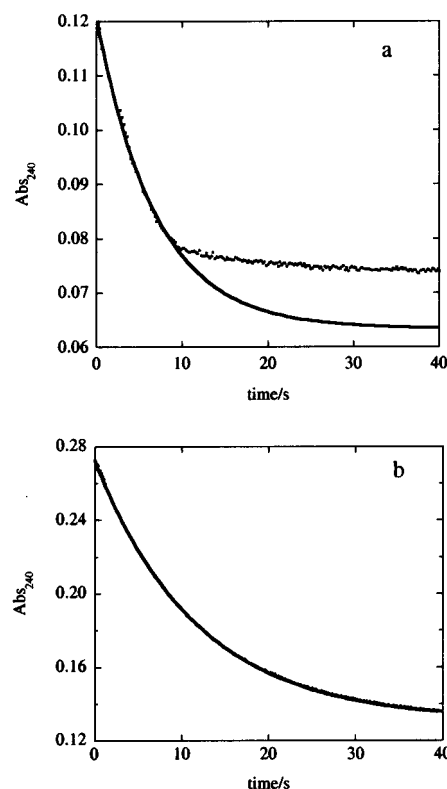**Figure 4.** Kinetic traces and exponential fits for the reactions of {47 μM $Cr_{aq}O^{2+}$ + 22 μM $Cr_{aq}OO^{2+}$} with 3.0 mM CH_3CHO (trace a) and of {60 μM $Cr_{aq}O^{2+}$ + 42 μM $Cr_{aq}OO^{2+}$} with 2.4 mM CH_3CHO (trace b) in O_2-saturated solution.

Product analysis was now carried out on O_2-saturated solutions, where most or all of $(CH_3)_3C^\bullet$ should be scavenged by O_2. The reaction solution had 60 μM $Cr_{aq}O^{2+}$, 40 μM $Cr_{aq}OO^{2+}$, and ~1.2 mM O_2. The yield of isobutene was comparable to that obtained in solutions having ~0.1 mM O_2, clearly ruling out the $(CH_3)_3C^\bullet$/$Cr_{aq}O^{2+}$ reaction as the source of isobutene.

The $Cr_{aq}O^{2+}$/aldehyde reactions also produced some chromate. The yield was ≤15% of the initial [$Cr_{aq}O^{2+}$] in the $C(CH_3)_3CHO$ reaction but much higher in the CH_3CHO reaction. An O_2-saturated solution of 61 μM $Cr_{aq}O^{2+}$, 42 μM $Cr_{aq}OO^{2+}$, and 3.0 mM CH_3CHO produced 25 μM $HCrO_4^-$.

Products of $Cr_{aq}OO^{2+}$/$C(CH_3)_3CHO$ Reaction. The major chromium product is believed to be Cr_{aq}^{3+}, which has a weak visible spectrum and is difficult to observe at the low concentrations used in this work. Chromate was also produced, consistently at the level of about 20% of the initial $Cr_{aq}OO^{2+}$, as determined by UV−visible spectrophotometry.

The Ce(IV) test for $Cr_{aq}OOH^{2+}$, the product of initial hydrogen atom transfer in reaction 6, was negative. In an attempt to trace the fate of $Cr_{aq}OOH^{2+}$, we tested various possibilities and discovered a surprisingly rapid reaction between $C(CH_3)_3CHO$ and $Cr_{aq}OOH^{2+}$, which produced chromate in ~10% yield in O_2-saturated solutions. Under a limited set of conditions, the rate was comparable to that of the $Cr_{aq}OO^{2+}$/$C(CH_3)_3CHO$ reaction.[26] This step is clearly a part of the kinetic scheme, but our kinetic simulations require an additional source of chromate and suggest it is produced in ~15% yield directly from $Cr_{aq}OO^{2+}$.

(26) Work in progress.

Table 1. Summary of Rate Constants Determined in This Work[a]

reaction	notation	$k/M^{-1} s^{-1}$
$Cr_{aq}OO^{2+} + CH_3C(O)OO^{\bullet}$	k_{Cr}	1.5×10^8
$L^1Ni^{2+} + CH_3C(O)OO^{\bullet}$	k_{18}	9.7×10^8
$ABTS^{\bullet-} + CH_3C(O)OO^{\bullet}$	k_A	1.2×10^9
$L^1Ni^{2+} + CH_3OO^{\bullet}$	k_{19}	2.7×10^7
$Cr_{aq}O^{2+} + CH_3CHO$	k_{20}	39
$Cr_{aq}O^{2+} + C(CH_3)_3CHO$	k_{10}	45^b

[a] At 25 °C and 0.10 M $HClO_4$. L^1 = 1,4,8,11-tetraazacyclotetradecane. [b] Reference 3.
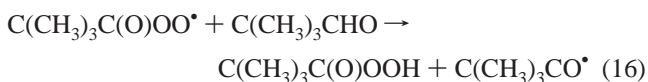
The test for CO_2 with Ba^{2+} was positive and produced large amounts of a white precipitate of $BaCO_3$. Isobutene was the only product detected in the gas phase by GC.

In several experiments, a small amount of L^1Ni^{2+} was added after completion of the $Cr_{aq}OO^{2+}/C(CH_3)_3CHO$ reaction ($[C(CH_3)_3CHO]$ = 0.03−0.05 M). The addition of L^1Ni^{2+} caused the solution to turn pink, and a new band appeared at 520 nm, signaling the formation of the binuclear nickel complex of the highly oxidized macrocycle, $(L_{ox}Ni_2)^{4+}$.[27]

The $Cr_{aq}O^{2+}/C(CH_3)_3CHO$ reaction failed to oxidize the macrocycle in L^1Ni^{2+} at the typical kinetic concentrations of $C(CH_3)_3CHO$, ≤ 2.5 mM. In an experiment having $[C(CH_3)_3CHO]$ = 0.045 M, however, the pink color of $(L_{ox}Ni_2)^{4+}$ appeared readily.

The species responsible for the overoxidation of L^1Ni^{2+} is probably the peracid $C(CH_3)_3C(O)OOH$. Other oxidants potentially present in spent reaction solutions (H_2O_2, O_2, or $HCrO_4^{-}$) either do not react with L^1Ni^{2+} under the conditions employed or do not produce $(L_{ox}Ni_2)^{4+}$. Another peracid, *m*-chloroperbenzoic acid (mcpba), on the other hand, rapidly oxidized L^1-Ni^{2+} to $(L_{ox}Ni_2)^{4+}$ in a control experiment.

From ϵ_{520} = 6500 M^{-1} cm^{-1} for $(L_{ox}Ni_2)^{4+}$,[27] and taking into account that each of the two macrocycles underwent a six-electron oxidation, one finds the concentration of peracid at high initial $[C(CH_3)_3CHO]$ to be comparable to or greater than the initial concentration of $Cr_{aq}OO^{2+}$ but much lower (or zero) at low initial $[C(CH_3)_3CHO]$. These findings lead us to suggest the side reaction in eqs 16 and 8 as the source of $C(CH_3)_3C$-$(O)OOH$. This chain reaction causes a slight depletion of O_2 and $C(CH_3)_3CHO$ but has otherwise no effect on the reactions of interest.
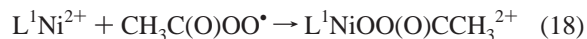
$$C(CH_3)_3C(O)OO^{\bullet} + C(CH_3)_3CHO \rightarrow$$
$$C(CH_3)_3C(O)OOH + C(CH_3)_3CO^{\bullet} \quad (16)$$

Products of $Cr_{aq}OO^{2+}/CH_3CHO$ Reaction. The yield of chromate was 48% when the reaction was conducted in the absence of Mn^{2+} and 35% in the presence of 5 mM Mn^{2+}. The effect of Mn^{2+} suggests that $Cr_{aq}O^{2+}$ plays a role in the formation of some but not all of the observed $HCrO_4^{-}$. Tests for CO_2 and CH_2O were negative.

The search for $CH_3OO^{\bullet}$ utilized the difference in reactivity of L^1Ni^{2+} toward alkylperoxyl and acylperoxyl radicals (Table 1). Laser flash photolysis of $L^1CoC(O)CH_3^{2+}$ in O_2-saturated solutions takes place according to eq 12. Carbon radicals are rapidly converted to $CH_3C(O)OO^{\bullet}$. The other fragment, L^1Co^{2+}, reacts with O_2 more slowly,[28] k_{17} = 1.2×10^7 M^{-1} s^{-1}, and is also accompanied by an absorbance increase at 360 nm.

(27) McAuley, A.; Xu, C. *Inorg. Chem.* **1992**, *31*, 5549−5554.
(28) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1990**, *112*, 2273−2278.

$$L^1Co^{2+} + O_2 \rightleftharpoons L^1CoOO^{2+} \quad (17)$$

Laser flash photolysis in the presence of L^1Ni^{2+} yielded a biexponential trace corresponding to the sum of reactions 17 (slow step) and 18 (fast step). The acylperoxonickel complex, $L^1NiOO(O)CCH_3^{2+}$, is expected to hydrolyze readily to L^1Ni^{3+} and $CH_3C(O)OOH$, in analogy to the methylperoxo complex $L^1NiOOCH_3^{2+}$.[20]

$$L^1Ni^{2+} + CH_3C(O)OO^{\bullet} \rightarrow L^1NiOO(O)CCH_3^{2+} \quad (18)$$

The reaction between L^1Ni^{2+} and $CH_3OO^{\bullet}$ behaved analogously, except that reaction 17 was now faster than reaction 19.

$$L^1Ni^{2+} + CH_3OO^{\bullet} \rightarrow L^1NiOOCH_3^{2+} \quad (19)$$

To test for $CH_3OO^{\bullet}$ in the reaction between $Cr_{aq}OO^{2+}$ and $CH_3C(O)OO^{\bullet}$, an O_2-saturated solution ($[O_2] \approx 1.2$ mM) 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, and the absorbance was monitored at 360 nm. At these concentrations, approximately 65% of $CH_3C(O)OO^{\bullet}$ should react with $Cr_{aq}OO^{2+}$, and the rest with L^1Ni^{2+}. If $CH_3OO^{\bullet}$ is produced, then the $CH_3OO^{\bullet}/L^1Ni^{2+}$ reaction of eq 19 should be observed well after the reactions of eqs 17 and 18 are completed. A small and slow absorbance change on the expected time scale (k = 600 ± 300 s^{-1}, ΔAbs ~0.01) was noticed, but it was comparable in size to that in a control experiment having no $Cr_{aq}OO^{2+}$. The amount of CH_3-$OO^{\bullet}$, and the absorbance change at 360 nm, should have been at least 3 times as large as the observed background amount had $CH_3OO^{\bullet}$ been produced quantitatively. On this basis, CH_3-$OO^{\bullet}$ was ruled out as an important intermediate in the $CH_3C(O)OO^{\bullet}/Cr_{aq}OO^{2+}$ reaction.

The observed $CH_3OO^{\bullet}$ is believed to have been generated photochemically from $L^1CoCH_3^{2+}$, a natural impurity identified by NMR in our samples of the acetylcobalt complex, which was prepared photochemically from $L^1CoCH_3^{2+}$ and CO.[15] The fact that the same amount of this independently generated CH_3-$OO^{\bullet}$ was available for the reaction with L^1Ni^{2+} in the presence and in the absence of $Cr_{aq}OO^{2+}$ shows that the reaction of CH_3-$OO^{\bullet}$ with $Cr_{aq}OO^{2+}$ is negligibly slow compared to that with L^1Ni^{2+} under the conditions employed.

Discussion

Any plausible mechanistic scheme for the reaction of $Cr_{aq}O^{2+}$ with aldehydes has to take into account the following. (1) Hydrogen abstraction and free radicals are involved, as amply demonstrated in previous work[3] and here. (2) The intermediate acylperoxyl radicals react rapidly with $Cr_{aq}OO^{2+}$. (3) The reaction of pivaldehyde produces Cr_{aq}^{3+}, isobutene, some $HCrO_4^{-}$, and probably carbon dioxide, although this was determined only for the $Cr_{aq}OO^{2+}$ reaction, which has all the other products identical with those for the $Cr_{aq}O^{2+}$ reaction. (4) Isobutene is produced even in O_2-saturated solutions. (5) Under a given set of conditions, the $Cr_{aq}O^{2+}/C(CH_3)_3CHO$ reaction consumes ~0.3 mol of $Cr_{aq}OO^{2+}$ per mole of $Cr_{aq}O^{2+}$, but the corresponding reaction with CH_3CHO requires >0.5 mol of Cr_{aq}-OO^{2+} per mole of $Cr_{aq}O^{2+}$. (6) The $Cr_{aq}O^{2+}/CH_3CHO$ reaction produces large amounts of chromate. (7) Tests for CO_2, CH_2O, and transient $CH_3OO^{\bullet}$ in the $Cr_{aq}OO^{2+}/CH_3CHO$ reaction were all negative.

To the best of our knowledge, the $Cr_{aq}OO^{2+}/CH_3C(O)OO^{\bullet}$ reaction is the first example[13] of a directly observed and kinetically characterized cross reaction between a superoxometal complex and acylperoxyl (or alkylperoxyl) radicals. The rate constant, $k = 1.5 \times 10^8$ M^{-1} s^{-1}, is much larger than the geometric mean of the individual rate constants for self-reactions, 6 M^{-1} s^{-1} for $Cr_{aq}OO^{2+}$ [7] and probably $>10^8$ M^{-1} s^{-1} for $CH_3C(O)OO^{\bullet}$.[29]

The geometric mean rule is used routinely to estimate rate constants for the cross combination reactions in the gas phase.[30,31] The agreement between the theory and experiment is reasonably good for alkyl radicals, although deviations have been noted, especially for polar radicals.[31] We are not aware of any systematic studies of cross reactions in solution, but our work clearly shows that this simple rule does not apply to the $Cr_{aq}OO^{2+}/CH_3C(O)OO^{\bullet}$ reaction, which is about 10^4 times faster than the geometric mean. Such a finding is reasonable[32] in view of the large driving force for the reaction and agrees with an extensive gas-phase study which concluded that all cross reactions of $CH_3C(O)OO^{\bullet}$ are fast and that all acylperoxyl radicals are as reactive as $CH_3C(O)OO^{\bullet}$.[33]

From the mechanistic point of view, the reactions of $Cr_{aq}O^{2+}$ and $Cr_{aq}OO^{2+}$ with CH_3CHO appear to be somewhat simpler than those with $C(CH_3)_3CHO$ and will be discussed first. Both oxidants engage in an initial hydrogen atom abstraction, followed by the capture of the radicals by O_2 and the cross reaction between $CH_3C(O)OO^{\bullet}$ and $Cr_{aq}OO^{2+}$ (Scheme 3).

Scheme 3

$$CrO^{2+} (CrOO^{2+}) + CH_3CHO \rightarrow$$
$$CrOH^{2+} (CrOOH^{2+}) + CH_3C^{\bullet}O \quad (20)$$

$$CH_3C^{\bullet}O + O_2 \rightarrow CH_3C(O)OO^{\bullet} \quad (21)$$

$$CH_3C(O)OO^{\bullet} + Cr_{aq}OO^{2+} \xrightarrow{H^+} Cr^VO^{3+} + CH_3COOH + O_2 \quad (22)$$

$$2CrO^{3+} \rightarrow CrO^{2+} + HCrO_4^- + 5H^+ \quad (23)$$

$$CrO^{2+} + CrO^{3+} \rightarrow HCrO_4^- + Cr^{3+} + 3H^+ \quad (24)$$
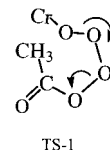
The large amounts of $HCrO_4^-$ produced, and the modest but real effect of Mn_{aq}^{2+} on the yields of chromate, strongly suggest that Cr(V) is involved. If Cr(IV) were the initial product of reaction 22, it would be scavenged completely by 5 mM Mn^{2+}, and no chromate would be produced. If, on the other hand, $HCrO_4^-$ were produced directly in eq 22, then Mn^{2+} should not affect the yield. Moreover, the large change in the geometry and degree of hydrolysis between $Cr_{aq}OO^{2+}$ and $HCrO_4^-$, and the need for other products of eq 22 to be reasonably stable, would require some very unusual chemistry to generate chromate directly.

Acetic acid is difficult to detect, especially at the small concentrations in this work and in the presence of excess aldehyde. For these reasons, acetate analysis was not attempted,

but all our results suggest that it is a major product. The failure to observe CO_2 or CH_2O, or to detect $CH_3OO^{\bullet}$, shows that the intermediate radical did not decarboxylate and that the product still contains both carbons from the aldehyde. The L^1Ni^{2+} test ruled out the peracid as a product.

A possible transition state for reaction 22 is shown below (TS-1). The products may form directly, or a peroxo intermedi-
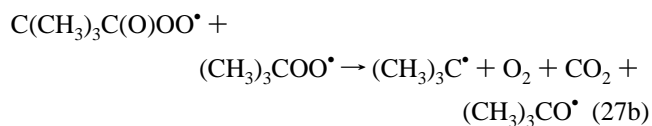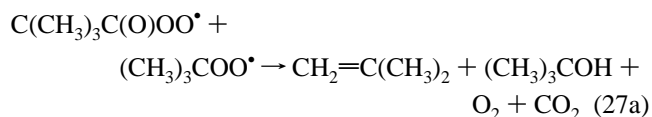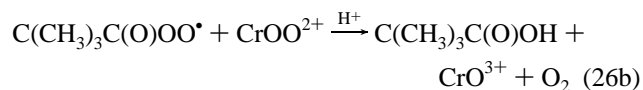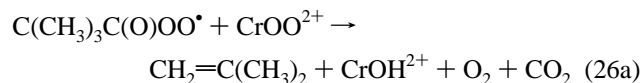

TS-1

ate $CrOOC(O)CH_3^{2+}$ may be generated first, followed by hydrolysis to $Cr_{aq}O^{3+}$ and acetic acid. Both cases are a variation of the Russell mechanism[8,9] for self-reactions of alkylperoxyl radicals. μ-Peroxides are produced in self-reactions of acylperoxyl radicals in organic solvents.[5]

The new mechanism for the $Cr_{aq}O^{2+}/C(CH_3)_3CHO$ reaction in Scheme 4 contains elements of Schemes 1–3, modified and expanded in accord with the new findings. Acyl radicals, generated by hydrogen abstraction in eq 10, disappear mainly in the reaction with O_2 (eq 8) and by decarbonylation ($k_7 \approx 2.5 \times 10^5$ s^{-1} in aqueous solutions),[34] which ultimately results in the formation of *tert*-butylperoxyl radicals (eq 25).

Scheme 4

$$CrO^{2+} + C(CH_3)_3CHO \rightarrow CrOH^{2+} + C(CH_3)_3C^{\bullet}O \quad (10)$$

$$C(CH_3)_3C^{\bullet}O \rightarrow {}^{\bullet}C(CH_3)_3 + CO \quad (7)$$

$$C(CH_3)_3C^{\bullet}O + O_2 \rightarrow C(CH_3)_3C(O)OO^{\bullet} \quad (8)$$

$$(CH_3)_3C^{\bullet} + O_2 \rightarrow (CH_3)_3COO^{\bullet} \quad (25)$$

$$C(CH_3)_3C(O)OO^{\bullet} + CrOO^{2+} \rightarrow$$
$$CH_2=C(CH_3)_2 + CrOH^{2+} + O_2 + CO_2 \quad (26a)$$

$$C(CH_3)_3C(O)OO^{\bullet} + CrOO^{2+} \xrightarrow{H^+} C(CH_3)_3C(O)OH + CrO^{3+} + O_2 \quad (26b)$$

$$C(CH_3)_3C(O)OO^{\bullet} +$$
$$(CH_3)_3COO^{\bullet} \rightarrow CH_2=C(CH_3)_2 + (CH_3)_3COH + O_2 + CO_2 \quad (27a)$$

$$C(CH_3)_3C(O)OO^{\bullet} +$$
$$(CH_3)_3COO^{\bullet} \rightarrow (CH_3)_3C^{\bullet} + O_2 + CO_2 + (CH_3)_3CO^{\bullet} \quad (27b)$$

$$(CH_3)_3COO^{\bullet}, C(CH_3)_3C(O)OO^{\bullet} \rightarrow \text{nonradical products} \quad (28)$$
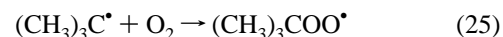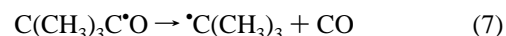
The cross reaction between $Cr_{aq}OO^{2+}$ and $C(CH_3)_3C(O)OO^{\bullet}$ branches to give two sets of products (eq 26). Reaction 26b is

(29) Precise data are not available for acylperoxyl radicals in aqueous solution, but rapid self-reactions have been reported in organic solvents.[5]
(30) Knyazev, V. D.; Slagle, I. R. *J. Phys. Chem. A* **2001**, *105*, 6490–6498.
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analogous to that shown in eq 22 for $CH_3C(O)OO^{\bullet}$ and is (together with eqs 23 and 24) the source of $HCrO_4^-$.

The lack of O_2 effect on the yield of isobutene is explained by the other branch, eq 26a, which is again a variation of the Russell mechanism for primary and secondary alkylperoxyl radicals involving intramolecular hydrogen transfer and elimination of O_2 to yield the disproportionation products. In the present case, CO_2 is also eliminated. Equation 26a has no counterpart in the CH_3CHO reaction, where it could not yield a stable organic product.

It is doubtful that reaction 26a takes place in a single step. More likely, in analogy with the self-reactions of acyl radicals,[5] O_2 is extruded to generate a μ-peroxide. Product elimination could then take place through a six-membered transition state, TS-2. The low kinetic stability of μ-peroxides of chromium-(III) has been noted before.[11,35]

TS-2
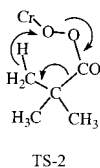
At typical O_2 concentrations of 0.1−0.2 mM, and using $k_7 = 2.5 \times 10^5$ s^{-1} [34] and $k_8 = 4 \times 10^9$ M^{-1} s^{-1}, about 60−80% of the acyl radicals in Scheme 4 are converted to $C(CH_3)_3C$-$(O)OO^{\bullet}$, only a fraction of which react with $Cr_{aq}OO^{2+}$, as judged by the absorbance decrease at 240 nm. The self-reactions of $C(CH_3)_3C(O)OO^{\bullet}$ are not competitive at the low steady-state concentrations. The most reasonable candidate that can compete with reaction 26 and explain the small consumption of Cr_{aq}-OO^{2+} despite the large value of k_{Cr} is the $(CH_3)_3COO^{\bullet}$/$C(CH_3)_3C(O)OO^{\bullet}$ cross reaction of eq 27.[5,33] One of the two radicals, $(CH_3)_3COO^{\bullet}$, is persistent ($k_{self} = 5 \times 10^3$ M^{-1} s^{-1}),[6] which allows its concentrations to build up and the rate of cross reaction 27 to increase relative to those of the other radical self-reactions in the system, in accord with the Ingold−Fischer persistent radical effect.[36,37]

If reaction 27 takes place as shown in eq 27b, then the persistent radical effect would be strongly enhanced by the catalytic nature of the reaction. This might explain the great efficiency of reaction 27 in competition with reaction 26, even though the latter uses a bulk reagent, $Cr_{aq}OO^{2+}$, and has a large rate constant.

More likely, however, reaction 27 will bypass free radicals by eliminating O_2 to generate $CH_2{=}C(CH_3)_2$, $(CH_3)_3COH$, and CO_2 either directly or via the peroxide $C(CH_3)_3COO(O)CC$-$(CH_3)_3$ in the uncatalyzed process of eq 27a, which was written in analogy with the other cross reaction, eq 26a. It is not clear whether or how quickly the μ-peroxide would eventually cleave to yield the proposed products. From the experimental data at hand, it is impossible to tell whether $CH_2{=}C(CH_3)_2$ and CO_2 come solely from reaction 26, or from the combination of eqs 26 and 27.

The mechanism in Scheme 4 is equally applicable to the Cr_{aq}-OO^{2+}/$C(CH_3)_3CHO$ reaction, once the hydrogen abstraction step of eq 10 is replaced by eq 6. Also, at the typically large

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concentrations of $Cr_{aq}OO^{2+}$, most of the $C(CH_3)_3C(O)OO^{\bullet}$ will react as in eq 26, making reaction 27 unimportant. Under these conditions, chromate yields can be used to estimate the relative proportions of reactions 26a and 26b. Of the observed 20% yield of chromate, 5% comes from the $C(CH_3)_3CHO$/$Cr_{aq}OOH^{2+}$ reaction (only about one-half of $Cr_{aq}OO^{2+}$ is converted to Cr_{aq}-OOH^{2+}), and the rest comes from eq 26b followed by eqs 23 and 24. After the allowance for the stoichiometry of $HCrO_4^-$ formation, the proportion of the two pathways, k_{26a} vs k_{26b}, is 2:3.

Experiments with CH_3CHO provide additional support for the mechanism in Scheme 4. Acetyl radicals, produced in reaction 20, do not dissociate CO readily and are converted quantitatively to $CH_3C(O)OO^{\bullet}$. No persistent radicals or catalytic reactions are involved, so that reaction 22 should be the major path for the disappearance of $CH_3C(O)OO^{\bullet}$. As expected, the amount of $Cr_{aq}OO^{2+}$ consumed is about twice as large as that in the $C(CH_3)_3CHO$ reaction, but the ratio $R = \Delta[Cr_{aq}OO^{2+}]$/$[Cr_{aq}O^{2+}]_0$ is still significantly smaller than 1. Several steps in Schemes 1 and 2 have an effect on this ratio. In the $C(CH_3)_3$-CHO reaction, the decarbonylation of eq 7 reduces the total amount of acylperoxyl radicals, depending on $[O_2]$, to 60−80% of $[Cr_{aq}O^{2+}]_0$. The oxidation of $Cr_{aq}O^{3+}$ by $Cr_{aq}O^{2+}$ further decreases that amount, but the major reason for the small value of R is reaction 27, which has no counterpart in the CH_3CHO reaction. In this case, the $Cr_{aq}O^{3+}$/$Cr_{aq}O^{2+}$ reaction is responsible for $R < 1$.

The absence of $RC(O)OOH$ among the products of the $Cr_{aq}O^{2+}$/$RCHO$ reactions at typical concentrations of RCHO shows that hydrogen atom transfer reactions of $RC(O)OO^{\bullet}$ do not play an important role in the mechanism. Specifically, these considerations rule out a reaction between $RC(O)OO^{\bullet}$ and Cr_{aq}-OOH^{2+} produced in eq 6. The dominant reaction of acylperoxyl radicals is that with $Cr_{aq}OO^{2+}$, as expected on the basis of the large value for k_{Cr} and reasonably large concentrations of Cr_{aq}-OO^{2+} in all the experiments.

To account for an assumed 2:1 stoichiometry in the $Cr_{aq}O^{2+}$/$C(CH_3)_3CHO$ reaction, we have previously[3] calculated the rate constant k_{10} by dividing the observed value by 2.[3] The new findings and the mechanism in Scheme 4 suggest that this may not be correct and that the ratio will depend on the fate of $Cr_{aq}O^{3+}$. Disproportionation, in fact, produces $Cr_{aq}O^{2+}$, and reaction 24 consumes additional amounts over the initial 1:1 stoichiometry. For this reason, Table 1 lists the uncorrected experimental values of the rate constants for both aldehydes.

Conclusions

There are close parallels in the chemistry of $Cr_{aq}OO^{2+}$ and organic peroxyl radicals. The superoxochromium complex participates in rapid cross-disproportionation reactions with $CH_3C(O)OO^{\bullet}$ ($k_{Cr} = 1.5 \times 10^8$ M^{-1} s^{-1}) and other acylperoxyl radicals. Our work strongly suggests that $(CH_3)_3COO^{\bullet}$ and Cr_{aq}-OO^{2+} adopt analogous mechanisms (eq 26 and 27) and even exhibit similar kinetics in their reactions with $RC(O)OO^{\bullet}$. The kinetic competition between $Cr_{aq}OO^{2+}$ and $(CH_3)_3COO^{\bullet}$ for $C(CH_3)_3C(O)OO^{\bullet}$ is responsible for the limited consumption of $Cr_{aq}OO^{2+}$ in the $Cr_{aq}O^{2+}$/$C(CH_3)_3CHO$ reaction.

Future mechanistic schemes for metal-catalyzed autoxidations will need to include the cross reactions between organic and metal-based peroxyl radicals. This requirement includes oxidations in biological environments, where the long lifetimes of

some superoxometal complexes, i.e., oxygen carriers, provide ample time for reactions with ROO$^\bullet$ to take place. Such interactions may produce high-valent, potentially damaging species by mechanisms similar to those in Schemes 3 and 4.

Supporting Information Available: Kinetic and k vs concentration plots, Figures S1 and S2 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA026365W