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Generation and Reactivity of Rhodium(IV) Complexes in Aqueous Solutions

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At pH = 1 and 25 °C, the Fenton-like reactions of Fe_{aq}^{2+} with hydroperoxorhodium complexes $LRh^{III}OOH^{2+}$ (L = $(H_2O)(NH_3)_4$, $k = 30\ M^{-1}\ s^{-1}$, and L = L^2 = (H_2O)(*meso*-Me_6-[14]aneN_4), $k = 31\ M^{-1}\ s^{-1}$) generate short-lived, reactive intermediates, believed to be the rhodium(IV) species $LRh^{IV}O^{2+}$. In the rapid follow-up steps, these transients oxidize Fe_{aq}^{2+}, and the overall reaction has the standard 2:1 $[Fe_{aq}^{2+}]/[LRhOOH^{2+}]$ stoichiometry. Added substrates, such as alcohols, aldehydes, and $(NH_3)_4(H_2O)RhH^{2+}$, compete with Fe_{aq}^{2+} for $LRh^{IV}O^{2+}$, causing the stoichiometry to change to <2:1. Such competition data were used to determine relative reactivities of $(NH_3)_4RhO^{2+}$ toward CH_3OH (1), CD_3OH (0.2), C_2H_5OH (2.7), 2-C_3H_7OH (3.4), 2-C_3D_7OH (1.0), CH_2O (12.5), C_2H_5CHO (45), and $(NH_3)_4RhH^{2+}$ (125). The kinetics and products suggest hydrogen atom abstraction for $(NH_3)_4RhO^{2+}$/alcohol reactions. A short chain reaction observed with C_2H_5CHO is consistent with both hydrogen atom and hydride transfer. The rate constant for the reaction between Tl_{aq}^{III} and L^2Rh^{2+} is $2.25 \times 10^5\ M^{-1}\ s^{-1}$.

Introduction

Compounds containing rhodium in the +4 oxidation state are rare but not completely unknown.[1,2] Examples include anionic polyhalogeno complexes, which readily hydrolyze in water,[3-6] and cationic polyhydroxo species.[7-15] The $Rh(OH)^{3+}$ ion, for example, can be produced in concentrated mineral acids, where it acts as a mild oxidant toward nitrous acid, hydroxylamine, hydrogen peroxide, Fe(II), and other substrates.[8-10,13] Several organometallic rhodium(IV) compounds have also been reported,[2] but a class of complexes such as Claus Blue, produced by oxidation of Rh(III) and initially believed to contain rhodium(IV), have been shown to be in fact mononuclear or binuclear superoxorhodium(III) ions.[16,17]

Despite the limited data on well-defined, stable Rh(IV) compounds, several reports have provided evidence for Rh(IV) species as intermediates in chemical[18] and electrochemical transformations.[19-21] Some of our own data on the reaction between (H_2O)(*meso*-Me_6-[14]aneN_4)$RhOO^{2+}$ (hereafter L^2RhOO^{2+}) and NO also support the involvement of a transient $L^2Rh(IV)$.[22,23] This finding encouraged us to look for ways to generate $L^2Rh(IV)$ and related species indepen-

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dently, and to study their reactivity, especially in the context of O_2 activation by transition metal complexes.

Previously, we have examined the reactivity of $Cr_{aq}OO^{2+}$ and $Cr_{aq}O^{2+}$ as H-atom abstracting agents.[24] The chromyl ion was found to be about 10^2 times more reactive than $Cr_{aq}OO^{2+}$. By way of comparison, an organic analogue, tert-BuO$^•$, is 10^7 times more reactive than tert-BuOO$^•$. This kinetic difference parallels the trend in thermodynamic driving forces for the two sets of reactions.[24]

In search of other examples of LMO/LMOO pairs (L = ligand) for our mechanistic studies, we decided to explore the tetraammine and macrocyclic rhodium complexes. The superoxo, $LRhOO^{2+}$, and hydroperoxo, $LRhOOH^{2+}$, compounds are known and reasonably stable and might provide access to Rh(IV). Guided by our earlier findings on the reduction of hydroperoxometal complexes with Fe_{aq}^{2+},[25] we expected $LRhOOH^{2+}$ to react with Fe_{aq}^{2+} in a Fenton-type reaction of eq 1 to generate LRh(IV). The results of these studies, both in the presence and absence of potential substrates for LRh(IV), are presented in this report.

$$Fe_{aq}^{\ 2+} + M^{III}OOH^{2+} \rightarrow Fe_{aq}OH^{2+} + M^{IV}O^{2+} \qquad (1)$$

The hydroperoxo complexes in this work are believed to be six-coordinate, but the sixth ligand, a molecule of water, is omitted in our notation.

Experimental Section

Materials. Perchloric acid, sodium hydroxide, zinc metal, mercury(II) chloride (all Fisher), hexaammineruthenium(III) chloride, thallium(III) sulfate, diammonium 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonate) ($ABTS^{2-}$), methanol, ethanol, 2-propanol, propionaldehyde, and paraformaldehyde (all Aldrich) were reagent grade or better and were used as received. Solutions of Fe_{aq}^{2+} and $Ru(NH_3)_6^{2+}$ were prepared by Zn/Hg reduction of the respective 3+ ions under anaerobic conditions.

Solid $[(NH_3)_5CoBr](ClO_4)_2$, *trans*-$[(H_2O)(NH_3)_4RhH](ClO_4)_2$, *meso*-$[(Me_6$-$[14]aneN_4)(H_2O)RhH](CF_3SO_3)_2$, and $[([14]aneN_4)Ni](ClO_4)_2$ were available from our previous work.[24,26] Solutions of formaldehyde were prepared by dissolving a known amount of paraformaldehyde in warm 1 M $HClO_4$. Deionized water was further purified by passage through a Millipore Milli-Q water purification system.

Oxygen saturated solutions of $Cr_{aq}OO^{2+}$ (0.1−0.3 mM) were prepared as described previously[24] and standardized spectrophotometrically ($\epsilon_{293} = 3.0 \times 10^3$ M^{-1} cm^{-1}). Kinetic solutions of $Cr_{aq}OOH^{2+}$ (35−50 μM) were prepared by reducing deaerated solutions of $Cr_{aq}OO^{2+}$ with $Ru(NH_3)_6^{2+}$. Such solutions contained 9 mM methanol that was left over from the preparation of superoxochromium(III).

Solutions of (*meso*-Me_6-$[14]aneN_4)(H_2O)RhOO^{2+}$ (hereafter L^2RhOO^{2+}) were prepared as described earlier.[22] The hydroperoxide $(NH_3)_4RhOOH^{2+}$ [26,27] ($\epsilon_{241} = 4.0 \times 10^3$ M^{-1} cm^{-1}, $\epsilon_{320} = 258$ M^{-1} cm^{-1}) was generated by the reaction of the corresponding hydride with O_2 in the presence of traces of the superoxo complex. This chemistry is described by the following equations.[28]

$$LRhH^{2+} + LRhOO^{2+} \rightarrow LRhOOH^{2+} + LRh^{2+}$$

$$LRh^{2+} + O_2 \rightarrow LRhOO^{2+}$$

Typically, a 0.3 mM solution of $(NH_3)_4RhH^{2+}$ in 4.8 mM $HClO_4$ was saturated with oxygen and photolyzed in a Rayonet UV photo reactor for 40 s, after which time ∼40 μM $(NH_3)_4RhOO^{2+}$ was detected ($\epsilon_{268} = 1.0 \times 10^4$ M^{-1} cm^{-1}). After the injection of an additional 0.74 mM $(NH_3)_4RhH^{2+}$, the reaction was allowed to proceed in the dark for 65 min under O_2 bubbling. The product was diluted 10-fold, and the yield (75%) was determined spectrophotometrically. In an alternative procedure, the reaction between oxygen and $(NH_3)_4RhH^{2+}$ was carried out at pH = 11.2, where the generation of $(NH_3)_4RhOOH^{2+}$ is instantaneous. After reacidification to pH = 2.3, the yield of the hydroperoxorhodium complex was typically 76%. Attempts to improve the yield by varying O_2 and base concentrations, reaction time, and temperature were unsuccessful. The samples of $(NH_3)_4RhOOH^{2+}$, prepared by the two methods, yielded identical kinetic results in the reactions with Fe_{aq}^{2+} and organic substrates. Unfortunately, this convenient and fast method is not suitable for the preparation of L^2RhOOH^{2+}, because an additional, unidentified species was produced which reacted with Fe_{aq}^{2+} more slowly than the authentic L^2RhOOH^{2+}. For this reason, kinetic solutions of L^2RhOOH^{2+} were prepared by controlled reduction of L^2RhOO^{2+} by $Ru(NH_3)_6^{2+}$.[22]

Most of the kinetic and spectral measurements were carried out by conventional UV−vis spectrophotometry with the use of a Shimadzu 3101 PC spectrophotometer. In some cases, when fast mixing was required, an Applied Photophysics DX-17MV stopped-flow apparatus was employed. Most of the experiments were conducted at 25 ± 0.5 °C and 0.10 M ionic strength, maintained with $HClO_4$. Nonlinear least-squares fittings of kinetic data were performed with the use of Kaleidagraph 3.09 for PC software. Kinetic simulations were carried out with Chemical Kinetics Simulator 1.01 (IBM) and Kinsim 4.0[29] software.

Results

Reactions of $LRhOOH^{2+}$ with Fe_{aq}^{2+} (L = $(NH_3)_4$ and L^2). The kinetics, monitored at λ 240 nm ($\epsilon_{Fe(III)} = 4160$ M^{-1} cm^{-1}), obeyed a pseudo-first-order rate law. Plots of the pseudo-first-order rate constants against $[Fe_{aq}^{2+}]$ yielded $k = 30.0 \pm 0.4$ M^{-1} s^{-1} for $(NH_3)_4RhOOH^{2+}$ and 31.0 ± 0.6 M^{-1} s^{-1} for L^2RhOOH^{2+}. The molar absorptivity changes, defined as $\Delta\epsilon = (Abs_\infty - Abs_0)/[LRhOOH^{2+}]_0 = \Delta Abs/[LRhOOH^{2+}]_0$, where Abs_∞ and Abs_0 represent final and initial absorbancies, increased somewhat with $[Fe_{aq}^{2+}]$ and reached saturation at 0.15 mM for the tetraammine and at 1.0 mM for the macrocyclic hydroperoxo complex, Figure 1. At the saturation limit, the values of $\Delta\epsilon$ were 5.0×10^3 M^{-1} cm^{-1} in the $(NH_3)_4RhOOH^{2+}/Fe_{aq}^{2+}$ reaction and 1.0×10^4 M^{-1} cm^{-1} in the $L^2RhOOH^{2+}/Fe_{aq}^{2+}$ reaction.

Effect of Alcohols, Formaldehyde, and $(NH_3)_4RhH^{2+}$ on $(NH_3)_4RhOOH^{2+}/Fe_{aq}^{2+}$ Reaction. These experiments had a large excess of Fe_{aq}^{2+} over $(NH_3)_4RhOOH^{2+}$ to ensure

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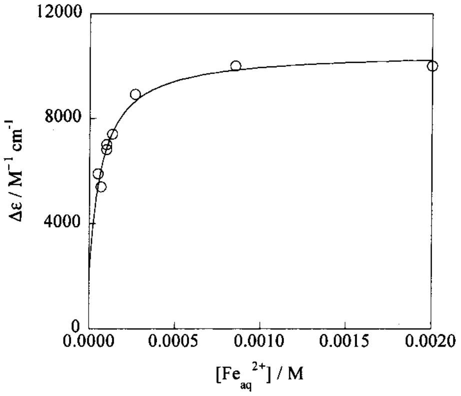

Figure 1. Plot of $\Delta\epsilon$ at 240 nm against [Fe_{aq}^{2+}] for the reaction of 22−30 μM L^2RhOOH^{2+} with Fe_{aq}^{2+} in air-saturated solutions at pH = 1 and 25 °C. Data were fitted to eq 15. L^2 = (*meso*-Me$_6$-[14]aneN$_4$).

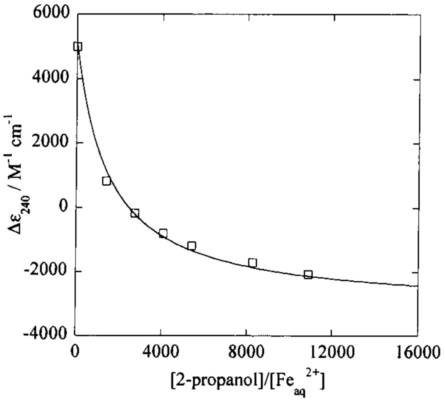

Figure 2. Plot of $\Delta\epsilon$ against the ratio [2-propanol]/[Fe_{aq}^{2+}] for the reaction between $(NH_3)_4RhOOH^{2+}$ (44 μM) and Fe_{aq}^{2+} (0.16−0.43 mM) in the presence of 2-propanol (0.42−1.68 M) and Fe_{aq}^{3+} (97 μM). Conditions: oxygen-free atmosphere, pH 1, 25 °C.

pseudo-first-order conditions, and an excess (0.10 mM) of externally added Fe_{aq}^{3+} to capture potential reducing transients. Kinetic traces were exponential, and the rate constants matched those obtained in the absence of substrates, but the amplitude and sign of the absorbance changes varied with the concentrations of the reducing substrates and Fe_{aq}^{2+}. Figure 2 shows a plot of $\Delta\epsilon$ against the ratio [2-propanol]/[Fe_{aq}^{2+}]. The data were fitted to eq 2, where m_1 represents $\Delta\epsilon$ at [RH]/[Fe_{aq}^{2+}] approaching infinity, ϵ_{Fe} is the molar absorptivity of Fe_{aq}^{3+} at 240 nm, and m_2 is the ratio of appropriate rate constants, as discussed later.

$$\frac{\text{Abs}_\infty - \text{Abs}_0}{[\text{LRhOOH}^{2+}]_0} = \Delta\epsilon = m_1 + \frac{2\epsilon_{\text{Fe}}}{1 + m_2\dfrac{[\text{RH}]}{[\text{Fe}_{\text{aq}}^{\;2+}]}} \qquad (2)$$

The numerical values of parameters m_1 and m_2 for different substrates are summarized in Table 1. The effect of alcohol deuteration was estimated in single-point experiments for CD_3OH and 2-C_3D_7OH in H_2O.

$(NH_3)_4RhOOH^{2+}$/Fe_{aq}^{2+} Reaction in the Presence of Propionaldehyde. Kinetics were pseudo-first-order and had negative absorbance changes at 240 nm. The rate constants were 2−9 times greater than in the absence of propionaldehyde, suggesting a chain mechanism. Fe_{aq}^{3+} showed a mild inhibiting effect; the rate constant decreased from 0.029 to 0.024 s^{-1} as [Fe_{aq}^{3+}] increased from 0.16 to 0.32 mM ([$(NH_3)_4RhOOH^{2+}$] = 22 μM, [C_2H_5CHO] = 44 mM, [Fe_{aq}^{2+}] = 0.16 mM). The large molar absorptivity of Fe_{aq}^{3+} at the monitoring wavelength prevented us from increasing [Fe_{aq}^{3+}] to the saturation limit (provided one existed), and all consecutive kinetic runs were carried out without added Fe_{aq}^{3+}.

Table 1. Parameters m_1[a] and m_2[b] for the Reactions between $LMOOH^{2+}$ and Fe_{aq}^{2+} in the Presence of RH and Fe_{aq}^{3+} at 25 °C, pH 1, and 0.10 M Ionic Strength

	LMOOH = $(NH_3)_4RhOOH^{2+}$		$Cr_{aq}OOH^{2+}$	
RH	$m_1/10^3$ M^{-1} cm^{-1}	$m_2/10^{-4}$	$m_1/10^3$ M^{-1} cm^{-1}	$m_2/10^{-4}$
CH_3OH	−3.0 ± 0.5	2.0 ± 0.6	−0.86 ± 0.5	170 ± 60
CD_3OH		0.39		
C_2H_5OH	−3.1 ± 0.2	5.4 ± 0.7	−0.88 ± 0.1	270 ± 40
i-C_3H_7OH	−3.1 ± 0.2	6.8 ± 0.8	−0.66 ± 0.3	17 ± 4
i-C_3D_7OH		2.1		
CH_2O	−3.4 ± 0.4	25 ± 6		
$(NH_3)_4RhH^{2+}$	−2.9	250		
C_2H_5CHO		89 ± 0.5		

[a] $m_1 = (\text{Abs}_\infty - \text{Abs}_0)/[\text{LMOOH}^{2+}]_0 = \Delta\epsilon$ at [RH]/[Fe_{aq}^{2+}] approaching infinity. [b] $m_2 = k_{RH}/k_{T1}$, see Scheme 1.

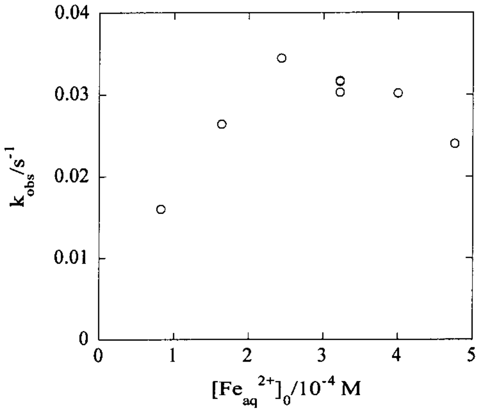

Figure 3. Plot of k_{obs} against [Fe_{aq}^{2+}] for the Fe_{aq}^{2+}/$(NH_3)_4RhOOH^{2+}$ reaction at 0.044 M C_2H_5CHO.

At a constant concentration of C_2H_5CHO, the rate first increased with Fe_{aq}^{2+}, and then decreased, as shown in Figure 3. The dependence on [C_2H_5CHO] was approximately linear. A plot of k_{obs} against [C_2H_5CHO] at 0.16 mM Fe_{aq}^{2+} had a slope of 0.39 ± 0.07 M^{-1} s^{-1} and an intercept of 0.005 s^{-1}. The intercept is in excellent agreement with the value calculated for the A_4RhOOH^{2+}/Fe_{aq}^{2+} reaction in the absence of substrates.

High concentrations of $(NH_3)_5CoBr^{2+}$ (1 mM) stabilized the rates of the $(NH_3)_4RhOOH^{2+}$/Fe_{aq}^{2+}/C_2H_5CHO reaction at values close to those obtained in the absence of the aldehyde (30 M^{-1} s^{-1}). This observation suggests that one or more of the chain carriers were scavenged by $(NH_3)_5CoBr^{2+}$. The amount of $(NH_3)_5CoBr^{2+}$ consumed in a given kinetic run was calculated from the absorbance changes at 320 nm, where only $(NH_3)_5CoBr^{2+}$ and $(NH_3)_4RhOOH^{2+}$ absorb. It was assumed that all of the hydroperoxorhodium was consumed and that no other highly absorbing products were formed. The quantity $\Delta[(NH_3)_5CoBr^{2+}]/[(NH_3)_4RhOOH^{2+}]_0$ is plotted against the ratio $y \equiv [C_2H_5CHO]/$

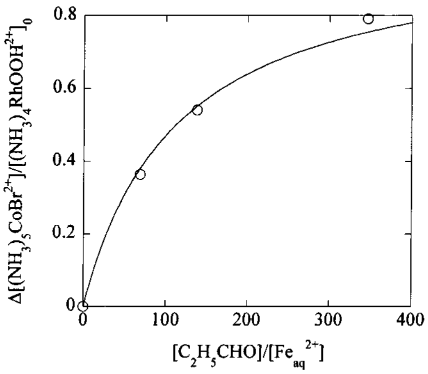

Figure 4. Plot of $\Delta[(NH_3)_5CoBr^{2+}]/[(NH_3)_4RhOOH^{2+}]_0$ against $[C_2H_5CHO]/[Fe_{aq}^{2+}]$ for the reaction between 60 μM $(NH_3)_4RhOOH^{2+}$ and 0.62 mM Fe_{aq}^{2+} in the presence of 0−0.21 M C_2H_5CHO and 1 mM $(NH_3)_5CoBr^{2+}$. Monitoring wavelength 320 nm, oxygen-free atmosphere, pH = 1, 25 °C. Data were fitted to eq 3.

$[Fe_{aq}^{2+}]$ in Figure 4. A fit of the experimental data to eq 3 yielded $m_4 = (8.9 \pm 0.05) \times 10^{-3}$.

$$\Delta[(NH_3)_5CoBr^{2+}]/[(NH_3)_4RhOOH^{2+}]_0 = \frac{m_4y}{m_4y + 1} \tag{3}$$

The $Cr_{aq}OOH^{2+}/Fe_{aq}^{2+}$ reaction in the presence of alcohols was used to confirm the methodology applied to the reactions of hydroperoxorhodium(III) ions. It was shown earlier that the $Fe_{aq}^{2+}/Cr_{aq}OOH^{2+}$ reaction generates $Cr_{aq}O^{2+}$, and the kinetics of the reactions of $Cr_{aq}O^{2+}$ with a number of substrates are known independently.[30] The comparison between the ratios of directly measured rate constants and the data obtained in the competition experiments described later will thus allow us to estimate the reliability of the approach used in the $LRhOOH/Fe_{aq}^{2+}$/substrate reactions.

A solution of 50 μM $Cr_{aq}OOH^{2+}$ was allowed to react with 0.63−1.45 mM Fe_{aq}^{2+} in the presence of 0.23 mM Fe_{aq}^{3+} and variable amounts of methanol, ethanol, or 2-propanol. The reactions were followed spectrophotometrically at 240 nm. The kinetic behavior of the $Cr_{aq}OOH^{2+}$ system was qualitatively the same as that of the hydroperoxorhodium complexes, but the precision and reproducibility of the data depended severely on experimental conditions, probably because both $Cr_{aq}OO^{2+}$ and $Cr_{aq}OOH^{2+}$ are significantly less stable than the rhodium analogues. The data treatment according to eq 2 yielded parameters m_1 and m_2 in Table 1.

The L^2Rh^{2+}/Tl(III) reaction was examined briefly as a potential source of L^2RhO^{2+} for direct kinetic studies. The two-electron oxidation of Cr_{aq}^{2+} by Tl(III) successfully produced $Cr_{aq}O^{2+}$ in our earlier work.[30] A spectrophotometric titration of 0.34 mM L^2Rh^{2+} with a 6.5 mM solution of Tl(III) at pH 1 afforded a 1.6:1 $[L^2Rh^{2+}]$/[Tl(III)] stoichiometry, suggesting that the oxidation proceeded beyond the Rh(III) stage.

The reaction of L^2Rh^{2+} with excess Tl(III) was also studied by stopped-flow at pH 1. The absorbance decrease at 280 nm obeyed first-order kinetics. A plot of k_{obs} against [Tl(III)] was linear with a zero intercept and a slope of $(2.25 \pm 0.08) \times 10^5$ M^{-1} s^{-1}. In a sequential stopped-flow experiment at pH 0.52, Fe_{aq}^{2+} (1.6−2.0 mM) was introduced 10−500 ms after L^2Rh^{2+} (0.075−0.15 mM) had been mixed with Tl_{aq}^{3+} (2.5 mM). No Fe_{aq}^{3+} could be detected, indicating that any potential intermediates in the L^2Rh^{2+}/Tl(III) reaction are exceedingly short-lived. The same conclusion was reached when $ABTS^{2-}$ or L^1Ni^{2+} was added immediately after the manual mixing of Tl(III) and L^2Rh^{2+}.

Discussion

A reasonable mechanism for the $Cr_{aq}OOH^{2+}/Fe_{aq}^{2+}$ reaction in the presence of alcohols is shown in eqs 4−7, all of which are known independently. The $Cr_{aq}O^{2+}$ ion, produced in eq 4 ($k_4 = 48$ M^{-1} s^{-1})[25a] reacts with the alcohol by hydride transfer, eq 5, and with Fe_{aq}^{2+} by electron transfer, $k_7 = 3.8 \times 10^3$ M^{-1} s^{-1}.[25b] The Cr_{aq}^{2+} produced in eq 5 is oxidized to Cr_{aq}^{3+} by Fe_{aq}^{3+}, eq 6. From the data at 1.0 M ionic strength,[31] the value of k_6 at 0.10 M ionic strength is estimated as ∼3×10^4 M^{-1} s^{-1}.

$$Cr_{aq}OOH^{2+} + Fe_{aq}^{2+}\ (+H^+) \rightarrow Cr_{aq}O^{2+} + Fe_{aq}^{3+} + H_2O \tag{4}$$

$$Cr_{aq}O^{2+} + R_2CHOH \rightarrow Cr_{aq}^{2+} + R_2CO + H_2O \quad k_{ROH} \tag{5}$$

$$Cr_{aq}^{2+} + Fe_{aq}^{3+} \rightarrow Cr_{aq}^{3+} + Fe_{aq}^{2+} \tag{6}$$

$$Cr_{aq}O^{2+} + Fe_{aq}^{2+}\ (+2H^+) \rightarrow Cr_{aq}^{3+} + Fe_{aq}^{3+} + H_2O \quad k_{Fe} \tag{7}$$

Other potential competing reactions, shown in eqs 8−10, can be ignored under our experimental conditions. Reaction 8, for which a rate constant of 10^8 M^{-1} s^{-1} was estimated earlier from the yields of $Cr_{aq}OO^{2+}$ in the $Cr_{aq}O^{2+}/CH_3OH/O_2$ reaction, involves two transient species, and reactions 9 (assumed to have $k \sim 10^4$−10^5 M^{-1} s^{-1}, comparable to the Cr_{aq}^{2+}/H_2O_2 reaction)[32] and 10 ($k_{10} = 1.3 \times 10^3$ M^{-1} s^{-1})[30] have a concentration disadvantage relative to eqs 5−7 at the large excesses of alcohols, Fe_{aq}^{3+}, and Fe_{aq}^{2+} used.

$$Cr_{aq}^{2+} + Cr_{aq}O^{2+}\ (+2H^+) \rightarrow 2Cr_{aq}^{3+} + H_2O \tag{8}$$

$$Cr_{aq}^{2+} + Cr_{aq}OOH^{2+}\ (+H^+) \rightarrow Cr_{aq}^{3+} + Cr_{aq}O^{2+} + H_2O \tag{9}$$

$$Cr_{aq}O^{2+} + Cr_{aq}OOH^{2+}\ (+H^+) \rightarrow Cr_{aq}^{3+} + Cr_{aq}OO^{2+} + H_2O \tag{10}$$

In the absence of alcohols, the reaction yields 2 equiv of Fe_{aq}^{3+}, eq 11. At high alcohol concentrations, reaction 5 dominates over reaction 7, the net result being the Fenton-like, Fe_{aq}^{2+}-catalyzed oxidation of the alcohols by $Cr_{aq}OOH^{2+}$, eq 12.

$$Cr_{aq}OOH^{2+} + 2Fe_{aq}^{2+}\ (+3H^+) \rightarrow Cr_{aq}^{3+} + 2Fe_{aq}^{3+} + 2H_2O \tag{11}$$

$$Cr_{aq}OOH^{2+} + R_2CHOH\ (+H^+) \xrightarrow{Fe_{aq}^{2+}} Cr_{aq}^{3+} + R_2CO + 2H_2O \tag{12}$$

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Table 2. Rate Constants for the Reaction between $Cr_{aq}O^{2+}$ and Alcohols Obtained in This Work and by Direct Measurement at 25 °C, pH 1, and 0.10 M Ionic Strength

R_2CHOH	$k_{ROH}/M^{-1}\ s^{-1}$ [a]	$k_{ROH}/M^{-1}\ s^{-1}$ [b]
CH_3OH	60 ± 23	22.7 ± 0.6
C_2H_5OH	104 ± 17	~40[c]
i-C_3H_7OH	6.6 ± 1.6	5.2 ± 0.2

[a] This work. [b] From ref 30. [c] Estimated from the rate constant at $\mu = 1.0$ M.

The amount of $Fe_{aq}{}^{3+}$ produced should depend on the relative proportion of the reactions in eqs 7 and 5. Because only $Fe_{aq}{}^{3+}$ and $Cr_{aq}OOH^{2+}$ absorb significantly at 240 nm, the molar absorptivity change can be expressed as in eq 13, where ϵ_{Cr} is the molar absorptivity of $Cr_{aq}OOH^{2+}$, and the rate constants k_{ROH} and k_{Fe} are defined in eq 5 and 7.

$$\Delta\epsilon = -\epsilon_{Cr} + 2\epsilon_{Fe}\frac{k_{Fe}[Fe_{aq}{}^{2+}]}{k_{Fe}[Fe_{aq}{}^{2+}] + k_{ROH}[R_2CHOH]} \quad (13)$$

Rearrangement yields the expression in eq 14.

$$\Delta\epsilon = -\epsilon_{Cr} + \frac{2\epsilon_{Fe}}{1 + \dfrac{k_{ROH}}{k_{Fe}}\dfrac{[R_2CHOH]}{[Fe_{aq}{}^{2+}]}} \quad (14)$$

Comparison with eq 2 identifies m_1 as $-\epsilon_{Cr}$ and m_2 as k_{ROH}/k_{Fe}. By substituting the known value for k_{Fe} (3.8×10^3 $M^{-1}\ s^{-1}$),[25b] we calculated the absolute rate constants k_{ROH} in Table 2, which also lists the values measured directly in our previous work.[30] The two sets of data agree reasonably well with each other, considering that widely different methods were used in the two studies. The absolute rate constants measured in the earlier work relied on the formation of $Cr_{aq}{}^{2+}$ by hydride transfer, and quantitative capture of $Cr_{aq}{}^{2+}$ by O_2 to generate $Cr_{aq}OO^{2+}$, a species used to monitor the progress of the reaction. The present work uses absorbance changes at 240 nm and the scheme based on eqs 4−7 to determine the ratios of rate constants k_5 and k_7. In addition, k_{ROH} in this work is probably subject to a systematic error caused by traces of hydrogen peroxide (from slow hydrolysis of $Cr_{aq}OOH^{2+}$) and chromate(VI) (from preparation and decomposition of $Cr_{aq}OO^{2+}$ during the degassing step), both of which would react with $Fe_{aq}{}^{2+}$ and alter the amount of $Fe_{aq}{}^{3+}$ produced. No correction for these side reactions was attempted because the exact amounts of interfering species could not be estimated with confidence, but they had to be small to yield the agreement within the estimated error in the best case (2-C_3H_7OH) and to within less than a factor of 3 in the worst case (C_2H_5OH).

Hydroperoxorhodium(III) complexes also react with $Fe_{aq}{}^{2+}$ to produce intermediates that discriminate between $Fe_{aq}{}^{2+}$ and various substrates. It is reasonable to assume that the rhodium complexes, like their chromium counterparts, react with $Fe_{aq}{}^{2+}$ in Fenton-type chemistry. This assumption is further supported by the similarity in rate constants, 48 M^{-1} s^{-1} for $Cr_{aq}OOH^{2+}$, 30 for $(NH_3)_4RhOOH^{2+}$, and 31 for L^2-$RhOOH^{2+}$. We have shown earlier that one-electron, that is, Fenton-type, reactions of H_2O_2 and metal hydroperoxides occur with similar rate constants for a given reductant.[30] The two-electron (O-atom transfer) reactions, on the other hand, show much greater kinetic selectivity and span a wide range of rate constants.[30]

On the basis of these considerations, we suggest that major mechanistic features of the $Cr_{aq}OOH^{2+}/Fe_{aq}{}^{2+}$ reaction are reproduced in the $LRhOOH^{2+}/Fe_{aq}{}^{2+}$ reaction. The more complicated behavior in the rhodium case is attributed to the short lifetime and complex chemistry of the intermediate $LRhO^{2+}$ species. The proposed mechanism is presented in Scheme 1, where L represents L^2 or $(NH_3)_4$.

Scheme 1

$$LRhOOH^{2+} + Fe_{aq}{}^{2+}\ (+H^+) \xrightarrow{k_I} LRhO^{2+} + Fe_{aq}{}^{3+} + H_2O$$

$$LRhO^{2+} \xrightarrow{k_d} L'Rh^{III}$$

$$LRhO^{2+} + Fe_{aq}{}^{2+}\ (+2H^+) \xrightarrow{k_{T1}} LRh^{3+} + Fe_{aq}{}^{3+} + H_2O$$

$$LRhO^{2+} + R_2CHOH \xrightarrow{k_{RH}} LRh^{2+} + R_2CO + H_2O\ (\text{or } LRhOH^{2+} + R_2C^{\bullet}OH)$$

$$LRh^{2+} + Fe_{aq}{}^{3+} \xrightarrow{k_{T2}} LRh^{3+} + Fe_{aq}{}^{2+}$$

$$R_2C^{\bullet}OH + Fe_{aq}{}^{3+} \xrightarrow{k_{T3}} R_2CO + Fe_{aq}{}^{2+} + H^+$$

We first consider the case of L^2RhOOH^{2+}. In addition to the bimolecular reactions with $Fe_{aq}{}^{2+}$ and RH, $LRhO^{2+}$ may (and, as shown later, does) undergo rapid decay, probably by intramolecular electron transfer to generate a Rh^{III}−(ligand radical) complex, which decays further to stable products. Similar chemistry has been reported for high-valent macrocyclic complexes of cobalt, nickel, and iron.[25c,33−35]

In the absence of added substrates, the reaction with $Fe_{aq}{}^{2+}$ should have a 2:1 stoichiometry, provided the excess of $Fe_{aq}{}^{2+}$ is large enough to avoid the loss of L^2RhO^{2+} in the decomposition reaction. This was confirmed by the data shown in Figure 1. At low $[Fe_{aq}{}^{2+}]$, the molar absorptivity change, $\Delta\epsilon$, increased with increasing $[Fe_{aq}{}^{2+}]$ until it reached a plateau. At $[Fe_{aq}{}^{2+}]$ approaching zero, the molar absorptivity change in the reaction, where decomposition of L^2-RhO^{2+} is the only possible outcome, is $\Delta\epsilon_0 = (\epsilon_{Fe} + \epsilon_{(L'Rh)} - \epsilon_{(L2RhOOH)})$. At $[Fe_{aq}{}^{2+}]$ approaching infinity, $\Delta\epsilon_\infty = (2\epsilon_{Fe} + \epsilon_{(L2Rh3+)} - \epsilon_{(L2RhOOH)})$. We define the difference in the molar absorptivity change caused by the decomposition of L^2RhO^{2+} as $\Delta\epsilon_{(decomp)} = \Delta\epsilon_\infty - \Delta\epsilon_0 = (\epsilon_{Fe} + \epsilon_{(L2Rh3+)} - \epsilon_{(L'Rh)})$, where L′ is the modified macrocyclic ligand. A derivation, similar to that for eq 14, results in an expression

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for $\Delta\epsilon$ in terms of $[Fe_{aq}^{2+}]$, $\Delta\epsilon_0$, and $\Delta\epsilon_{decomp}$, eq 15. A fit of the experimental data to eq 15, see Figure 1, afforded $k_d/k_{T1} = (8 \pm 4) \times 10^{-5}$ M.

$$\Delta\epsilon = \Delta\epsilon_0 + \frac{\Delta\epsilon_{(decomp)}}{1 + \dfrac{k_d}{k_{T1}[Fe_{aq}^{2+}]}} \qquad (15)$$

Scheme 1 is also applicable to the reactions of $(NH_3)_4RhOOH^{2+}$, except for the chemistry of the decomposition step(s). An intramolecular electron transfer to generate a Rh^{III}−(ammine radical) complex is considered unlikely for this purely inorganic ion. Instead, $(NH_3)_4RhO^{2+}$ probably undergoes disproportionation and/or hydrolysis to stable products. Surprisingly, $(NH_3)_4RhO^{2+}$ does not appear to be more persistent than L^2RhO^{2+}. The somewhat lower concentrations of Fe_{aq}^{2+} required for the stoichiometry of $(NH_3)_4RhOOH^{2+}/Fe_{aq}^{2+}$ reaction to reach saturation can probably be accounted for by the larger rate constant for the capture of the Rh(IV) intermediate compared to that formed in the L^2Rh^{2+}/Fe_{aq}^{2+} reaction. Here, we assume that the reactivity difference is caused mostly by steric effects and is thus similar to that observed in the reactions of L^1Rh^{2+} and L^2Rh^{2+} with Fe_{aq}^{3+}.[28] In those reactions, the rate constant for the L^1 complex, which we believe to be a good approximation for the tetraammine complex, was ∼6 times larger than that for the L^2 compound. This result is comparable to the ∼7 times smaller amount of Fe_{aq}^{2+} required to scavenge $(NH_3)_4RhO^{2+}$ in this work.

Some of the intermediates produced during the self-decay, such as partially hydrolyzed Rh(IV) and transient Rh(V) species, may themselves react with added substrates and, thus, affect the outcome of competition experiments. To avoid these complications, the self-decay was prevented by using >0.2 mM Fe_{aq}^{2+}, an amount that is even larger than that required for the 2:1 ($[Fe_{aq}^{2+}]/[(NH_3)_4RhOOH^{2+}]$) stoichiometry in the absence of added substrates. Thus, the data in Table 1 and Figure 2 are believed to represent the competition ratio for the first intermediate formed, which we suggest is $(NH_3)_4RhO^{2+}$.

As one might expect, alcohols are the weakest, and $(NH_3)_4RhH^{2+}$ is the strongest, competitor for Rh(IV), as shown by the data in Table 1. The kinetic isotope effect, k_H/k_D, for the reaction with methanol (5.0) and 2-propanol (3.2) clearly indicates the involvement of the alcohol C−H bonds in the transition state.

The relative reactivities of various substrates toward $(NH_3)_4RhO^{2+}$ and $Cr_{aq}O^{2+}$, calculated from the data in Tables 1 and 2, are summarized in Table 3. In the rhodium series, the reactivity increases smoothly within the series of alcohols. In the chromium case, all of the organic materials have similar rate constants, and only $(NH_3)_4RhH^{2+}$ is significantly faster than the rest of the substrates. We note that all of the substrates in Table 3, except $(NH_3)_4RhH^{2+}$ and propionaldehyde, react with $Cr_{aq}O^{2+}$ by hydride transfer.[30] It is tempting to suggest that the different reactivity pattern for $(NH_3)_4RhO^{2+}$ reflects a different mechanism, such as hydrogen atom transfer, but the data are insufficient for such a conclusion.

Table 3. Relative Reactivities of $(NH_3)_4RhO^{2+}$ and $Cr_{aq}O^{2+}$ toward Substrates X at pH 1 and 25 °C

X	k_X/k_{MeOH}	
	$(NH_3)_4RhO^{2+\,a}$	$Cr_{aq}O^{2+\,b}$
CH_3OH	1	1
C_2H_5OH	2.7	1.7
i-C_3H_7OH	3.4	0.23
CH_2O	12.5	1.8
C_2H_5CHO	45	
$C(CH_3)_3CHO$		0.71
$(NH_3)_4RhH^{2+}$	125	
$([14]\text{-aneN}_4)RhH^{2+}$		430[a,c]

[a] Ionic strength = 0.10 M. [b] Ionic strength = 1.0 M. Data from ref 30. [c] From ref 24.

Of all the substrates in Table 1, only C_2H_5CHO exhibited a significant effect on the kinetics of $(NH_3)_4RhOOH^{2+}$ disappearance, clearly signaling a mechanistic change. Two of the most likely possibilities are discussed here.

In one scenario, the $(NH_3)_4RhO^{2+}$/substrate reaction takes place by H-atom abstraction for all the substrates except C_2H_5CHO, which reacts by hydride transfer. Even the lowest concentrations of Fe_{aq}^{3+} are capable of scavenging alcohol-derived radicals ($k = 10^8$ M^{-1} s^{-1})[36] produced by H-atom abstraction, and Scheme 1 holds for the alcohols. No $(NH_3)_4Rh^{2+}$ is produced by this mechanism.

In contrast, the hydride transfer from C_2H_5CHO would generate $(NH_3)_4Rh^{2+}$, which reacts with Fe_{aq}^{3+} more slowly[37] than reducing carbon radicals do. At the low concentrations of Fe_{aq}^{3+} present in C_2H_5CHO experiments, the $(NH_3)_4Rh^{2+}/(NH_3)_4RhOOH^{2+}$ reaction becomes important ($k = 4 \times 10^5$ M^{-1} s^{-1} for L^1Rh^{2+}/tert-BuOOH reaction)[26] and creates a chain, Scheme 2. The competing $(NH_3)_4RhO^{2+}/Fe_{aq}^{2+}$ reaction is responsible for the modest chain length observed.

Scheme 2

$$(NH_3)_4RhOOH^{2+} + Fe_{aq}^{2+} (+H^+) \xrightarrow{k_I} (NH_3)_4RhO^{2+} + Fe_{aq}^{3+}$$

$$(NH_3)_4Rh^{2+} + (NH_3)_4RhOOH^{2+} \xrightarrow{k_{P1}} (NH_3)_4RhOH^{2+} + (NH_3)_4RhO^{2+}$$

$$(NH_3)_4RhO^{2+} + C_2H_5CHO \xrightarrow{k_{P2}} (NH_3)_4Rh^{2+} + C_2H_5C(O)OH$$

$$(NH_3)_4RhO^{2+} + Fe_{aq}^{2+} (+2H^+) \xrightarrow{k_{T1}} (NH_3)_4Rh^{3+} + Fe_{aq}^{3+} + H_2O$$

$$(NH_3)_4Rh^{2+} + Fe_{aq}^{3+} \xrightarrow{k_{T2}} (NH_3)_4Rh^{3+} + Fe_{aq}^{2+}$$

The efficiency of the chain reaction (and hence the chain length and absolute rates) strongly depends on the degree of competition between the propagating $(NH_3)_4RhO^{2+}/C_2H_5CHO$ reaction and the termination steps T1 and T2. At low

[Fe_{aq}^{2+}], the main chain-terminating step is probably T2, so that the overall rate constant is proportional to [Fe_{aq}^{2+}]. At higher [Fe_{aq}^{2+}], termination by step T1 becomes important, and the overall rate decreases. Both phenomena were qualitatively reproduced in our kinetic simulations, and the results at low [Fe_{aq}^{2+}] (0.08−0.24 mM) were in excellent quantitative agreement with experimental data.

Clearly, the long chain approximation is not strictly applicable in this case, but such a treatment does provide some insight and allows a reasonable analysis of the kinetic data. Ignoring reaction T_2 at the low [Fe_{aq}^{3+}] used, the sequence of steps I, P1, P2, and T1 yields the rate law in eq 16.

$$\text{rate} = \frac{k_I k_{P2}}{k_{T1}}[(NH_3)_4RhOOH^{2+}][C_2H_5CHO] \tag{16}$$

After substitution for $k_I = 30\ M^{-1}\ s^{-1}$, one obtains the ratio $k_{P2}/k_{T1} = 0.013$, which is shown in Table 1 as parameter m_2.

In another option, it is the strongly reducing nature of acyl radicals that is responsible for the chain. This possibility is shown in Scheme 3, which retains the one-electron mechanism of the alcohol reactions but uses acyl radicals as chain carriers. The chemistry shown has a precedent in the reactions of H_2O_2 with hydroxyalkyl[38] and hydrated acyl radicals.[39] In the present work, the chain was observed only in the propionaldehyde reaction, presumably because (hydrated)[40] acyl radicals are more reactive than α-hydroxyalkyl radicals in reaction P3, and also because the reactions with alcohols and CH_2O were carried out in the presence of added Fe_{aq}^{3+}, which would readily terminate the chain.

Scheme 3

$$(NH_3)_4RhOOH^{2+} + Fe_{aq}^{2+}\ (+H^+) \xrightarrow{k_I} (NH_3)_4RhO^{2+} + Fe_{aq}^{3+} + H_2O$$

$$C_2H_5C^{\bullet}O + (NH_3)_4RhOOH^{2+} \xrightarrow{k_{P3}} C_2H_5COOH + (NH_3)_4RhO^{2+}$$

$$(NH_3)_4RhO^{2+} + C_2H_5CHO\ (+H^+) \xrightarrow{k_{P4}} (NH_3)_4Rh^{3+} + C_2H_5C^{\bullet}O + H_2O$$

If chain propagation takes place by reactions P3 and P4, then the observed rate constant is $k_I k_{P4}/k_{T1}$, which gives $k_{P4}/k_{T1} = 0.013$.

To confirm the validity of this data analysis, we conducted the $Fe_{aq}^{2+}/(NH_3)_4RhOOH^{2+}/C_2H_5CHO$ reaction in the presence of $(NH_3)_5CoBr^{2+}$, which reacts rapidly with both Rh(II) complexes and hydrated acyl radicals.[24] Under these conditions, there is no chain reaction, and the amount of $(NH_3)_5CoBr^{2+}$ consumed is a function of the competition between reactions T1 and P2 (and/or P4), eq 17, which upon rearrangement gives eq 18.

$$\Delta[(NH_3)_5CoBr^{2+}] = [(NH_3)_4RhOOH^{2+}]_0 \frac{k_{P2}[C_2H_5CHO]}{k_{P2}[C_2H_5CHO] + k_{T1}[Fe_{aq}^{2+}]} \tag{17}$$

$$\frac{\Delta[(NH_3)_5CoBr^{2+}]}{[(NH_3)_4RhOOH^{2+}]_0} = \frac{\dfrac{k_{P2}}{k_{T1}}\dfrac{[C_2H_5CHO]}{[Fe_{aq}^{2+}]}}{\dfrac{k_{P2}}{k_{T1}}\dfrac{[C_2H_5CHO]}{[Fe_{aq}^{2+}]} + 1} \tag{18}$$

Comparison with eq 3 identifies parameter m_4 as the ratio $k_{P2}/k_{T1} = 8.9 \times 10^{-3}$. The agreement with the value obtained under the chain conditions (1.3×10^{-2}) is satisfactory and supports our approach.

Both possibilities presented here adequately explain the faster reaction with the aldehyde, but it is not clear why either possibility should apply. The sudden switch from H-atom transfer to hydride transfer for C_2H_5CHO is difficult to justify. If anything, the opposite might be expected; that is, alcohols and formaldehyde would appear more likely to react by hydride transfer, and higher aldehydes by hydrogen atom transfer, as observed for $Cr_{aq}O^{2+}$. However, our kinetic simulations show that such an explanation would require that all of the substrates *except* C_2H_5CHO exhibit chain kinetics, contrary to the observations. At this stage, it is reasonable to suggest that $(NH_3)_4RhO^{2+}$ reacts by hydrogen atom abstraction in most cases, but no clear distinction can be made for propionaldehyde.

In the absence of absolute rate constants for the reactions of Rh(IV) species in this work, a direct comparison with $Cr_{aq}O^{2+}$ is not feasible, but some interesting points have emerged. The relative rate constants in Table 3 for rhodium reactions show a clear trend, as opposed to the $Cr_{aq}O^{2+}$ case. One feature that separates $Cr_{aq}O^{2+}$ from the rhodium complexes is the presence of water ligands in equatorial positions. Normally, one would not expect equatorial ligands to play a major role in hydrogen atom or hydride transfer to the axial site, but the cis-aqua ligands may participate in hydrogen-bonded transition-state structures and attenuate the effects of other rate-influencing factors. The dramatic role of hydrogen bonding in hydrogen transfer reactions has been demonstrated.[41]

The observed 1.6:1 stoichiometry for the L^2RhH^{2+}/Tl_{aq}^{3+} reaction shows that it is not a clean two-electron oxidation of the rhodium. It is not clear whether the reaction occurs in one- or two-electron steps and what kind of intermediates are involved. The inability to oxidize Fe_{aq}^{2+}, L^1Ni^{2+}, and $ABTS^{2-}$ immediately after mixing L^2Rh^{2+} with Tl_{aq}^{3+} clearly shows that L^2RhO^{2+} either was not produced or it decayed

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rapidly on its own or in reactions with the rhodium and/or thallium species in solution. If the latter is true, and a reasonable upper limit of $\sim 10^8$ M^{-1} s^{-1} is placed on all the potential competing bimolecular reactions of L^2RhO^{2+}, the sequential stopped-flow data provide an estimate of $k_d > 100$ s^{-1}. Obviously, this analysis assumes that the L^2Rh^{2+}/Tl_{aq}^{3+} reaction involves the same intermediate as the $L^2RhOOH^{2+}/Fe_{aq}^{2+}$ reaction. From the k_d/k_{T1} value previously described, we then calculate $k_{T1}(L^2RhO^{2+}) > 10^6$ M^{-1} s^{-1}. This rate constant is rather large for electron-transfer involving Fe_{aq}^{2+}, showing that either the oxidizing power of L^2RhO^{2+} is comparable to those of Tl_{aq}^{2+} [42] or $Br_2^{\bullet-}$,[43] or our analysis does not apply because the two types of experiments yielded different intermediates. Further work is needed to resolve this issue.

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