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Hydrogen Atom Abstraction by Metal−Oxo and Metal−Superoxo Complexes: Kinetics and Thermodynamics

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Abstract: The superoxochromium complex $Cr_{aq}OO^{2+}$ abstracts a hydrogen atom from CMe_3CHO in acidic aqueous solution with $k = 0.16\ M^{-1}\ s^{-1}$. This rate constant is only $\sim 10^2$ times smaller than that for the reaction of $Cr_{aq}O^{2+}$ with the same aldehyde, $k = 23\ M^{-1}\ s^{-1}$, in contrast to the much greater reactivity difference between alkoxyl and alkylperoxyl radicals, $k_{t-BuO}/k_{t-BuOO} \approx 10^6$. The absolute rate constants for hydrogen atom abstraction from a common reagent by metal-oxo and -superoxo species and the corresponding organic oxygen-centered radicals, $RO^\bullet$ and $ROO^\bullet$, can now be compared for the first time: k_{BuO} ($9 \times 10^7\ M^{-1}\ s^{-1}$) > $k_{CrO}(23) \geq k_{BuOO}(8) > k_{CrOO}$ (0.16). The reactivity of individual species is explained by the energetics of the O−H bonds in ROH, ROOH, $Cr_{aq}OH^{2+}$, and $Cr_{aq}OOH^{2+}$.

Introduction

The superoxochromium complex $Cr_{aq}OO^{2+}$ (hereafter $CrOO^{2+}$) and the aquachromium(IV) ion, $Cr_{aq}O^{2+}$ (hereafter CrO^{2+}), react with rhodium(III) hydrides $L(H_2O)RhH^{2+}$ (L = $(NH_3)_4$, cyclam, and *meso*-Me_6-cyclam) by hydrogen atom abstraction, eqs 1 and 2.[1,2] The reactions of CrO^{2+} are faster than those of $CrOO^{2+}$, as one would intuitively expect, although the rate constants for the two sets of reactions differ by a factor of only about 10^2.

$$CrOO^{2+} + LRhH^{2+} \rightarrow CrOOH^{2+} + LRh^{2+} \qquad (1)$$

$$CrO^{2+} + LRhH^{2+} \rightarrow CrOH^{2+} + LRh^{2+} \qquad (2)$$

There are no other examples of the reactions of oxo and superoxo complexes of the same metal with which to compare our data, so we turned to the chemistry of the related alkoxyl and alkylperoxyl radicals, $RO^\bullet$ and $ROO^\bullet$. These radicals, just like the metal−oxo and −superoxo complexes, are crucial intermediates in metal-catalyzed oxidations of hydrocarbons.[3−5] Both $RO^\bullet$ and $ROO^\bullet$ engage in hydrogen atom abstraction, but alkoxyl radicals are much more reactive, typically by 6−7 orders of magnitude.[6−10]

It is not clear whether this amazing difference between the metal-based intermediates and O-centered organic radicals is related to the choice of the element-hydrogen bonds examined—C−H for $RO^\bullet$ and $ROO^\bullet$,[6−9] and Rh−H for CrO^{2+} and $CrOO^{2+}$ [1,2]—or whether the observed reactivity pattern is a general feature governed by the thermodynamics of the O−H bonds in ROH, ROOH, $CrOH^{2+}$, and $CrOOH^{2+}$.

The present work addresses this question by examining hydrogen atom abstractions by CrO^{2+} and $CrOO^{2+}$ from the aldehydic C−H bond in pivalaldehyde. This compound is one of the few that have been shown[11,12] to react with CrO^{2+} in a 1-e process, believed to be hydrogen atom abstraction. Many other organic materials, including alcohols, ethers, and carboxylic acids, react by hydride transfer and would not provide a suitable comparison for $RO^\bullet$ reactions. Also, pivalaldehyde turned out to be sufficiently reactive so that both CrO^{2+} and $CrOO^{2+}$ undergo reduction at convenient rates. Finally, there are special features in the radical chemistry of aldehydes, which could be explored to obtain useful mechanistic information in the complicated reactions with $CrOO^{2+}$.

All of the work was carried out in acidic aqueous solutions, where pivalaldehyde exists as a 4:1 mixture of CMe_3CHO and $CMe_3CH(OH)_2$.[13] The kinetic data provide no information on separate reactivities of the two forms, but the knowledge of the overall reactivity is sufficient in a comparative study of two reactions under identical experimental conditions. Similarly, the radicals derived from the two forms probably exist as a rapidly equilibrating mixture of $CMe_3C^\bullet O$ and $CMe_3C^\bullet(OH)_2$, eq 3, as is the case with the parent acetyl radicals, $CH_3C^\bullet O/CH_3C^\bullet(OH)_2$.[14] We are not aware of any kinetics or equilibrium data for reaction 3, but the analogous equilibrium for acetyl radicals is established rapidly ($k_f = 2 \times 10^4\ s^{-1}$, $k_r \approx 3 \times 10^4\ s^{-1}$)[14] and has an equilibrium constant ($K_{hydr} \approx 1$) comparable to that of the aldehyde itself ($K_{hydr} = 1.2$). Extrapolated to the case of pivaloyl radicals, these data suggest that both forms exist in solution. To simplify the notation, the aldehyde and acyl radicals

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are denoted CMe_3CHO and $CMe_3C^{\bullet}O$ throughout the paper.

$$CMe_3C^{\bullet}O + H_2O \underset{k_r}{\overset{k_f}{\rightleftharpoons}} CMe_3C^{\bullet}(OH)_2 \; K_{hydr} \qquad (3)$$

Experimental Section

Stock solutions of $CrOO^{2+}$ were prepared from Cr^{2+} and O_2, kept in ice, and used within 2 h of preparation, as previously described.[15] Except in special cases, such solutions were stabilized[11] with 0.01−0.3 M methanol. For air-free kinetic experiments, solutions of $CrOO^{2+}$ were purged with Ar in a spectrophotometric cell for 10 min at 0 °C. The cell was then immersed into a thermostating bath inside the spectrophotometer cell compartment which was kept at 25 °C. The reaction was initiated 10 min later by injecting the aldehyde. Approximately 10% of $CrOO^{2+}$ usually decomposed during the degassing and thermostating procedure. Solutions of CrO^{2+} were prepared from Cr^{2+} and air at 25 °C and used immediately.[16]

Solid $[(NH_3)_5CoBr](ClO_4)_2$ was available from previous work.[17] $Mn(ClO_4)_2{,}6H_2O$ (G. F. Smith) was used as received. Commercial pivalaldehyde (Aldrich) contained an impurity that readily oxidized Fe_{aq}^{2+}. The aldehyde was purified[18] by treatment with $SnCl_2$ followed by distillation, and stored over basic alumina in a refrigerator. Stock solutions of CMe_3CHO in CH_3CN were prepared daily and kept in ice under argon. The in-house distilled and ion-exchanged water was further purified by a passage through a Milli-Q purification system.

Kinetic solutions for the reaction of $CrOO^{2+}$ with CMe_3CHO contained ≤14% CH_3CN, introduced air-free with the aldehyde. Because of this small but variable volume of added CH_3CN, experiments with "O_2-saturated" solutions had $[O_2]$ up to 14% below the solubility limit in H_2O (1.26 mM). The kinetics of the reactions of $CrOO^{2+}$ were monitored at 245 nm, where the spectrum of $CrOO^{2+}$ exhibits a maximum.[19−21] This wavelength is also conveniently close to the minimum in the spectrum of pivalaldehyde (0.1 M $HClO_4$, 14% acetonitrile in water, $\lambda_{min} = 240$ nm, $\epsilon = 3.1$ M^{-1} cm^{-1}). The kinetics in the presence of $(NH_3)_5CoBr^{2+}$ were monitored at 290 nm, where the absorbance change was still acceptable and the background absorbance of $(NH_3)_5CoBr^{2+}$ smaller than at 245 nm. The kinetics of CrO^{2+}/CMe_3CHO reaction were monitored at 240 nm, where CrO^{2+} has an estimated molar absorptivity of ~3000 M^{-1} cm^{-1}.

A Shimadzu 3101 PC spectrophotometer was used for all the spectral and kinetic measurements. Gaseous products were determined with use of a Hewlett-Packard model 4790 gas chromatograph.

Results and Discussion

Kinetics. The overall rate and even the shape of the kinetic traces at 240 nm for the reaction between $CrOO^{2+}$ and CMe_3CHO depended strongly on reaction conditions, Figure 1. Initially, the stock solutions of $CrOO^{2+}$ contained ≤0.2 M methanol to scavenge any CrO^{2+}, a standard impurity in the absence of alcohols.[11] Under pseudo-first-order conditions ($[CMe_3CHO] \gg [CrOO^{2+}]$) in O_2-saturated solutions containing methanol the kinetic traces were not exponential, and the rate was $[CH_3OH]$-dependent, Figure 1a. In the absence of oxygen, the traces became even more unusual and suggestive of autocatalysis, Figure 1b.

When methanol was omitted, reasonably good pseudo-first-order kinetics were obtained at high (~1mM) O_2, Figure 1a, but at low $[O_2]$ the reaction still appeared autocatalytic, Figure 1b.

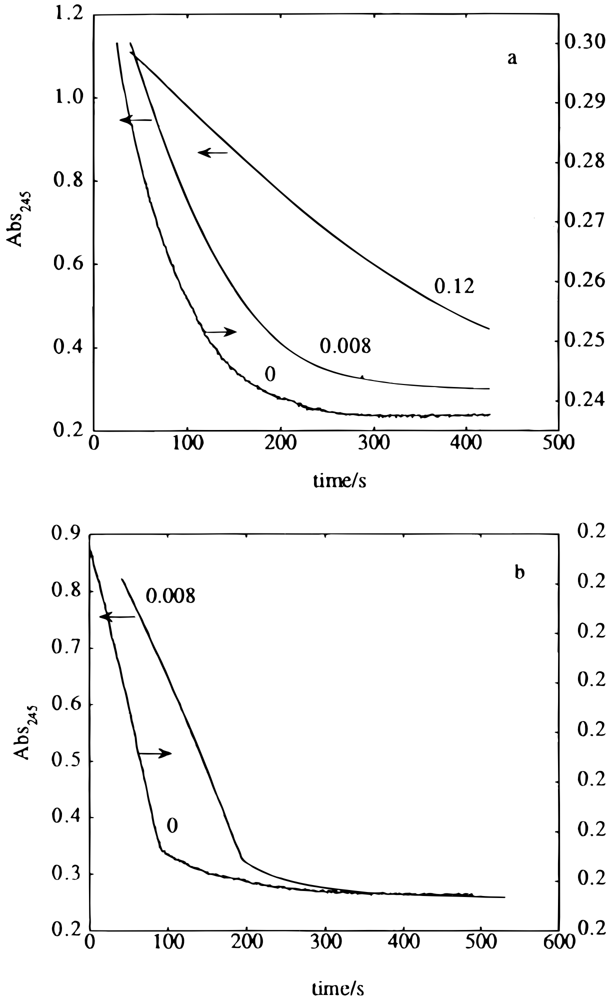

Figure 1. Effect of methanol and O_2 on the kinetic traces at 245 nm. Conditions: 30 mM CMe_3CHO, 0.10 M $HClO_4$. (a) 0.03 mM $CrOO^{2+}$, 1 mM O_2, no MeOH (bottom trace, right ordinate), 0.12 mM $CrOO^{2+}$, 0.008 M MeOH (middle trace, left ordinate), and 0.12 mM $CrOO^{2+}$, 0.12 M MeOH (top trace, left ordinate). (b) Air-free, 0.03 mM $CrOO^{2+}$, 8 mM MeOH (left ordinate), and no MeOH (right ordinate).

The complicated kinetic behavior indicated the involvement of reactive intermediates, such as CrO^{2+} and/or the radicals derived from CMe_3CHO. Judged by the methanol effect, CrO^{2+} is not only a left-over impurity from the preparation, but is probably generated in the course of the reaction as well. The large methanol effect stems from the fact that reactions 4−5 not only remove CrO^{2+} but also regenerate the reactant $CrOO^{2+}$.[3]

$$CrO^{2+} + CH_3OH \rightarrow CH_2O + Cr^{2+} + H_2O \; k = 52 \; M^{-1} \; s^{-1} \; {}^{12} \qquad (4)$$

$$Cr^{2+} + O_2 \rightarrow CrOO^{2+} \qquad (5)$$

The expected mechanism for the reaction between $CrOO^{2+}$ and CMe_3CHO produces $CrOOH^{2+}$ and acyl radicals $CMe_3C^{\bullet}O$ at an early stage, eq 6, followed by the chemistry in eq 7−8. The decarbonylation of $CMe_3C^{\bullet}O$ (eq 7a)[22,23] and reaction with O_2 (eq 7b)[22,24] are both well documented, even if precise kinetic data are not available for this particular acyl radical in aqueous solution. The evidence for reactions 7c and 8 will be presented shortly.

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$$\mathrm{CrOO^{2+} + CMe_3CHO \rightarrow CrOOH^{2+} + CMe_3C^{\bullet}O} \quad k_6 \quad (6)$$

$$\mathrm{CMe_3C^{\bullet}O \rightarrow {}^{\bullet}CMe_3 + CO} \quad k < 7 \times 10^5\ \mathrm{s^{-1}} \quad (7a)$$

$$\xrightarrow{\mathrm{O_2}} \mathrm{CMe_3C(O)OO^{\bullet}} \quad \sim 10^9\ \mathrm{M^{-1}\ s^{-1}} \quad (7b)$$

$$\xrightarrow{\mathrm{CrOO^{2+}}} \text{products} \quad (7c)$$

$$\mathrm{CMe_3C(O)OO^{\bullet} + CrOO^{2+} \rightarrow \rightarrow \rightarrow CrO^{2+}} \quad (8)$$

If a competent scavenger for $\mathrm{CMe_3C^{\bullet}O}$ or $\mathrm{CMe_3C(O)OO^{\bullet}}$ could be found, then the system should become kinetically simple and yield the desired rate constant for reaction 6. The scavenger should not absorb strongly in the UV and should react rapidly with acyl or acylperoxyl radicals, but not with $\mathrm{CrOO^{2+}}$.

Several candidates were examined. The free radical 4-hydroxy-tetramethylpiperidinoxyl (HO-TEMPO) reacts readily with C-centered radicals, but it turned out to be too reactive toward $\mathrm{CrOO^{2+}}$ ($k \approx 200\ \mathrm{M^{-1}\ s^{-1}}$) to be useful in the present system. 3-Methyl-1,4-cyclohexadiene and $\mathrm{Ni(cyclam)^{2+}}$, both of which react with acylperoxyl radicals,[25–27] also did not work out. Solutions containing $\mathrm{CrOO^{2+}}$, $\mathrm{CMe_3CHO}$, and 3-methyl-1,4-cyclohexadiene turned cloudy within seconds, eliminating the possibility of using the olefin as a trap in kinetic measurements. The macrocyclic nickel complex reacted too rapidly with $\mathrm{CrOO^{2+}}$.

The next set of experiments was conducted in the presence of $\mathrm{Mn^{2+}}$, which scavenges $\mathrm{CrO^{2+}}$ according to eq 9,[28,29] $k_9 \approx 10^6\ \mathrm{M^{-1}\ s^{-1}}$.[11] Unlike MeOH, $\mathrm{Mn^{2+}}$ does not regenerate $\mathrm{CrOO^{2+}}$ and would appear to be a better scavenger for $\mathrm{CrO^{2+}}$ for kinetic purposes.

$$\mathrm{Mn^{2+} + CrO^{2+} \xrightarrow{H^+} Mn^{3+} + Cr^{3+}} \quad k_9 \approx 10^6\ \mathrm{M^{-1}\ s^{-1}} \quad (9)$$

At $[\mathrm{Mn^{2+}}] = 2-10$ mM, Figure 2, the reaction obeyed pseudo-first-order kinetics precisely, and yielded rate constants that were independent of the concentration of $\mathrm{Mn^{2+}}$ and methanol. This result strongly supports the mechanism in eqs 4−9 and clearly implicates $\mathrm{CrO^{2+}}$ as the intermediate responsible for the complicated kinetic behavior in Figure 1. Under the conditions in this work, reaction 9 is so much faster than reaction 4 that methanol cannot compete for $\mathrm{CrO^{2+}}$, resulting in well-behaved kinetics. The sequence of reactions 5−6, 7b, 8−9 defines the observed rate constant in the presence of $\mathrm{Mn^{2+}}$ and $\mathrm{O_2}$ as $2k_6$. From the plot in Figure 3, the value is $2k_6 = 0.28 \pm 0.04\ \mathrm{M^{-1}\ s^{-1}}$.

Additional kinetics experiments were carried out under air-free conditions in the presence of $\mathrm{Co(NH_3)_5Br^{2+}}$ as a potential scavenger for acyl radicals $\mathrm{CMe_3C^{\bullet}O}$, as in eq 10. The complete scavenging of $\mathrm{CMe_3C^{\bullet}O}$ should yield k_6 directly.

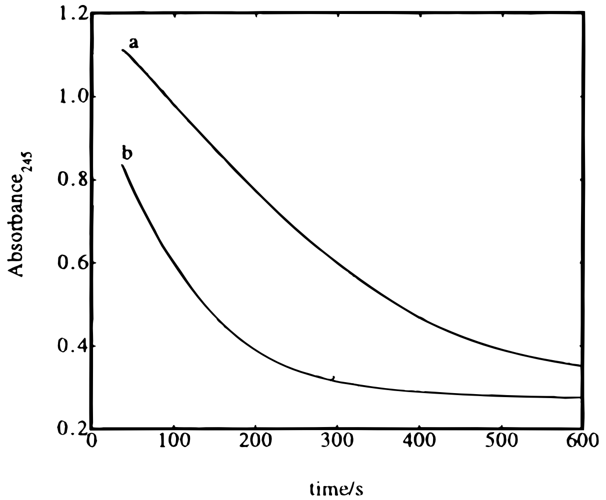

Figure 2. Effect of $\mathrm{Mn^{2+}}$ on the reaction between $\mathrm{CrOO^{2+}}$ (0.12 mM) and $\mathrm{CMe_3CHO}$ (30 mM) in 0.10 M $\mathrm{HClO_4}$ in the presence of 0.12 M MeOH at (a) $[\mathrm{Mn^{2+}}] = 0$, $[\mathrm{CrOO^{2+}}] = 0.16$ mM and (b) $[\mathrm{Mn^{2+}}] = 10$ mM, $[\mathrm{CrOO^{2+}}] = 0.12$ mM.

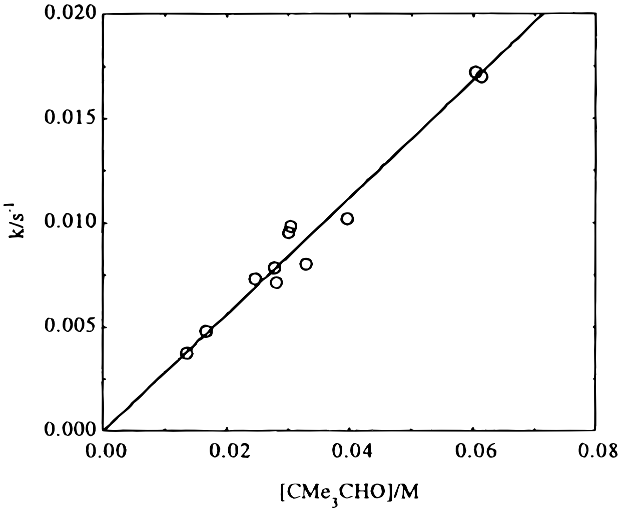

Figure 3. Plot of the rate constants for the reaction between $\mathrm{CrOO^{2+}}$ and $\mathrm{CMe_3CHO}$ in the presence of added $\mathrm{Mn^{2+}}$ (2−10 mM). Conditions: $[\mathrm{CrOO^{2+}}] = 0.05-0.13$ mM, $[\mathrm{MeOH}] = 0-0.3$ M, $[\mathrm{H^+}] = 0.10$ M, $T = 25.0$ °C.

$$\mathrm{CMe_3C^{\bullet}O + (NH_3)_5CoBr^{2+} \xrightarrow{H^+} CMe_3C(O)Br + Co^{2+} + 5\ NH_4^{+}} \quad (10)$$

Because of the intense UV absorption by $\mathrm{(NH_3)_5CoBr^{2+}}$ ($\lambda_{\max}$ 270 nm, $\epsilon = 1.7 \times 10^4\ \mathrm{M^{-1}\ cm^{-1}}$), only limited amounts can be used in kinetic experiments. The rate constant k_{10} needs to be $> 5 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$ if $\mathrm{(NH_3)_5CoBr^{2+}}$ is to compete successfully with $\mathrm{CrOO^{2+}}$ for $\mathrm{CMe_3C^{\bullet}O}$, $k_{7c} \approx 10^9\ \mathrm{M^{-1}\ s^{-1}}$, see later. Known reactions of alkyl radicals with $\mathrm{Co(NH_3)_5Br^{2+}}$ have rate constants of only $\sim 10^6\ \mathrm{M^{-1}\ s^{-1}}$,[17,30] but acyl radicals, especially when hydrated, are strongly reducing[31] and should react at least as fast as hydroxyalkyl radicals ($k > 10^8\ \mathrm{M^{-1}\ s^{-1}}$).[30] This turned out to be the case, so that small amounts of $\mathrm{(NH_3)_5CoBr^{2+}}$ added to argon-saturated reaction mixtures caused the kinetic traces to become first order, as shown in Figure 4. The rate constant, measured at 290 nm, was independent of the

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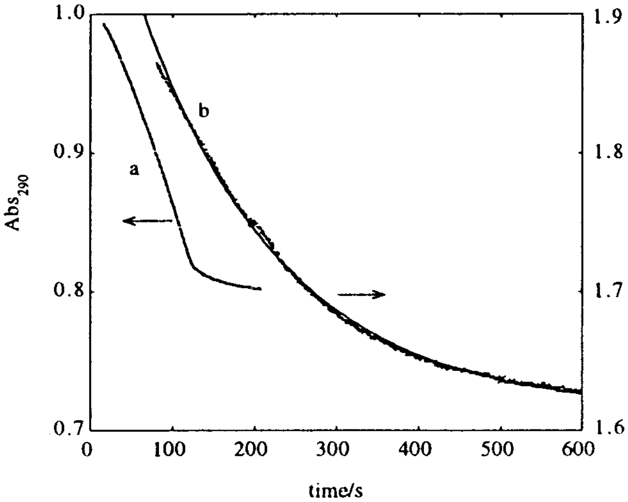

Figure 4. Effect of $(NH_3)_5CoBr^{2+}$ on the reaction between $CrOO^{2+}$ (0.1 mM) and CMe_3CHO (49 mM) in 0.10 M $HClO_4$ under Ar. (a) $[(NH_3)_5CoBr^{2+}] = 0$. (b) $[(NH_3)_5CoBr^{2+}] = 0.69$ mM. The first-order fit to the data in (b) is also shown.

concentration of $(NH_3)_5CoBr^{2+}$ in the narrow range accessible (0.28−0.69 mM). The value, which we assign to k_6, is 0.16 $M^{-1}\ s^{-1}$, close to half of that obtained in the presence of Mn^{2+} and O_2 (0.28 $M^{-1}\ s^{-1}$), in full agreement with the predictions. Additional support for the role of $(NH_3)_5CoBr^{2+}$ comes from the fact that it has no effect in O_2-saturated solutions, in the presence or absence of Mn^{2+}, where the radicals are preferentially captured by O_2.

All of the experimental data strongly support the proposed mechanism, including the operation of reaction 8 or a similar process which produces CrO^{2+} from $CMe_3C(O)OO^•$ and $CrOO^{2+}$. The role of Mn^{2+} is to remove the CrO^{2+}, and the role of $(NH_3)_5CoBr^{2+}$ to prevent its formation by removing $CMe_3C^•O$. The 1:1 stoichiometry for reaction 8 is indicated by the doubling of the rate constant when Ar and $(NH_3)_5CoBr^{2+}$ are replaced by O_2 and Mn^{2+}.

A reasonable mechanism for reaction 8 may involve an S_H2 attack by $CMe_3C(O)OO^•$ at $CrOO^{2+}$, producing a peroxo complex and molecular O_2, eq 11, followed by homolytic O−O bond cleavage in $CMe_3C(O)OOCr^{2+}$, decarboxylation of O-centered radicals, and formation of much less reactive[32,33] *tert*-butylperoxyl radicals, eqs 12−13.

$$CMe_3C(O)OO^• + CrOO^{2+} \rightarrow CMe_3C(O)OOCr^{2+} + O_2 \quad (11)$$

$$CMe_3C(O)OOCr^{2+} \rightarrow CMe_3C(O)O^• + CrO^{2+} \quad (12)$$

$$CMe_3C(O)O^• \xrightarrow{-CO_2} {}^•CMe_3 \xrightarrow{O_2} CMe_3OO^• \quad (13)$$

In support of reaction 11, indirect evidence for bimolecular homolytic activity of $CrOO^{2+}$ has been obtained earlier,[34] and the facile cleavage of the peroxidic O−O bond in $CrOOCr^{4+}$ is believed responsible for the formation of CrO^{2+} from Cr^{2+} and O_2.[11] It is plausible then that $CrOOR^{2+}$ may also yield CrO^{2+}, especially if R is a bulky alkyl group like CMe_3CO. A similar O−O bond cleavage in some acylperoxonickel complexes has been invoked recently.[27]

Table 1. Summary of the Rate Constants ($M^{-1}\ s^{-1}$)[1] for the Reactions of Oxochromium(IV) (k_{CrO}) and Superoxochromium (k_{CrOO}) Complexes with Rhodium Hydrides and Pivalaldehyde in Aqueous Solution[a]

	k_{CrO}	k_{CrOO}	k_{CrO}/k_{CrOO}	k_{t-BuO}/k_{t-BuOO}
L^1RhH^{2+}	$\sim 10^4$	129	78	
L^1RhD^{2+}	2.70×10^3	17	160	
$(NH_3)_4RhH^{2+}$		135		
L^2RH^{2+}	1.12×10^3	24	47	
L^2RhD^{2+}	338			
$(CH_3)_3CCHO$	23	0.16	140	$\sim 10^7$[b]
m- and *p*-$XC_6H_4CH_3$				$\sim 10^7$[c]
DHA[d]				3×10^5[e]

[a] $[H^+]$ = ionic strength = 0.10 M, 25 °C. For rhodium hydrides, identical rate constants were obtained in H_2O and 10% H_2O/90% D_2O.[2] [b] Calculated from $k_{t-BuOO} \approx 8\ M^{-1}\ s^{-1}$ in heptane[9] and $k_{t-BuO} = 8.9 \times 10^7\ M^{-1}\ s^{-1}$ in 1:2 benzene/di-*tert*-butyl peroxide. Data are for propionaldehyde.[50] [c] References 6 and 43. [d] DHA = Dihydroanthracene. [e] Estimated from the data for *t*-BuO$^•$ and *s*-BuOO$^•$ in ref 8.

The complicated kinetic behavior under air-free conditions in the absence of scavengers, Figure 1b, is probably caused by a combination of steps initiated by rapid reduction of $CrOO^{2+}$ and/or $CrOOH^{2+}$ by $CMe_3C^•O$, eventually producing Cr^{2+}, as observed in some other air-free reactions of $CrOO^{2+}$.[15] It is the elimination of such steps by the removal of $CMe_3C^•O$ and/or Cr^{2+} that is responsible for the effect of $(NH_3)_5CoBr^{2+}$ in Figure 4. From the fact that the reaction of $CMe_3C^•O$ with 10^{-4} M $CrOO^{2+}$, eq 7c, can successfully compete with decarbonylation, and taking $k_{7a} \approx 10^5\ s^{-1}$ in aqueous solution, we estimate $k_{7c} \approx 10^9\ M^{-1}\ s^{-1}$.

The kinetics of the reaction between CrO^{2+} and CMe_3CHO, eq 14, were redetermined in 0.10 M $HClO_4$. As reported earlier,[12] the reaction in O_2-containing solutions failed to produce $CrOO^{2+}$, signaling a 1-e mechanism which does not produce free Cr^{2+}. The rate constant obtained here, 45.2 ± 0.3 s^{-1}, is close to the value reported earlier at 1 M ionic strength, 37.1 ± 6.4 $M^{-1}\ s^{-1}$.[12] Based on the products, see below, we believe that $k_{obs} = 2k_{14}$, and Table 1 lists the corrected value, $k_{14} = 23$ $M^{-1}\ s^1$.

$$CrO^{2+} + CMe_3CHO \rightarrow CrOH^{2+} + CMe_3C^•O \quad (14)$$

Products. The main gaseous product of the reaction between 0.05 mM CrO^{2+} and 0.4 mM CMe_3CHO was isobutene. Small amounts of isobutane were also observed. The yield of isobutene was greatly reduced when the reaction was conducted in the presence of 0.6 mM $(NH_3)_5CoBr^{2+}$. These results are easily rationalized by a scheme whereby the decarbonylation of acyl radicals, produced in reaction 14, is followed by the oxidation of the newly generated *tert*-butyl radicals by CrO^{2+}, eq 15. Similarly, acyl radicals themselves are probably also oxidized by CrO^{2+}, but the resulting carboxylic acid is not volatile and would not be detected by GC. Regardless of the proportion of acyl radicals that undergo decarbonylation, for every rate determining step (eq 14) an additional mole of CrO^{2+} is consumed, and thus $k_{obs} = 2k_{14}$. This would not be true if a significant portion of $CMe_3C^•O$ reacted with O_2 (eq 7b), an unlikely possibility at typical oxygen concentrations of ≤0.2 mM[16] in solutions of CrO^{2+}. Consistent with this picture, 0.6 mM $(NH_3)_5CoBr^{2+}$ caused a large drop in the yield of CH_2CMe_2.

$${}^•CMe_3 + CrO^{2+} \xrightarrow{\text{fast}} CH_2{=}CMe_2 + CrOH^{2+} \quad (15)$$

Large concentrations of CMe_3CHO (>0.02 M) were required to make reaction 6 significantly faster than the background

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decomposition of $CrOO^{2+}$.[19] This presented no problem in kinetic experiments, but did complicate product analysis. The gas phase above the ice-cold reaction solutions still contained large amounts of CMe_3CHO which decomposed in the injector of the gas chromatograph into equimolar amounts of isobutene and isobutane, making it impossible to determine whether any additional amounts of these hydrocarbons were produced.

All of the data point to hydrogen atom transfer as the mechanism for the reactions of CMe_3CHO with both CrO^{2+} and $CrOO^{2+}$. The effect of O_2 and $(NH_3)_5CoBr^{2+}$ on the $CrOO^{2+}$ reaction, and the effect of $(NH_3)_5CoBr^{2+}$ on the products of CrO^{2+} reaction clearly show that acetyl radicals are involved. An alternative route to the radicals, electron transfer followed by deprotonation of the aldehydic C−H bond, appears highly unlikely in aqueous solution.

As shown in Table 1, the ratio k_{CrO}/k_{CrOO} for the reactions of CrO^{2+} and $CrOO^{2+}$ with CMe_3CHO is 140, close to that obtained in the reactions with rhodium hydrides and very much smaller than k_{t-BuO}/k_{t-BuOO} of $\sim 10^7$ observed for propionaldehyde or $10^{6\pm1}$ for a number of other organic molecules.[6,8] The data for the reactions of pivalaldehyde with t-BuO$^\bullet$ and t-BuOO$^\bullet$ are not available, but they are expected to be very similar to those for propionaldehyde.

The choice of rhodium hydrides as substrates in our earlier work is clearly not responsible for the small k_{CrO}/k_{CrOO} ratio observed. Instead, the data suggest that the energy of the O−H bonds being formed determines the reactivity ratio and the energy of the bonds being broken (Rh−H or C−H) plays a minor role at best. Such a behavior is predicted by Marcus theory[35−39] for atom transfer,[40] because the properties of the common reactant ($LRhH^{2+}$ or CMe_3CHO) for the pairs RO$^\bullet$/ROO$^\bullet$ and $CrO^{2+}/CrOO^{2+}$ cancel out.

The application of Marcus equation to the reactions of CrO^{2+} and $CrOO^{2+}$ with a common reagent, say CMe_3CHO, yields eq 16, where k_{12} ($= k_{CrO}$) and k_{13} ($= k_{CrOO}$) represent the rate constants for the cross reactions with CrO^{2+} and $CrOO^{2+}$, respectively, K_{12} and K_{13} are the equilibrium constants for the same reactions, and k_{11}, k_{22}, and k_{33} are the rate constants for the identity reactions of the couples $CMe_3CHO/CMe_3C^\bullet O$, $CrO^{2+}/CrOH^{2+}$, and $CrOO^{2+}/CrOOH^{2+}$, respectively. The work terms and f factors[39] in the numerator and denominator of eq 16 are not shown because the treatment assumes that they are similar and cancel out. Because of the negligible entropy difference in reaction 17, the free energy difference ΔG_{23} can be approximated as the difference in bond energies between $CrOO{-}H^{2+}$ and $CrO{-}H^{2+}$.

$$\frac{k_{12}}{k_{13}} = \frac{[k_{11}k_{22}K_{12}]^{0.5}}{[k_{11}k_{33}K_{13}]^{0.5}} = \left(\frac{k_{22}}{k_{33}}\right)^{0.5}(K_{23})^{0.5} = \left(\frac{k_{22}}{k_{33}}\right)^{0.5}[\exp(-0.5\Delta G_{23}/RT)] \quad (16)$$

$$CrO^{2+} + CrOOH^{2+} \rightarrow CrOH^{2+} + CrOO^{2+} \quad \Delta G_{23} \quad (17)$$

The bond energy for $CrO{-}H^{2+}$ is estimated as ≥ 373 kJ/mol from the thermodynamic cycle shown below at 1 M H^+ and setting ΔS^0 for the net reaction equal to $-S^0$ for $H_{aq}^\bullet$.[1] The combination with the previously estimated bond energy for $CrOO{-}H^{2+}$ of 330 kJ/mol[1] yields $\Delta G_{23} \approx -43$ kJ/mol.

$$Cr_{aq}O^{2+} + 2\,H_{aq}{}^{+} + e^- \rightleftarrows Cr_{aq}H_2O^{3+} \qquad \Delta G \leq -165 \text{ kJ/mol}^{11}$$

$$Cr_{aq}H_2O^{3+} \rightleftarrows Cr_{aq}OH^{2+} + H_{aq}{}^{+} \qquad 23 \text{ kJ/mol } (pK_a = 4)$$

$$H_{aq}{}^{\bullet} \rightleftarrows H_{aq}{}^{+} + e^- \qquad -221 \text{ kJ/mol}^{41}$$

Net:

$$Cr_{aq}O^{2+} + H_{aq}{}^{\bullet} \rightleftarrows Cr_{aq}OH^{2+} \qquad \Delta G \leq -363 \text{ kJ/mol } (\Delta H \leq -373 \text{ kJ/mol})$$

The uncertainty in ΔG_{23} is large, because two of the constituent parameters, the potential for CrO^{2+}/Cr^{3+}[11] and the bond energy[1] for $LRh{-}H^{2+}$ are only estimates. With this in mind, and assuming for the moment that $k_{22}/k_{33} \approx 1$, we calculate k_{12}/k_{13} ($= k_{CrO}/k_{CrOO}$) $\geq 6 \times 10^3$. The agreement with the observed value of $\sim 10^2$ is not unreasonable within the framework of Marcus theory. Similar calculations for t-BuO$^\bullet$/t-BuOO$^\bullet$, using bond energies of 440 kJ/mol (BuO−H)[42] and 369 (BuOO−H)[33] and again assuming similar rate constants for the identity reactions for BuO$^\bullet$/BuOH and BuOO$^\bullet$/BuOOH yields $k_{BuO}/k_{BuOO} \approx 10^6$. The close agreement between the calculated and observed values for the organic radicals, Table 1, and the acceptable agreement in the case of chromium complexes supports the assumptions built into the calculations and points to the O−H bond energies as a factor most responsible for the observed reactivities. Interestingly, a strong correlation has also been found between the energy of the O−H bond formed and the kinetics of oxidation of organic materials with CrO_2Cl_2 and MnO_4^-.[43]

The finding that $CrOO^{2+}$ is only 10^2 times slower than CrO^{2+} in hydrogen abstraction reactions may require some of the catalytic oxidation schemes to be rethought. With some exceptions,[44−48] the existing mechanisms usually have metal−superoxo species as (relatively unreactive) precursors to the more reactive oxidizing intermediates,[49] including metal−oxo species. With the reactivity differences smaller than previously thought, at least in the chromium case, it becomes possible for some superoxo complexes to be actively involved in substrate oxidation. Clearly, more data are needed on the reactivity of oxo and superoxo complexes of the same metal and ligand systems. Unfortunately, not too many examples of such pairs are known and we are currently exploring new methods for their generation.

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Table 2. Thermodynamic Data for Chromium-Based Intermediates and O−Centered Radicals

	O−H BDE (kJ/mol)	source
t-BuOH	440	ref 42
$CrOH^{2+}$	>373[a]	this work
t-BuOOH	369	ref 33
$CrOOH^{2+}$	330[a]	ref 1

[a] Solution phase.

Now that kinetic data are available for hydrogen atom abstraction from similar compounds, the absolute rate constants for organic and metal-based intermediates can be compared for the first time. As expected, *t*-$BuO^\bullet$ is by far the most reactive ($k = 9 \times 10^7$ M^{-1} s^{-1}) and $CrOO^{2+}$ the least (0.16 M^{-1} s^{-1}). On the basis of the perception that transient, high-valent metal−oxo complexes are highly reactive whereas alkylperoxyl radicals are not, one might find the similarity between k_{CrO} (23 M^{-1} s^{-1}) and k_{BuOO} (8 M^{-1} s^{-1}) surprising. Metal−oxo complexes may indeed be more reactive than alkylperoxyl radicals in electron transfer and oxo-transfer reactions. The energies of the element-hydrogen bonds for CrO^{2+}/$CrOH^{2+}$ and *t*-$BuOO^\bullet$/*t*-BuOOH are, however, quite comparable (Table 2), and the similarity between the two rate constants simply supports the picture whereby the reactivity in hydrogen abstraction reactions is indeed determined by the energy of the OH bonds.

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