



Superoxometal-catalyzed co-oxidation of alcohols and nitrous acid with molecular oxygen

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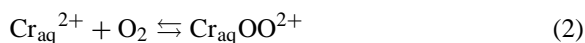
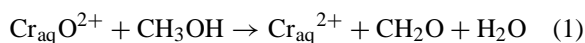
Abstract

A superoxochromium(III) ion, $\text{Cr}_{\text{aq}}\text{OO}^{2+}$, acts as a catalyst for the co-oxidation of alcohols and nitrous acid with molecular oxygen according to the stoichiometry: $\text{CH}_3\text{OH} + \text{HNO}_2 + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{NO}_3^- + \text{H}_2\text{O} + \text{H}^+$. The kinetics are second order in $[\text{HNO}_2]$ and independent of the concentrations of the superoxochromium catalyst, substrate, and O_2 . The proposed mechanism features the disproportionation of HNO_2 to NO and NO_2 , both of which react rapidly with $\text{Cr}_{\text{aq}}\text{OO}^{2+}$. The $\text{Cr}_{\text{aq}}\text{OO}^{2+}/\text{NO}$ reaction generates another equivalent of NO_2 and a mole of $\text{Cr}_{\text{aq}}\text{O}^{2+}$, the active oxidant. The two-electron oxidation of the alcohol by $\text{Cr}_{\text{aq}}\text{O}^{2+}$ produces $\text{Cr}_{\text{aq}}^{2+}$, which reacts rapidly with O_2 to regenerate the catalyst, $\text{Cr}_{\text{aq}}\text{OO}^{2+}$. The $\text{NO}_2/\text{Cr}_{\text{aq}}\text{OO}^{2+}$ reaction yields the peroxy-nitrate complex, $\text{Cr}_{\text{aq}}\text{OONO}_2^{2+}$, in a dead-end equilibrium process that has no effect on the catalytic reaction. The disproportionation of NO_2 yields the final nitrogen-containing product, NO_3^- , and regenerates an equivalent of HNO_2 . Under a fixed set of conditions, the relative catalytic efficiency (CE) of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ decreases as its concentration increases owing to the competition between O_2 and $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ for the intermediate $\text{Cr}_{\text{aq}}^{2+}$. © 2003 Elsevier Science B.V. All rights reserved.

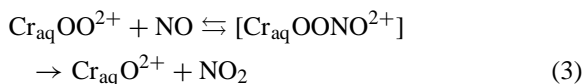
Keywords: Superoxochromium; Oxidation; Nitrous acid; Nitric oxide; Chromium(IV)

1. Introduction

The one-step, two-electron oxidation of organic substrates by aquachromyl(IV) ions, $\text{Cr}_{\text{aq}}\text{O}^{2+}$, is fast and quantitative [1,2]. The chromium product, $\text{Cr}_{\text{aq}}^{2+}$, is readily converted to a superoxochromium(III) complex in the presence of molecular oxygen [3,4]. This chemistry is described in Eqs. (1) and (2) using methanol as a reductant for $\text{Cr}_{\text{aq}}\text{O}^{2+}$.



If superoxochromium(III) ions could be converted back to $\text{Cr}_{\text{aq}}\text{O}^{2+}$, then a catalytic cycle would be created for the oxidation of methanol and other organic substrates by O_2 . So far we have identified only one reagent—nitrogen monoxide—that can carry out this transformation [5] (Eq. (3)).



In view of the rapid oxidation of nitric oxide by molecular oxygen in a process that is kinetically second order in NO [6] (Eqs. (4) and (5)) reaction (3) is not useful for catalytic oxidations unless the concentrations of NO are very low. Under such conditions, the rates of reactions (3) and (4) could be adjusted to make the NO auto-oxidation negligibly slow in comparison

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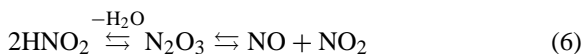
with the NO/Cr_{aq}OO²⁺ reaction of Eq. (3).



$$-\frac{d[\text{NO}]}{dt} = 4k_{\text{NO}}[\text{NO}]^2[\text{O}_2],$$

$$k_{\text{NO}} = 2 \times 10^6 \text{ M}^{-2} \text{ s}^{-1} \quad (5)$$

To avoid the handling of dilute solutions of air-sensitive NO, we explored the use of HNO₂ as a source of NO for reaction (3). The disproportionation of HNO₂ to NO and NO₂ takes place according to Eq. (6). In the presence of reagents that react rapidly with NO and/or NO₂, the reverse reaction is blocked and the rate of formation of NO in 0.1 M HClO₄, the preferred medium for Cr_{aq}OO²⁺, is 28 [HNO₂]² M s⁻¹ [7].



This paper describes our efforts to utilize Cr_{aq}OO²⁺ as a catalyst for the co-oxidation of organic substrates and nitrous acid with molecular oxygen according to Eqs. (1)–(3) and (6).

The following abbreviations will be used throughout the paper: CE = catalytic efficiency = [product]_∞/[Cr_{aq}OO²⁺]₀, AN = acetonitrile, en = diaminoethane, Ph = C₆H₅.

2. Experimental

Reagent grade perchloric acid, zinc metal, mercury(II) chloride, methanol, ethanol, 2-propanol, acetonitrile (all Fisher), and benzyl alcohol (Aldrich) were used as received. Nitrous acid was generated in situ by injecting the desired amount of sodium nitrite (Aldrich) into acidic aqueous solutions containing all the other components. Pentaamminenitrocobalt(III) triflate and chromium(III) perchlorate were available from our previous studies [5]. Solutions of Cr_{aq}²⁺, Cr_{aq}OO²⁺, and Cr_{aq}OOH²⁺ were prepared as previously described [5]. In-house deionized water was further purified by passage through a Millipore Milli-Q system.

UV-Vis spectra were recorded by use of a Shimadzu 3101 PC spectrophotometer. Laser flash photolysis experiments utilized an applied photophysics Nd-YAG laser system (λ_{exc} = 355 nm) which was described

elsewhere [8]. Steady state photolysis was performed with the use of a Sperti Del Sol sunlamp, λ_{exc} = 366 nm (~75%) and 313 nm (~25%) at ambient temperature.

3. Results

3.1. General observations

The reaction between Cr_{aq}OO²⁺ (13–20 μM), HNO₂ (0.34–1.75 mM) and methanol (0.007–0.87 M) in oxygen-saturated aqueous solutions was monitored by the loss of superoxochromium complex at 293 nm. The final absorbance reading yielded an apparent molar absorptivity for Cr-containing products of 4.0 × 10² M⁻¹ cm⁻¹. Formaldehyde was quantitated at the end of the reaction by chromotropic acid analysis [9] after purging the solution with argon for several minutes to remove CH₃ONO. The reaction was clearly catalytic, and the catalytic efficiency (CE), defined as [CH₂O]_∞/[Cr_{aq}OO²⁺]₀, ranged from 1 to 33 (Table 1). The order of addition of the reagents had no effect on the yield of formaldehyde, but lower concentrations of Cr_{aq}OO²⁺ resulted in higher CEs. The initial concentration of HNO₂ was of marginal importance.

Methanol affected the reaction in two ways. At concentrations below ~0.8 M, the yields of CH₂O increased with [MeOH] until they reached a plateau. The kinetics of disappearance of Cr_{aq}OO²⁺ and formation of CH₂O, on the other hand, slowed down as [CH₃OH] increased in the range 0.007–2 M. The decrease in rates was traced to the formation of methyl nitrite (Eq. (7)) which has K_{RONO} = 3.5 M⁻¹ [10].

Table 1
Yields of CH₂O obtained by Cr_{aq}OO²⁺-catalyzed oxidation of HNO₂/CH₃OH^a

[MeOH] (M)	[HNO ₂] (mM)	[CH ₂ O] _∞ /[Cr _{aq} OO ²⁺] ₀
0.007	0.84	1
0.40	1.0	15
0.81	0.34	15
0.81	0.84	20
0.87	1.75	20
0.84	1.2	33 ^b

^a Room temperature, 0.10 M HClO₄, [Cr_{aq}OO²⁺] = 20 μM.

^b [Cr_{aq}OO²⁺] = 13 μM.

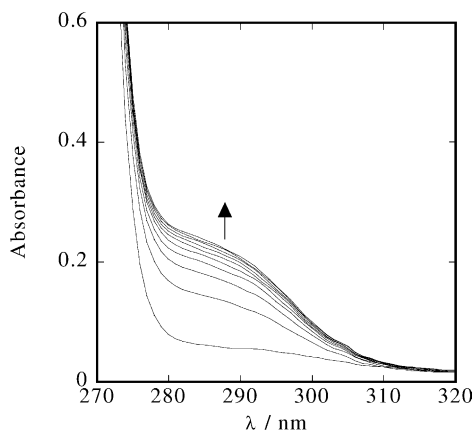


Fig. 1. Spectral scans showing the formation of benzaldehyde in the reaction between $20 \mu\text{M Cr}_{\text{aq}}\text{OO}^{2+}$, $0.11 \text{ M PhCH}_2\text{OH}$, and 0.14 mM HNO_2 in oxygen saturated aqueous solution at pH 1. Time interval between successive spectra is 150 s.

The ester is unreactive, probably because it does not disproportionate.



Similar effects were observed in the oxidation of benzyl alcohol. The reaction was followed at 287 nm, where the spectrum of benzaldehyde exhibits a shoulder (Fig. 1). The concentration of PhCHO was determined directly after a minor correction for the absorption by Cr-containing products ($\epsilon_{287} \sim 400 \text{ M}^{-1} \text{ cm}^{-1}$).

At low concentrations of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ ($10 \mu\text{M}$), the reaction was limited by $[\text{Cr}_{\text{aq}}\text{OO}^{2+}]$ as no more PhCH_2OH could be oxidized by addition of extra HNO_2 . The number of CE under these conditions was 8–10. At higher $[\text{Cr}_{\text{aq}}\text{OO}^{2+}]$ ($40 \mu\text{M}$), significant amounts of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ remained unreacted. Under such conditions of limiting HNO_2 , the reaction stoichiometry, expressed as $[\text{PhCHO}]_{\infty}/[\text{HNO}_2]_0$, was precisely 1:1 at $[\text{PhCH}_2\text{OH}] \geq 0.1 \text{ M}$. The addition of more HNO_2 produced more PhCHO. The maximum amount was again 8–10 times greater than $[\text{Cr}_{\text{aq}}\text{OO}^{2+}]_0$.

The yields of benzaldehyde were determined under different experimental conditions as a measure of the efficiency of the catalytic substrate oxidation versus catalyst decomposition. Fig. 2 shows the dependence of the yields of PhCHO on pH, solvent composition,

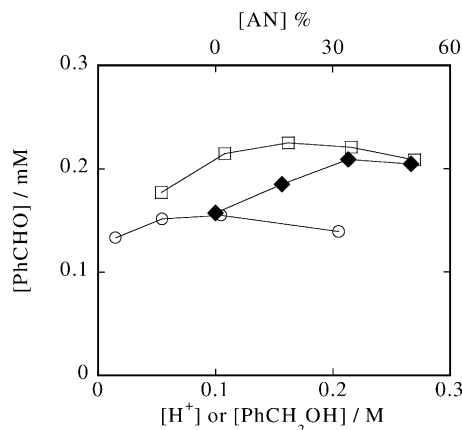


Fig. 2. Yields of benzaldehyde in the reaction between $\text{Cr}_{\text{aq}}\text{OO}^{2+}$, HNO_2 and PhCH_2OH as a function of reagent concentrations: (O) dependence on $[\text{H}^+]$ ($20 \mu\text{M Cr}_{\text{aq}}\text{OO}^{2+}$, 0.28 mM HNO_2 , $0.11 \text{ M PhCH}_2\text{OH}$); (□) dependence on $[\text{PhCH}_2\text{OH}]$ ($37 \mu\text{M Cr}_{\text{aq}}\text{OO}^{2+}$, 0.21 mM HNO_2); (◆) dependence on $[\text{AN}]$ ($20 \mu\text{M Cr}_{\text{aq}}\text{OO}^{2+}$, 0.28 mM HNO_2 , $0.11 \text{ M PhCH}_2\text{OH}$). All the experiments were run in aqueous solutions at pH 1 and 25°C .

and concentration of benzyl alcohol. The yields were insensitive to $[\text{HNO}_2]$ in the range $0.14\text{--}0.28 \text{ mM}$. The small effect of $[\text{H}^+]$ paralleled its known effect on the stability of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$, i.e. the maximum yield of PhCHO (CE = 8) was obtained at 0.10 M H^+ . The effect of AN as a cosolvent was significant. The yields of PhCHO increased with AN content, but reached saturation at 40% AN, where the maximum CE was 10.

A series of experiments with different $[\text{PhCH}_2\text{OH}]$ was carried out at $[\text{Cr}_{\text{aq}}\text{OO}^{2+}] = 37 \mu\text{M}$ and $[\text{HNO}_2] = 0.21 \text{ mM}$. Under these conditions, the reaction was limited by $[\text{HNO}_2]$ and the changing yields of PhCHO were indicative of deviations from the 1:1 ($[\text{PhCHO}]_{\infty}/[\text{HNO}_2]_0$) stoichiometry. The yields increased sharply as PhCH_2OH increased from 0.05 to 0.15 M . At this point, the stoichiometry was 1:1. At even higher alcohol concentrations, the aldehyde yields decreased slightly (Fig. 2).

3.2. Effect of added alcohols

To find out whether $\text{Cr}_{\text{aq}}\text{O}^{2+}$ is the active oxidant, competition experiments with several alcohols were carried out. Provided the reaction between $\text{Cr}_{\text{aq}}\text{O}^{2+}$ and PhCH_2OH is the only product-forming step

in the catalytic system, one should be able to affect the yields of PhCHO in a predictable way on the basis of the known rate constants and concentrations of the competing alcohols. Three different alcohols—methanol (0.080 M), ethanol (0.048 M) and 2-propanol (0.36 M)—were used in three separate experiments. At the concentrations chosen, the yield of PhCHO was predicted to be 58% of that obtained in the absence of competing alcohols, i.e. $k_{\text{MeOH}}[\text{methanol}] = k_{\text{EtOH}}[\text{ethanol}] = k_{2\text{-PrOH}}[2\text{-propanol}] = 0.72k_{\text{PhCH}_2\text{OH}}[\text{PhCH}_2\text{OH}]$, where k_{MeOH} , k_{EtOH} , $k_{2\text{-PrOH}}$, and $k_{\text{PhCH}_2\text{OH}}$ are the second-order rate constants for the reactions of $\text{Cr}_{\text{aq}}\text{O}^{2+}$ with the respective alcohols. The values of all the rate constants were taken from our previous work at $\mu = 1.0\text{ M}$ [1]. Fig. 3 shows the kinetic traces for the formation of PhCHO at 287 nm in the presence of the alcohols. The alcohol concentrations are sufficiently high to maintain the pseudo-first-order conditions, and the relative rates for the $\text{Cr}_{\text{aq}}\text{O}^{2+}$ /alcohol reactions are largely independent of ionic strength [1] so that the ratio of rate constants at 1 and 0.1 M ionic strength should be comparable. As can be seen from the figure, the concentration of PhCHO produced was nearly identical in the three experiments, as pre-

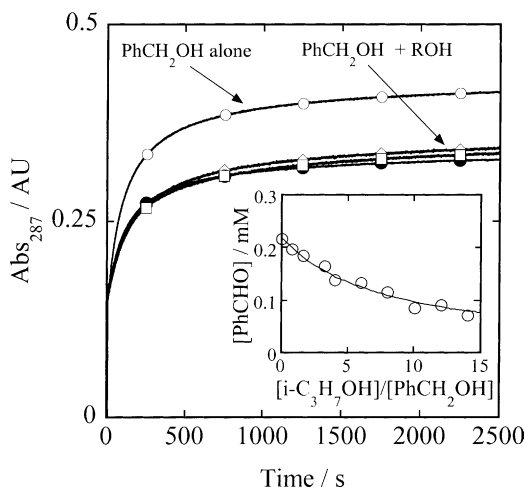


Fig. 3. Formation of benzaldehyde by oxidation of 0.11 M benzyl alcohol in the presence of competing alcohols. Conditions: $[\text{Cr}_{\text{aq}}\text{OO}^{2+}] = 37\ \mu\text{M}$, $[\text{HNO}_2] = 0.21\ \text{mM}$, oxygen saturated 0.1 M HClO_4 , $\lambda = 287\ \text{nm}$. (○) Benzyl alcohol alone; (◇) 0.080 M methanol; (●) 0.048 M ethanol; (□) 0.36 M 2-propanol. Inset: yields of benzaldehyde as a function of the concentration ratio $[2\text{-propanol}]/[\text{PhCH}_2\text{OH}]$. Solid line represents a fit to Eq. (8).

dicted. This result strongly supports our contention that $\text{Cr}_{\text{aq}}\text{O}^{2+}$ is the active oxidant.

Another set of experiments examined the effect of varying concentrations of 2-propanol (0.087–1.52 M) on the yield of PhCHO. As expected, higher concentrations of 2-propanol lowered the yields of PhCHO. The data were fitted to Eq. (8) for competition kinetics where Abs_{287} is the final absorbance reading, and Abs_0 and Abs_∞ denote the readings at $[2\text{-propanol}] = 0$ and $[2\text{-propanol}] \gg [\text{PhCH}_2\text{OH}]$, respectively.

$$\text{Abs}_{287} = \text{Abs}_\infty + \frac{\text{Abs}_0 - \text{Abs}_\infty}{1 + (k_{2\text{-PrOH}}[2\text{-PrOH}]/k_{\text{PhCH}_2\text{OH}}[\text{PhCH}_2\text{OH}])} \quad (8)$$

This equation is valid if chromyl is the only oxidizing species, and the degree of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ decomposition, which contributes to the absorbance changes at 287 nm, is the same at all the concentrations of 2-propanol. The fit in Fig. 3 gives $k_{2\text{-PrOH}}/k_{\text{PhCH}_2\text{OH}} = 0.12 \pm 0.01$, reasonably close to the directly determined value of 0.21 at $\mu = 1.0\text{ M}$. The less than perfect agreement is probably caused by changes in the reaction medium at high concentrations of 2-propanol.

The formation of benzyl nitrite from HNO_2 and benzyl alcohol in a reaction analogous to that in Eq. (7) was studied by observing the build-up of the ester at 375 nm (water) or 366 nm (40% AN in H_2O). At typical concentrations (0.01 M HNO_2 and 0.05–1.0 M PhCH_2OH at pH 1), the reaction was complete in mixing time (several seconds) in water and in several minutes in AN/ H_2O . The data were fitted to Eq. (9), where $\Delta\varepsilon$ represents the molar absorptivity change at a given $[\text{PhCH}_2\text{OH}]$, and $\Delta\varepsilon_0$ is the difference in molar absorptivity between the products and the reactants. The data afforded $K_{\text{RONO}} = 0.44 \pm 0.17\ \text{M}^{-1}$ (H_2O) and $0.49 \pm 0.02\ \text{M}^{-1}$ (AN/ H_2O), $\varepsilon_{375}(\text{PhCH}_2\text{ONO}) = 160 \pm 40\ \text{M}^{-1}\ \text{cm}^{-1}$ (H_2O), and $\varepsilon_{366}(\text{PhCH}_2\text{ONO}) = 195 \pm 5\ \text{M}^{-1}\ \text{cm}^{-1}$ (AN/ H_2O). The large errors in water are caused by limited solubility of PhCH_2OH which resulted in small conversions to PhCH_2ONO .

$$\Delta\varepsilon = \Delta\varepsilon_0 \frac{K_{\text{RONO}}[\text{PhCH}_2\text{OH}]}{1 + K_{\text{RONO}}[\text{PhCH}_2\text{OH}]} \quad (9)$$

3.3. Kinetics of the catalytic reaction

The oxidation of methanol is not accompanied by measurable absorbance changes in the UV-Vis

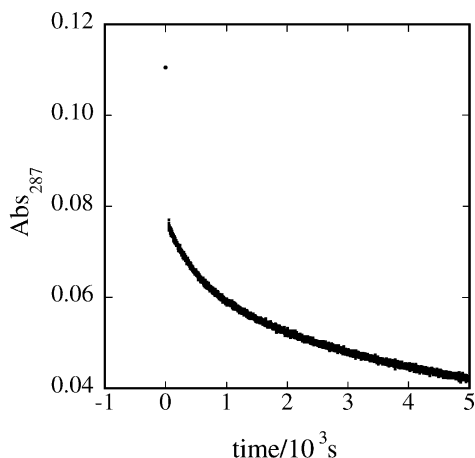


Fig. 4. Kinetic trace at 293 nm for the disappearance of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ ($37 \mu\text{M}$) during the catalytic co-oxidation of methanol (0.11 M) and HNO_2 (0.21 mM) in 0.10 M aqueous HClO_4 . The concentration of stock HNO_2 was 2.4 mM . The rapid drop in absorbance in mixing time signals the conversion of a portion of superoxochromium catalyst to the nonabsorbing peroxyxynitrate complex, see text.

spectrum, and only the disappearance of the catalyst, $\text{Cr}_{\text{aq}}\text{OO}^{2+}$, could be observed. All the experiments exhibited a rapid, initial absorbance decrease at 293 nm , followed by a slower decrease (Fig. 4). The timescale ($8\text{--}10 \text{ s}$) and the magnitude ($20\text{--}25\%$ of the $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ absorbance) of the initial decrease were approximately constant under all the conditions. Clearly, a portion of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ was consumed much more rapidly than the rest.

Nitrous acid was the last reagent to be injected in all the kinetic experiments, and one might suggest that some $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ was consumed in the reaction with high local concentrations of HNO_2 during the imperfect, manual mixing of the reagents. The effect could be especially serious because of the second-order dependence on $[\text{HNO}_2]$, see later. This hypothesis was ruled out in a set of kinetic runs using lower concentrations of HNO_2 stock solutions. A proportionately larger volume was injected so as to maintain the same final concentration. Under our typical conditions ($37 \mu\text{M}$ $\text{Cr}_{\text{aq}}\text{OO}^{2+}$, 0.21 mM HNO_2 , and 0.11 M methanol) the fast absorbance decrease remained virtually unchanged when 21.3 , 7.1 , and 2.4 mM HNO_2 stock solutions were used, suggesting that the observed phenomenon is an inherent feature of the catalytic system rather than a result of high local concentrations of HNO_2 at early times.

The oxidation of PhCH_2OH was monitored at 287 nm , where PhCHO absorbs strongly. These traces also exhibited the initial absorbance decrease followed by an increase as PhCHO grew in. The kinetic analysis of the slower portion is described below. At low $[\text{Cr}_{\text{aq}}\text{OO}^{2+}]$, a sudden break in the kinetic traces signaled the moment when all the $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ was consumed. In those cases, the kinetic treatment used the data points preceding the break.

The reaction was second order in $[\text{HNO}_2]$ ($0.10\text{--}0.28 \text{ mM}$), but at higher concentrations of benzyl alcohol ($>0.2 \text{ M}$), small deviations toward first-order kinetics were observed. All the data were fitted to the second-order integrated rate law in Eq. (10),

$$\text{Abs}_t = \text{Abs}_\infty + \frac{\text{Abs}_0 - \text{Abs}_\infty}{1 + k[\text{HNO}_2]_0 t} \quad (10)$$

The rate constants were independent of $[\text{Cr}_{\text{aq}}\text{OO}^{2+}]$ ($10\text{--}40 \mu\text{M}$). The minor observed rate retardation by PhCH_2OH in the range $0.05\text{--}0.21 \text{ M}$ disappeared once the concentration of $[\text{HNO}_2]$ was corrected for the small amount of the ester, PhCH_2ONO , formed under these conditions. Kinetic calculations assumed that PhCH_2ONO was unreactive, and yielded a constant value for k , $34 \text{ M}^{-1} \text{ s}^{-1}$ at 0.10 M H^+ . At higher concentrations of PhCH_2OH , the imperfect fits produced larger apparent rate constants. At the largest concentration of PhCH_2OH used, 0.27 M , the value of the rate constant was $44 \text{ M}^{-1} \text{ s}^{-1}$. We explain these results by the presence of low levels of an unidentified, reactive impurity in PhCH_2OH . For this explanation to be valid, the reaction with the impurity must regenerate the catalyst less efficiently than the oxidation of PhCH_2OH does, or not at all, thus increasing the apparent rate constant and decreasing the yield of PhCHO , as observed. The level of impurity is clearly very low, so that its effects show up only at the largest amounts of the alcohol used.

The $[\text{H}^+]$ dependence was studied in the range $0.015\text{--}0.20 \text{ M}$ at variable ionic strength ($\mu = [\text{H}^+]$). The fit to Eq. (11) [7] yielded $k_1 = 12 \pm 2 \text{ M}^{-1} \text{ s}^{-1}$ and $k_2 = 200 \pm 20 \text{ M}^{-2} \text{ s}^{-1}$, in good agreement with our previous data for the disproportionation of HNO_2 , $k_1 = 10.9 \text{ M}^{-1} \text{ s}^{-1}$, $k_2 = 175 \text{ M}^{-2} \text{ s}^{-1}$.

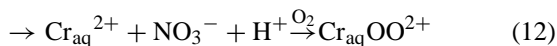
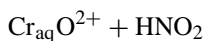
$$\text{rate} = k_{\text{obs}}[\text{HNO}_2]^2 = (k_1 + k_2[\text{H}^+])[\text{HNO}_2]^2 \quad (11)$$

Solvent polarity also affected the rate of the catalytic reaction. At $[\text{HNO}_2] = 0.28 \text{ mM}$ and $[\text{Cr}_{\text{aq}}\text{OO}^{2+}] =$

20 μM at pH 1, the kinetics of PhCHO formation in AN/water mixtures remained second order in $[\text{HNO}_2]$, but the rate constants decreased as the proportion of AN increased. The following values were obtained: $34 \text{ M}^{-1} \text{ s}^{-1}$ (0% AN), $17 \text{ M}^{-1} \text{ s}^{-1}$ (17% AN), $6.0 \text{ M}^{-1} \text{ s}^{-1}$ (34% AN), and $1.6 \text{ M}^{-1} \text{ s}^{-1}$ (50% AN).

3.4. Reaction between $\text{Cr}_{\text{aq}}\text{O}^{2+}$ and HNO_2

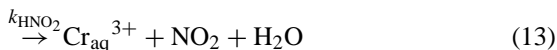
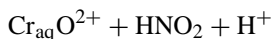
A solution containing $33 \mu\text{M}$ $\text{Cr}_{\text{aq}}\text{O}^{2+}$ and $13 \mu\text{M}$ $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ was mixed with 1–2 mM HNO_2 in oxygen saturated aqueous 15% AN at pH 1. The monitoring wavelength was set at 293 nm to check for the formation of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ as a test for two-electron oxidation of HNO_2 (Eq. (12)).



No absorbance increase was observed. Instead, the absorbance decreased slowly (100 s) in the known reaction between HNO_2 and $\text{Cr}_{\text{aq}}\text{OO}^{2+}$, the latter being always present in our solutions of $\text{Cr}_{\text{aq}}\text{O}^{2+}$.

In the next set of experiments, $35 \mu\text{M}$ $\text{Cr}_{\text{aq}}\text{O}^{2+}$ and $13 \mu\text{M}$ $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ were mixed with HNO_2 in the presence of 2.5 mM methanol in oxygen saturated 6.7% AN in water at pH 1. The formation of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ in the reaction between $\text{Cr}_{\text{aq}}\text{O}^{2+}$ and methanol (Eqs. (1) and (2)) and the subsequent disappearance of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ in the reaction with HNO_2 were observed at 293 nm (Fig. 5).

The timescales for both processes depended strongly on $[\text{HNO}_2]$ and varied between 10 and 80 s for the first stage and 200–1000 s for the second stage. The production of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ in the first stage was accelerated by the presence of HNO_2 , but the overall amount of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ produced was smaller at higher $[\text{HNO}_2]$. This behavior is consistent with competition between reaction (1) and a one-electron oxidation of HNO_2 with $\text{Cr}_{\text{aq}}\text{O}^{2+}$ (Eq. (13)). The rate of formation of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ is the sum of the rates in Eqs. (1) and (13).



Exponential fits to the first stage yielded the values of k_{obs} , which were in turn fitted to Eq. (14) to

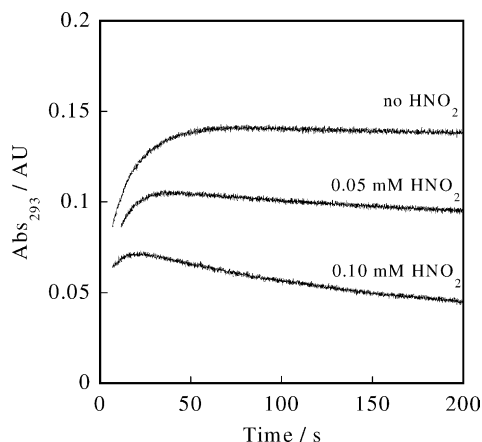


Fig. 5. Effect of 0–0.10 mM HNO_2 on formation and decay of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ at 293 nm for the reaction between 30 and $35 \mu\text{M}$ $\text{Cr}_{\text{aq}}\text{O}^{2+}$ (in the presence of $13 \mu\text{M}$ $\text{Cr}_{\text{aq}}\text{OO}^{2+}$) and 2.5 mM methanol in oxygen saturated 6.7% aqueous AN, pH 1.

yield $k_{\text{HNO}_2} = 950 \pm 160 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{MeOH}} = 24 \pm 4 \text{ M}^{-1} \text{ s}^{-1}$, the latter in excellent agreement with our previous determination, $23 \text{ M}^{-1} \text{ s}^{-1}$ [1].

$$k_{\text{obs}} = k_{\text{MeOH}}[\text{CH}_3\text{OH}] + k_{\text{HNO}_2}[\text{HNO}_2] \quad (14)$$

3.5. Search for other potential catalysts

Several other metal complexes were probed for their ability to catalyze the oxidation of benzyl alcohol with HNO_2/O_2 . A typical set of conditions had 0.11 M PhCH_2OH and 0.14–0.21 mM HNO_2 in oxygen-saturated aqueous solutions at pH 1. No catalytic activity was observed with $28 \mu\text{M}$ $(\text{H}_2\text{O})(\text{Me}_6\text{-cyclam})\text{RhOO}^{2+}$, $37 \mu\text{M}$ $(\text{NH}_3)_4(\text{H}_2\text{O})\text{RhOOH}^{2+}$, or $37 \mu\text{M}$ HCrO_4^- .

A hydroperoxochromium complex, $\text{Cr}_{\text{aq}}\text{OOH}^{2+}$, on the other hand, was as efficient a catalyst as $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ itself (Fig. 6). Kinetic traces at 293 nm showed an initial jump suggesting that some $\text{Cr}_{\text{aq}}\text{OOH}^{2+}$ had been converted to $\text{Cr}_{\text{aq}}\text{OO}^{2+}$. Moreover, the oxidation of (nonabsorbing) methanol instead of benzyl alcohol made it possible to observe the characteristic spectrum of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ ($\lambda_{\text{max}} = 293$ and 245 nm) (inset in Fig. 6).

The potential oxidant for $\text{Cr}_{\text{aq}}\text{OOH}^{2+}$ in the catalytic reaction is NO_2 , believed to be one of the reaction intermediates. To test this possibility, NO_2 was generated by flash photolysis of $(\text{NH}_3)_5\text{CoNO}_2^{2+}$ in

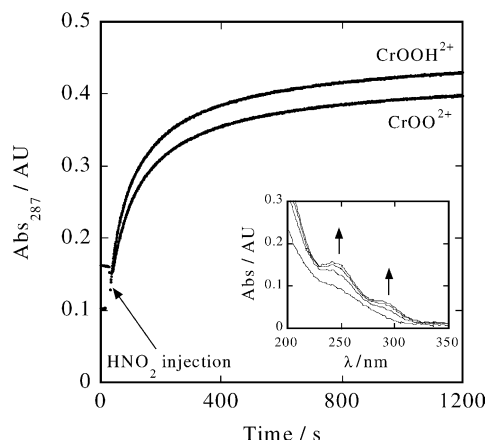
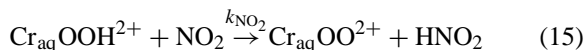


Fig. 6. Co-oxidation of 0.11 M benzyl alcohol and 0.21 mM HNO₂, catalyzed by 37 μM Cr_{aq}OO²⁺ or 37 μM Cr_{aq}OOH²⁺ in oxygen saturated 0.1 M HClO₄. Inset: oxidation of 0.11 M methanol + 0.21 mM HNO₂ catalyzed by Cr_{aq}OOH²⁺ (37 μM) produces Cr_{aq}OO²⁺ (λ_{max} = 245 and 293 nm). Time interval between successive spectra is 200 s.

the presence of Cr_{aq}OOH²⁺ and the absorbance was monitored at 293 nm. A series of experiments with 0.1–0.3 mM Cr_{aq}OOH²⁺ and 5 μM NO₂ did not produce measurable amounts of Cr_{aq}OO²⁺, placing a limit of <10⁶ M⁻¹ s⁻¹ for k_{NO₂} (Eq. (15)).



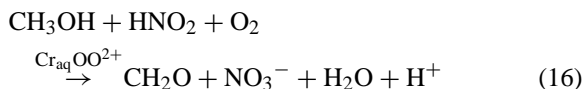
In another experiment, NO₂ (a total of 80 μM) was generated by continuous photolysis of 100 μM (NH₃)₅CoNO₂²⁺ in the presence of 100 μM Cr_{aq}OOH²⁺. About 25 μM Cr_{aq}OO²⁺ was detected by UV-Vis spectrophotometry. Since the spectrophotometric measurement takes ~30 s to complete, the actual amount of Cr_{aq}OO²⁺ produced was higher, but a portion was lost in the reaction with HNO₂. This was confirmed by nitrite analysis. Only 16 μM HNO₂ was detected, much less than the 40 μM observed in a control experiment in the absence of Cr_{aq}OOH²⁺. The photolysis of Cr_{aq}OOH²⁺ alone did not yield significant amounts of the superoxo complex.

To rule out the possibility that Cr_{aq}OO²⁺ is converted to Cr_{aq}OOH²⁺ in the Cr_{aq}OO²⁺-catalyzed oxidations, the reaction with methanol was carried out in the presence of (en)₂Co(SCH₂CH₂NH₂)₂²⁺ (en = 1,2-diaminoethane) which is known to be oxidized by Cr_{aq}OOH²⁺ to a strongly absorbing

sulfinato complex [2]. The experiment using 20 μM Cr_{aq}OO²⁺, 0.11 M methanol, 0.21 mM HNO₂, and 1.63 mM (en)₂Co(SCH₂CH₂NH₂)₂²⁺ in oxygen saturated aqueous solution at pH 1 produced no observable absorbance increase, which allows us to place a limit on the amount of Cr_{aq}OO²⁺ converted to Cr_{aq}OOH²⁺ during the catalytic reaction at less than 10%.

4. Discussion

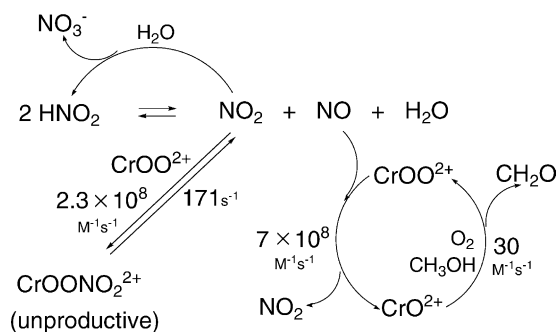
The co-oxidation of alcohols and HNO₂ with O₂ in the presence of Cr_{aq}OO²⁺ is clearly catalytic. The catalytic efficiency of up to 30 was observed for the oxidation of CH₃OH and ~10 for PhCH₂OH. The stoichiometry of the reaction is shown in Eq. (16) using methanol as an example.



The kinetics, studied in detail for PhCH₂OH as a substrate, are strictly second order in [HNO₂] and independent of [O₂] and [Cr_{aq}OO²⁺]. The results of competition between PhCH₂OH and three other alcohols for which the kinetics of reaction with Cr_{aq}OO²⁺ are independently known (Fig. 3) provide compelling evidence for Cr_{aq}O²⁺ as active oxidant.

All the observations are readily explained by the mechanism in Scheme 1.

The catalytic process begins with the disproportionation of HNO₂ to generate NO, a species that reduces Cr_{aq}OO²⁺ to Cr_{aq}O²⁺, which in turn oxidizes the substrate and regenerates Cr_{aq}OO²⁺ in the presence of O₂.

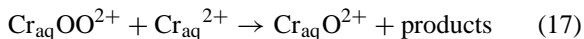


Scheme 1.

For the reaction to be catalytic, the other disproportionation product, NO_2 , must not deplete $\text{Cr}_{\text{aq}}\text{OO}^{2+}$. Initially this seemed unlikely in view of our earlier finding that NO_2 reacts rapidly with $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ [5]. Our recent work [11] has shown, however, that the reaction is reversible and that the initially formed peroxynitrate complex disappears only by homolysis of the N–O bond to regenerate $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ and NO_2 , followed by disproportionation of NO_2 to nitrite and nitrate. The catalysis observed here clearly shows that $\text{Cr}_{\text{aq}}\text{OONO}_2^{2+}$ again displays no chemistry other than the homolysis, making this complex a dead-end intermediate.

If Scheme 1 is applicable, then significant amounts of $\text{Cr}_{\text{aq}}\text{OONO}_2^{2+}$ should be produced in the early stages of the reaction. This calculation is based on the rate constants for the formation and homolysis of $\text{Cr}_{\text{aq}}\text{OONO}_2^{2+}$ and the levels of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ used. As shown in Fig. 4, this prediction is confirmed by the sudden initial drop in absorbance at 290 nm, where $\text{Cr}_{\text{aq}}\text{OONO}_2^{2+}$ does not absorb [11].

The kinetic data in Fig. 6 were simulated with the program Chemical Kinetics Simulator (IBM) using as a basis the mechanism in Scheme 1 (adapted for PhCH_2OH) and the associated rate constants. In addition, the equivalent of reaction (7), and reactions (13) and (17) were included.



The products of reaction (17) are not known precisely, although it has been shown [12] that substoichiometric amounts of $\text{Cr}_{\text{aq}}\text{O}^{2+}$ are formed. The rate constant k_{17} has a value of $8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at 1 M ionic strength [2]. At $\mu = 0.10 \text{ M}$, used in the present work, the value will be smaller, probably about $(3\text{--}5) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The results of the simulations were virtually unaffected when k_{17} was varied in this range.

The simulated traces reproduce the experimental ones to within 20% in terms of both absorbance changes and rate constants, lending strong support to the proposed mechanism.

The catalysis by $\text{Cr}_{\text{aq}}\text{OOH}^{2+}$ was unexpected until it became clear that a substantial portion of the hydroperoxo complex is converted rapidly to the active catalyst $\text{Cr}_{\text{aq}}\text{OO}^{2+}$, as shown in Fig. 6. The absorbance increase at 287 nm brings the initial absorbance to the approximately same level as that in a parallel experiment that started with $\text{Cr}_{\text{aq}}\text{OO}^{2+}$. Given that both

$\text{Cr}_{\text{aq}}\text{OOH}^{2+}$ and $\text{Cr}_{\text{aq}}\text{OONO}_2^{2+}$ are practically transparent at 287 nm, the data are consistent with the chemistry of NO_2 being responsible for all the observations. The absorbance drop when $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ is the catalyst has already been explained by the formation of $\text{Cr}_{\text{aq}}\text{OONO}_2^{2+}$. In $\text{Cr}_{\text{aq}}\text{OOH}^{2+}$ -catalyzed reaction, the NO_2 appears to be the oxidant yielding $\text{Cr}_{\text{aq}}\text{OO}^{2+}$. The experimental data show unequivocally that the reaction (15) takes place with a rate constant $k_{15} < 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Our simulations show that the real value must be close to this limit. The calculated traces reproduce the experimental data extremely well (to within 5%) with k_{15} in the range 10^5 to $10^6 \text{ M}^{-1} \text{ s}^{-1}$. Values around $10^4 \text{ M}^{-1} \text{ s}^{-1}$ are clearly much too low and predict a slow formation of $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ and an s-shaped trace for the growth of PhCHO , very different from the observed absorbance jump in mixing time followed by second-order kinetic traces for the formation of PhCHO . The results clearly show that the catalysis by the $\text{Cr}_{\text{aq}}\text{OOH}^{2+}$ relies exclusively on its prior oxidation to $\text{Cr}_{\text{aq}}\text{OO}^{2+}$.

The use of molecular oxygen at atmospheric pressures poses serious limitations on the catalytic efficiency. At $20 \mu\text{M}$ $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ and 1.2 mM O_2 , the theoretical limit on CE is 60. The observed numbers are smaller, 20 for the oxidation of methanol and 10 for benzyl alcohol. The main factor that reduces the CE is the competition between O_2 and $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ for the intermediate $\text{Cr}_{\text{aq}}^{2+}$. As the concentration of O_2 decreases during the course of the reaction, greater proportions of $\text{Cr}_{\text{aq}}^{2+}$ react in the catalyst-wasting side reaction with $\text{Cr}_{\text{aq}}\text{OO}^{2+}$ (Eq. (17)). This reaction is clearly the main route for the deactivation of the catalyst. The importance of the competition between reactions (2) and (17) was further demonstrated by the increase in CE as the ratio $[\text{O}_2]/[\text{Cr}_{\text{aq}}\text{OO}^{2+}]$ was increased by decreasing $[\text{Cr}_{\text{aq}}\text{OO}^{2+}]$ (Table 1).

The CEs for the oxidation of benzyl alcohol are even smaller than for methanol. The main reason is the low solubility and thus lower concentrations of PhCH_2OH in kinetic experiments. Such conditions slow the reaction of $\text{Cr}_{\text{aq}}\text{O}^{2+}$ with PhCH_2OH and make other competing reactions proportionately more important. The most serious competing reaction is the one-electron oxidation of HNO_2 (Eq. (13)) which converts a mole of active oxidant into the inactive $\text{Cr}_{\text{aq}}^{3+}$ and uses up a mole of nitrous acid in the process.

Work at higher pressures of O₂ should increase the turnover numbers by favoring reaction (2) over (17). Similar effects should be expected from the use of cosolvents, such as AN, which contain higher concentrations of dissolved O₂. Indeed, for a given set of conditions, the CEs in aqueous AN increased with the AN content of the solvent (Fig. 2). After a certain point, however, the CEs leveled-off, as the increased solubility of O₂ was offset by a decrease in the lifetime of Cr_{aq}OO²⁺.

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