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Transition Metal Ion Initiated Chain Reactions between *tert*-Butyl Hydroperoxide and Rhodium Hydrides. Rapid Hydrogen Atom Abstraction from Rhodium Hydrides by Methyl Radicals

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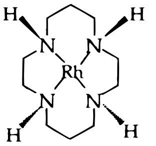
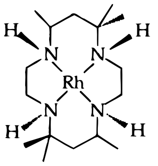
In the absence of catalysts, there is no reaction between *t*-BuOOH and macrocyclic rhodium hydrides $LRhH^{2+}$ (L^1 = [14]aneN$_4$, L^2 = Me$_6$-[14]aneN$_4$). The addition of Fe_{aq}^{2+} to such solutions results in rapid and catalytic oxidation of rhodium hydrides ($LRhH^{2+} + (CH_3)_3COOH + H^+ \rightarrow LRh^{3+} + CH_4 + (CH_3)_2CO$). This reaction occurs by a chain mechanism featuring methyl radicals and LRh^{2+} as reactive intermediates. The rates are independent of the absolute concentrations of iron but vary with the ratio of the two oxidation states, $-d[LRhH^{2+}]/dt = k_{obs}[t\text{-BuOOH}]^2[Fe^{2+}]/[Fe^{3+}]$. The rate constants k_{obs} are directly proportional to $[H^+]$. In 0.10 M aqueous $HClO_4$ at 25 °C, the values are 80.8 $M^{-1}\ s^{-1}$ (L^1RhH^{2+}) and 7.0 $M^{-1}\ s^{-1}$ (L^2RhH^{2+}). A macrocyclic cobalt(II) complex, L^2Co^{2+}, is also an effective chain initiator. The reaction occurs according to the rate law $-d[L^1RhH^{2+}]/dt = 254[t\text{-BuOOH}][L^1RhH^{2+}]$, independent of $[H^+]$. This reaction is not catalytic in L^2Co^{2+}, which is slowly consumed in the initiation and termination steps. Methyl radicals react rapidly with L^1RhH^{2+} ($k = 1.0 \times 10^9$ $M^{-1}\ s^{-1}$), L^2RhH^{2+} (1.4×10^8), and L^1Rh^{2+} (8.6×10^8).

Introduction

Our earlier work[1] on photochemical generation of LRh^{2+} from $LRhH^{2+}$ ($L = L^1$ = [14]aneN$_4$ and L^2 = *meso*-Me$_6$-[14]aneN$_4$) led us to suggest that a fast S_H2 reaction between hydrogen atoms and rhodium hydrides follows the initial cleavage of the Rh−H bond, eqs 1 and 2. The rate constant k_2 was estimated as $>3 \times 10^8$ $M^{-1}\ s^{-1}$ on the basis of our inability to trap hydrogen atoms with submillimolar concentrations of methyl viologen dication.



L^1Rh



L^2Rh

No suitable method was found to measure k_2 directly. In the absence of pulse radiolysis instrumentation, hydrogen atoms would almost certainly have to be generated by flash photolysis, possibly from $LRhH^{2+}$, as in eq 1. Unfortunately, the reaction of interest, eq 2, occurs with only a small absorbance change at $\lambda > 250$ nm, and UV-absorbing chromophores and competition kinetics are of limited use for the required $\lambda_{irr} < 300$ nm.

$$LRhH^{2+} \xrightarrow{h\nu(\mathrm{uv})} LRh^{2+} + H^{\bullet} \qquad (1)$$

$$H^{\bullet} + LRhH^{2+} \rightarrow LRh^{2+} + H_2 \qquad (2)$$

In their reactions with transition metal complexes, alkyl radicals, especially methyl, often exhibit chemistry similar to that of hydrogen atoms.[2,3] Alkyl radicals can be generated by visible photolysis of a number of precursors, which enables one to use spectroscopic probes and measure the kinetics precisely.[4−6] Even though hydrogen atom abstraction from metal hydrides by carbon-centered radicals is known[7−15] and has been used successfully to generate 17-e metal-centered radicals,[13,16−18] the kinetic data for such reactions are limited.[9−15] Most of the kinetic studies utilized radical clock reactions,[9−11,15,19] whereby bimolecular hydrogen abstraction and unimolecular radical rearrangement occur simultaneously. This approach has proven useful in radical kinetics,[20] but the number of suitable radicals is limited. Other authors[12,13] worked with stable radicals, such

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as trityl, and measured the kinetics directly. These studies revealed the dominance of steric factors, which are so severe that some metal hydrides barely react with the large trityl radicals.

The complexes $LRhH^{2+}$ are good candidates for direct kinetic measurements, because these hydrides are stable in acidic aqueous solutions and compatible with many radical-generating systems. In the present work, laser flash photolysis of alkyl cobalt complexes was used as a source of radicals for rapid kinetic measurements.

Reaction 2 and the equivalent reaction of methyl radicals, P1,[21] generate LRh^{2+}, which may engage in reactions with added substrates. Alkyl hydroperoxides appeared especially promising because of their potential to regenerate alkyl radicals and transform the stoichiometric reaction into a chain oxidation of $LRhH^{2+}$.

$$LRhH^{2+} + {}^{\bullet}CH_3 \rightarrow LRh^{2+} + CH_4 \qquad (P1)$$

To examine this possibility, methyl radicals were generated in a slow thermal reaction of eq I and β.[21] The Fe^{2+}/*t*-BuOOH combination not only provided a clean source of methyl radicals but also added an interesting mechanistic twist, resulting in a highly efficient catalytic chain reaction.

$$Fe^{2+} + (CH_3)_3COOH \rightarrow FeOH^{2+} + (CH_3)_3CO^{\bullet} \qquad (I)$$

$$(CH_3)_3CO^{\bullet} \rightarrow (CH_3)_2CO + {}^{\bullet}CH_3 \qquad (\beta)$$

Experimental Section

The complexes trans-$([14]aneN_4)(H_2O)RhH]^{2+}$ (hereafter L^1RhH^{2+}) and β-trans-[*meso*-$(Me_6$-$[14]aneN_4)(H_2O)RhH]^{2+}$ (hereafter L^2RhH^{2+}) in dilute aqueous perchloric acid were prepared by ion exchange of the chloride salts, as described previously.[1,22] Dilute solutions of LRh^{2+} ($L = L^1$ and L^2) were prepared by UV photolysis (Rayonet reactor) of the corresponding rhodium hydrides under strictly air-free conditions, eqs 1 and 2.[1] A 2−3 min photolysis of 0.1−0.2 mM $LRhH^{2+}$ typically produced LRh^{2+} in ~67% yield as determined by spectrophotometric titrations of solutions of LRh^{2+} with $(NH_3)_5CoBr^{2+}$. Most of the remaining rhodium was present as LRh^{3+}. Some of it may have been produced by oxidation of LRh^{2+} with traces of O_2, but the persistency of the 67% yield in a large number of experiments suggests that other reactions, perhaps those shown in eqs 3−5, are involved.[1−6]

$$LRhH^{2+} \xrightarrow{LRh^{2+},\ H^+} LRh^{3+} + H_2 \qquad (3)$$

$$LRh^{2+} \xrightarrow{h\nu} LRh^{3+} + e_{aq}^{-} \qquad (4)$$

$$e_{aq}^{-} + H^+ \rightarrow H^{\bullet} \qquad k = 2.3 \times 10^{10}\ M^{-1}\ s^{-1} \qquad (5)$$

It was difficult to determine from the UV spectra whether any $LRhH^{2+}$ remained in the photolyzed solutions. This issue became important in the study of the reaction of L^1Rh^{2+} with methyl radicals, because both L^1RhH^{2+} and L^1Rh^{2+} react at close to diffusion-controlled rates, and the true rate constant for L^1Rh^{2+} may be smaller than that calculated if some of the "missing" Rh is present as L^1RhH^{2+}, see Results and Discussion.

Solutions of Fe^{2+} were prepared by Zn/Hg reduction of Fe^{3+} in dilute $HClO_4$ and stored under Ar. Stock solutions of *tert*-butyl hydroperoxide were prepared by dilution of the commercial 70% $(CH_3)_3COOH$ (Aldrich) and standardized by spectrophotometric titration with Cr_{aq}^{2+} at 260 nm, where the product $(H_2O)_5CrCH_3^{2+}$ has a molar absorptivity of 2520 M^{-1} cm^{-1}.[23]

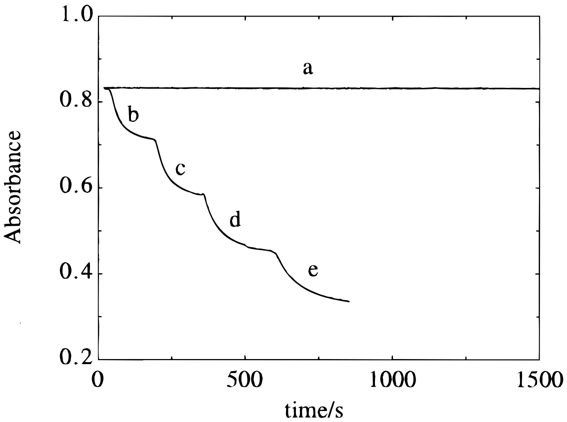

Figure 1. Absorbance vs time traces at 290 nm for the Fe^{2+}-catalyzed reaction between L^1RhH^{2+} and *t*-BuOOH. (a) 1.7 mM L^1RhH^{2+} + 0. 4 mM *t*-BuOOH in 0.10 M $HClO_4$. (b) After addition of 10 μM Fe_{aq}^{2+} to a. (c, d, e) Addition of more *t*-BuOOH (0.4 mM/shot) consumes all of L^1RhH^{2+}. $L^1 = [14]aneN_4$.

Kinetic data for the chain reactions were collected by use of a Shimadzu 3100 PC spectrophotometer equipped with a thermostated cell compartment. The reaction of L^1RhH^{2+} was monitored at 290 and 235 nm, where the values of apparent $\Delta\epsilon$ ($=\epsilon_{reactants} - \epsilon_{products}$) were determined to be 314 M^{-1} cm^{-1} and 3000 M^{-1} cm^{-1}, respectively. The rate constants obtained at the two wavelengths agreed to within 5%. The reaction of L^2RhH^{2+} was monitored at 235 nm ($\Delta\epsilon = 5140\ M^{-1}\ cm^{-1}$).

The kinetics of the reaction of $LRhH^{2+}$ ($L = L^1$ and L^2) and L^1Rh^{2+} with alkyl radicals were determined by laser flash photolysis utilizing a dye laser system described previously.[24] All experiments used λ_{irr} 490 nm (Exciton LD-490 dye). Gaseous products were analyzed by use of a Hewlett-Packard 5790A gas chromatograph.

All the experiments were carried out under argon in acidic aqueous solutions. The kinetic data were obtained at 25.0 °C and 0.10 M ionic strength ($HClO_4 + LiClO_4$).

Results and Discussion

In the absence of catalysts, no reaction was observed between 0.4 mM *t*-BuOOH and 1.7 mM L^1RhH^{2+} in 1500 s under air-free conditions at pH 1, trace a in Figure 1. The addition of small amounts of Fe_{aq}^{2+} (10 μM) to this solution caused a rapid decrease in absorbance at 290 nm, corresponding to the loss of one mole of L^1RhH^{2+} ($\epsilon_{290} = 470\ M^{-1}\ cm^{-1}$)[1] per mole of *t*-BuOOH, eq 6. The ready consumption of additional aliquots of *t*-BuOOH (traces c, d, and e in Figure 1) showed that most of the added iron persisted as Fe^{2+}. Methane was the only gaseous product found.

$$L^1RhH^{2+} + (CH_3)_3COOH + H^+ \xrightarrow{Fe^{2+}} L^1Rh^{3+} + CH_4 + (CH_3)_2CO \qquad (6)$$

Reaction 6 is extremely sensitive to the presence of O_2 and takes place only in thoroughly degassed solutions. This required the purging of all the solutions with Ar for at least 30−40 min prior to any kinetic measurements. Shorter purging times resulted in an induction period, after which the reaction proceeded with the same rate constant as that obtained with carefully degassed solutions.

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[21] The equation labels I, P, T, and β stand for initiation, propagation, termination, and β-elimination steps in Schemes 1 and 2.

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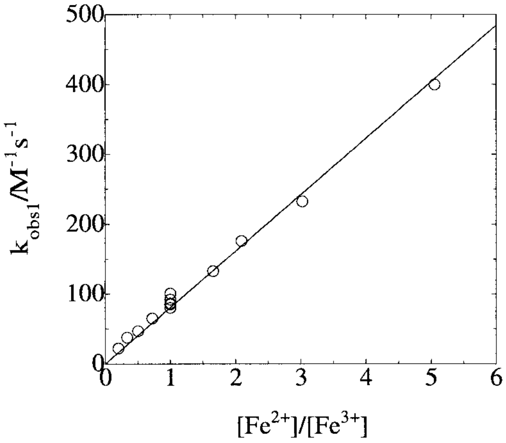

Figure 2. Plot of k_{obs1} (eqs 7 and 9) against the ratio $[Fe^{2+}]/[Fe^{3+}]$ for the reaction between L^1RhH^{2+} and *t*-BuOOH in 0.10 M aqueous $HClO_4$ at 25 °C. L^1 = [14]aneN$_4$.

Scheme 1

$$Fe^{2+} + (CH_3)_3COOH \xrightarrow{H^+} Fe^{3+} + (CH_3)_3CO^\bullet \qquad (I)$$

$$(CH_3)_3CO^\bullet \rightarrow (CH_3)_2CO + {}^\bullet CH_3 \qquad (\beta)^{25}$$

$$L^1RhH^{2+} + {}^\bullet CH_3 \rightarrow L^1Rh^{2+} + CH_4 \qquad (P1)$$

$$L^1Rh^{2+} + (CH_3)_3COOH \xrightarrow{H^+} L^1Rh^{3+} + (CH_3)_3CO^\bullet \qquad (P2)$$

$$L^1Rh^{2+} + Fe^{3+} \rightarrow L^1Rh^{3+} + Fe^{2+} \qquad (T)$$

Kinetics of the Chain Reaction. The buildup of small amounts of Fe^{3+} in the course of the reaction had a retarding effect and resulted in complicated kinetic behavior such that the apparent rate constants decreased with time. To keep $[Fe^{3+}]$ approximately constant during the reaction, controlled amounts of Fe^{3+} were added to all kinetic solutions. Under these conditions and using L^1RhH^{2+} (0.1−2.7 mM) in excess over *t*-BuOOH (0.08−0.9 mM), the kinetics were strictly second-order, eq 7.

$$-d[t\text{-BuOOH}]/dt = -d[L^1RhH^{2+}]/dt = k_{obs1}[t\text{-BuOOH}]^2 \qquad (7)$$

The rate constant k_{obs1} is independent of L^1RhH^{2+} and directly proportional to the ratio $[Fe^{2+}]/[Fe^{3+}]$, as shown in Figure 2, $k_{obs1}/M^{-1}\ s^{-1} = (80.8 \pm 1.3)[Fe^{2+}]/[Fe^{3+}]$ in 0.10 M H^+. In the absence of added Fe^{3+}, the ratio $[Fe^{2+}]/[Fe^{3+}]$ changes dramatically when even a small percentage of Fe^{2+} is oxidized. This explains the need for added Fe^{3+} to keep the system kinetically well behaved.

The dependence of k_{obs} on $[Fe^{2+}]/[Fe^{3+}]$ holds over a large range of absolute concentrations. Eventually, at $[Fe^{2+}] = [Fe^{3+}] < 0.5\ \mu M$, the reaction slowed, presumably because the concentration of O_2 in "air-free" solutions began to approach that of the catalyst. Consistent with this interpretation is the fact that the reaction at the lowest concentrations of Fe ($<1\ \mu M$) exhibited an induction period, as expected if O_2 was a problem.

All the data are consistent with the catalytic chain reaction of Scheme 1.

The steady-state approximation for the intermediates ${}^\bullet CH_3$ and L^1Rh^{2+} results in the rate law of eq 8, which, under a long-chain approximation, reduces to eq 9 and identifies k_{obs1} of eq 7 as $k_Ik_{P2}[Fe^{2+}]/k_T[Fe^{3+}]$.

$$\text{rate} = -d[BuOOH]/dt = -d[L^1RhH^{2+}]/dt = k_I[Fe^{2+}][BuOOH] + \frac{k_Ik_{P2}[Fe^{2+}]}{k_T[Fe^{3+}]}[BuOOH]^2 \qquad (8)$$

$$\text{rate} = k_{obs1}[BuOOH]^2 = \frac{k_Ik_{P2}[Fe^{2+}]}{k_T[Fe^{3+}]}[BuOOH]^2 \qquad (9)$$

Equation 9 describes the kinetics well under all conditions, as demonstrated by excellent fits to second-order kinetics and by the linearity of the plot in Figure 2. The minor positive deviations exhibited by the points close to the origin in Figure 2 may indicate a contribution from the initiation step, which would be noticeable only at the lowest $[Fe^{2+}]/[Fe^{3+}]$ ratios, i.e., under the conditions that cause a major decrease in the chain length and may require the complete rate law of eq 8 to describe the data. Importantly, the quality of the second-order fits did not deteriorate as the ratio $[Fe^{2+}]/[Fe^{3+}]$ decreased, showing that reaction I consumed, at best, only a small fraction of *t*-BuOOH.

The acid dependence of the catalytic reaction was investigated at $0.009 \le [H^+] \le 0.10$ M. The rate increases with $[H^+]$, as shown in Figure 3. Assuming that the only reason for acid dependence is the retarding effect of H^+ on the termination step and that $FeOH^{2+}$ is the only form of Fe(III) that reacts in that step, one obtains eq 10, where k_{FeOH} represents the rate constant for the reaction of L^1Rh^{2+} with $FeOH^{2+}$ (modified termination step) and $[Fe(III)]_T$ is the total concentration of iron(III). The value of K_a, the acid dissociation constant of Fe^{3+}, was fixed at 2.5×10^{-3} M.[26] The fit, shown in Figure 3, yields $k_Ik_{P2}/k_{FeOH} = 1.96 \pm 0.04$.

$$k_{obs1}[Fe(III)]_T/[Fe^{2+}] = k_Ik_{P2}(K_a + [H^+])/k_{FeOH}K_a \qquad (10)$$

The assumptions built into eq 10 are consistent with the known tendency of Fe^{3+} to react with transition metal complexes by inner-sphere mechanisms utilizing HO-bridged pathways.[27,28] The slowdown of the termination step should speed up the chain reaction, which should thus be catalyzed by $[H^+]$, as observed experimentally. The rest of Scheme 1 is either known (reactions I, β, and P1) or believed (P2) to be independent of $[H^+]$.

The complex L^2RhH^{2+} behaves much like L^1RhH^{2+} in its reaction with *t*-BuOOH. The Fe^{2+} catalysis, second-order dependence on [*t*-BuOOH], and kinetic dependencies on $[Fe^{2+}]/[Fe^{3+}]$ and $[H^+]$ are qualitatively the same as those observed for L^1RhH^{2+}. A limited number of kinetic experiments yielded $k_{obs1}/M^{-1}\ s^{-1} = (7.0 \pm 0.4)[Fe^{2+}]/[Fe^{3+}]$ at 0.1 M H^+, and $(2.9 \pm 0.3)[Fe^{2+}]/[Fe^{3+}]$ at 0.05 M H^+.

Other Chain Initiators. Numerous metal reductants produce methyl radicals in their reactions with *t*-BuOOH. In principle, such reductants might be able to replace Fe^{2+} and induce the oxidation of $LRhH^{2+}$ complexes. A successful catalyst should not react rapidly with methyl radicals, and the oxidized form should be reduced by LRh^{2+} in the equivalent of reaction T to regenerate the catalyst. Preferably, the catalyst should be air-

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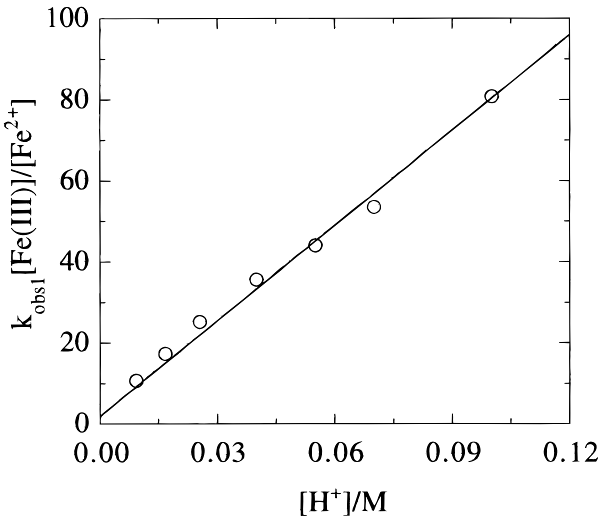
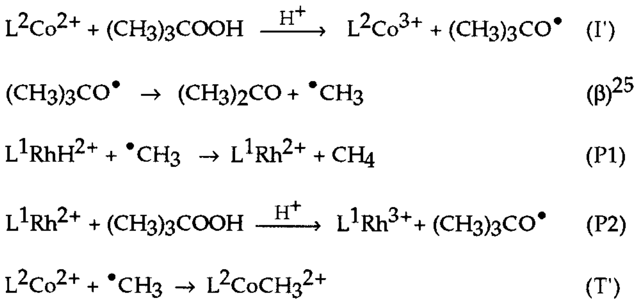


Figure 3. Plot of $k_{obs1}[Fe^{III}]/[Fe^{2+}]$ against $[H^+]$ for the reaction of L^1RhH^{2+} with *t*-BuOOH at 25 °C and 0.10 M ionic strength. The line was calculated by use of eq 10. L^1 = [14]aneN_4.

Scheme 2



stable to prevent trace amounts of O_2 from inducing uncontrollable changes in reaction rates.

None of the complexes considered (V^{2+}, Cr^{2+}, Ti^{3+}, Cu^+, and macrocyclic cobalt complexes) had all the required properties. The reaction using L^2Co^{2+} did, however, exhibit some interesting features, as described below.

As was the case with Fe^{2+}, even small concentrations of L^2Co^{2+} initiated a rapid reaction between *t*-BuOOH and L^1RhH^{2+}. In the presence of an excess of *t*-BuOOH (0.3−1 mM) over L^1RhH^{2+} (0.05−0.1 mM), the reaction of interest was followed by the oxidation of L^2Co^{2+} with excess *t*-BuOOH, $2k_{I'} = 22.8\ M^{-1}\ s^{-1}$.[29] The two stages were resolved by consecutive kinetic treatment.

The kinetics of the faster step were independent of the concentration of L^2Co^{2+} (5−40 μM) and H^+ (0.01−0.10 M) and obeyed the mixed second-order rate law of eq 11, where $k_{obs} = 254 \pm 10\ M^{-1}\ s^{-1}$.

$$-d[L^1RhH^{2+}]/dt = k_{obs2}\,[t\text{-BuOOH}][L^1RhH^{2+}] \quad (11)$$

The mechanism of L^2Co^{2+}-induced reaction is clearly different from that induced by Fe^{2+}. The L^2Co^{2+} reaction is described well by Scheme 2, which retains the chain-propagating sequence of Scheme 1 but replaces the initiation and termination steps with reactions I′ and T′.

Scheme 2 yields the rate law of eq 12 which reduces to eq 11 under the long-chain approximation, with $k_{obs2} = (k_{I'}k_{P1}/k_{T'})$.

$$-d[L^1RhH^{2+}]/dt = k_{I'}[L^2Co^{2+}][t\text{-BuOOH}] + (k_{I'}k_{P1}/k_{T'})[L^1RhH^{2+}][t\text{-BuOOH}] \quad (12)$$

Several experiments were carried out with a large excess of L^1RhH^{2+} (2−3 mM) at low $[L^2Co^{2+}]$ (3−10 μM). The reaction was still first-order in [*t*-BuOOH], but the measured rate constants were smaller than those obtained with *t*-BuOOH in excess. Also, the dependence on $[L^1RhH^{2+}]$ became less than first order, and the reaction showed some dependence on $[L^2Co^{2+}]$. The results are consistent with the introduction of an additional termination step, reaction 13.[30] As shown later,

$$L^1Rh^{2+} + {}^\bullet CH_3 \rightarrow L^1RhCH_3^{2+} \quad (13)$$

the rate constant for the capture of ${}^\bullet CH_3$ by L^1Rh^{2+}, k_{13}, is about 20 times greater than that for the corresponding reaction of L^2Co^{2+} ($k_{T'} = 4.2 \times 10^7\ M^{-1}\ s^{-1}$).[5] At $[L^1RhH^{2+}] > 2$ mM, the steady-state concentration of L^1Rh^{2+} is >0.3 μM, sufficiently high to compete with 3−10 μM L^2Co^{2+}.

The critical difference between L^2Co^{2+} and Fe^{2+} lies in the inability of L^2Co^{3+} to be reduced rapidly with LRh^{2+} (equivalent of reaction T), which prevents the reaction from becoming catalytic. Also, the rapid reaction between L^2Co^{2+} and methyl radicals (reaction T′) keeps the chain length at ~200 under most of the conditions used in this work. For comparison, the chain length in the Fe^{2+}-catalyzed reaction varied much more with the conditions, from ~8 at low $[Fe^{2+}/[Fe^{3+}]$ and low [*t*-BuOOH] to >2000 under more standard conditions ($[Fe^{2+}/[Fe^{3+}] \approx 1$ and [*t*-BuOOH] > 0.3 mM at 0.10 M H^+). Finally, the rates of L^2Co^{2+}-induced reactions are not affected by changes in $[H^+]$.

Kinetics of Individual Steps. The reaction between Fe^{2+} and *t*-BuOOH, eq I, takes place with a rate constant $k_I = 18.7 \pm 0.1\ M^{-1}\ s^{-1}$, regardless of which reagent is in excess, and independent of $[H^+]$ in the range 0.01 to 0.10 M.[31]

The rate constants for the reactions of rhodium hydrides with methyl radicals were determined by laser flash photolysis utilizing methyl viologen radical cation ($MV^{\bullet +}$) as a kinetic probe[5,6,32,33] and $L^1CoCH_3^{2+}$ [5] as a photochemical source of methyl radicals. The values obtained are $k_{P1} = (1.0 \pm 0.1) \times 10^9\ M^{-1}\ s^{-1}$ for L^1RhH^{2+} and $(1.4 \pm 0.1) \times 10^8\ M^{-1}\ s^{-1}$ for L^2RhH^{2+}, both independent of $[H^+]$ in the range 4−10 mM.

The same kinetic probe method was used to determine the rate constant k_{13} for the capture of ${}^\bullet CH_3$ by L^1Rh^{2+}. The range of $[L^1Rh^{2+}]$, 0.060−0.095 mM, was limited on one end by the large reaction rates and on the other by uncertainties in the actual concentrations of the highly air-sensitive L^1Rh^{2+}. The value, $k_{13} = (8.6 \pm 1.0) \times 10^8\ M^{-1}\ s^{-1}$, was calculated under the assumption that no L^1RhH^{2+} was present in solutions of L^1Rh^{2+}, see Experimental Section. Since the photochemical yields of L^1Rh^{2+} were ~67% of initial L^1RhH^{2+}, the presence of small amounts of unreacted L^1RhH^{2+} cannot be ruled out entirely. On the other hand, any contribution from traces of L^1RhH^{2+} was probably offset by air oxidation of some L^1Rh^{2+} during the manipulations and kinetic measurements following steady-state photolysis. In view of the two potentially opposing sources

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[30] In the limit where reaction 13 is the only termination step, the rate law is $-d[t\text{-BuOOH}]/dt = [t\text{-BuOOH}]\{k_{I'}k_{P1}k_{P2}[L^2Co^{2+}][L^1RhH^{2+}]/2k_{13}\}^{0.5}$. When $k_\beta \ll k_{P1}[L^1RhH^{2+}]$, the dependence on $[L^1RhH^{2+}]$ disappears, $-d[t\text{-BuOOH}]/dt = [t\text{-BuOOH}]\{k_{I'}k_\beta k_{P2}[L^2Co^{2+}]/2k_{13}\}^{0.5}$.

[31] Bakac, A.; Wang, W.-D. *Inorg. React. Mech.* **1988**, *1*, in press.

[32] Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739.

[33] Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520.

Table 1. Summary of Kinetic Data Obtained in This Work[a]

reaction	notation	k/M^{-1} s^{-1} [b]
$^{\bullet}CH_3 + L^1RhH^{2+} \rightarrow CH_4 + L^1Rh^{2+}$	P1	$1.0(1) \times 10^9$
$^{\bullet}CH_3 + L^2RhH^{2+} \rightarrow CH_4 + L^2Rh^{2+}$	P1(L^2)	$1.4(1) \times 10^8$
$^{\bullet}CH_3 + L^1Rh^{2+} \rightarrow L^1RhCH_3{}^{2+}$	13	$8.6(22) \times 10^8$
$^{\bullet}CH_3 + L^2Co^{2+} \rightarrow L^2CoCH_3{}^{2+}$	T′	$4.2(4) \times 10^7$ [c]
$L^1Rh^{2+} + Fe^{3+} \rightarrow L^1Rh^{3+} + Fe^{2+}$	T	$9(4) \times 10^4$ [d]
$L^2Rh^{2+} + Fe^{3+} \rightarrow L^2Rh^{3+} + Fe^{2+}$	T(L^2)	$1.6(3) \times 10^4$ [d]
$L^1Rh^{2+} + t\text{-BuOOH} \rightarrow L^1RhOH^{2+} + t\text{-BuO}^{\bullet}$	P2	$>4 \times 10^4$ $\sim 4 \times 10^5$ [e]
$L^2Rh^{2+} + t\text{-BuOOH} \rightarrow L^2RhOH^{2+} + t\text{-BuO}^{\bullet}$	P2(L^2)	$4(2) \times 10^3$
$Fe^{2+} + t\text{-BuOOH} \rightarrow Fe^{3+} + \text{t-BuO}^{\bullet}$	I	18.7(1)[f]
$L^1Co^{2+} + Fe^{3+} \rightarrow L^1Co^{3+} + Fe^{2+}$		4100(100)[d]
$L^2Co^{2+} + Fe^{3+} \rightarrow L^2Co^{3+} + Fe^{2+}$		274(2)[d]
$L^1Co^{2+} + t\text{-BuOOH} \rightarrow L^1CoOH^{2+} + t\text{-BuO}^{\bullet}$		52.0(15)[g]
$L^2Co^{2+} + t\text{-BuOOH} \rightarrow L^2CoOH^{2+} + t\text{-BuO}^{\bullet}$	I′	11.4(14)[g]
Scheme 1, $L = L^1$	$I \times P2/T$	80.8(13)[d]
Scheme 1, $L = L^2$	$I \times P2/T$	7.0(4)[d]
Scheme 2, $L = L^1$	$I' \times P1/T'$	254(10) 285(86)[h]

[a] At 25 °C and 0.10 M ionic strength ($HClO_4 + LiClO_4$). L^1 = [14]aneN$_4$, L^2 = Me$_6$-[14]aneN$_4$. [b] Numbers in parentheses represent one standard deviation of the last significant figure. [c] Reference 5. [d] The reaction is acid-dependent. The value quoted is for 0.10 M H$^+$. [e] Calculated from the kinetic data for the chain reaction, eq 9. [f] Reference 31. [g] Reference 29. [h] Calculated from independently measured $k_{I'}$, k_{P1}, and $k_{T'}$.

of error, an uncertainty of ~25% seems reasonable, i.e., $k_{13} = (8.6 \pm 2.2) \times 10^8$ M^{-1} s^{-1}.

The reactions of LRh^{2+} complexes with t-BuOOH and with Fe^{3+} are fast and could not be measured accurately without the use of a stopped-flow instrument. Unfortunately, the handling of <0.2 mM LRh^{2+} in our stopped-flow apparatus resulted in rapid air oxidation of all the LRh^{2+} before the measurements could be made. The rate constants were therefore estimated by conventional spectrophotometry using low concentrations of all the reagents. Only the last 10−30% of the reaction was usually observed, and the oxidation of L^{1}Rh^{2+} by t-BuOOH was too fast to measure under any conditions. The data were used to estimate the following rate constants (M^{-1} s^{-1}): $k_T = (9 \pm 4) \times 10^4$, $k_{T(L2)} = (1.6 \pm 0.3) \times 10^4$, $k_{P2} > 4 \times 10^4$, and $k_{P2(L2)} = (4 \pm 2) \times 10^3$, all in 0.10 M HClO$_4$. In calculating the rate constants for the reactions with t-BuOOH, the measured rates were corrected for an assumed, but unconfirmed, factor of 2, i.e., $-d[LRh^{2+}]/dt = 2k_{P2}[LRh^{2+}][t\text{-BuOOH}]$. All the kinetic data are summarized in Table 1.

The reactions of LCo^{2+} complexes with Fe^{3+} also were studied. At [H$^+$] = 0.02−0.10 M, the data for L^{2}Co^{2+} obeyed the rate law of eq 14, where $k_{14} = 26.4 \pm 0.1$ s^{-1}. The measured value in 0.10 M HClO$_4$ was 274 M^{-1} s^{-1}. The L^{1}Co^{2+}/Fe^{3+} reaction in 0.10 M H$^+$ has $k = 4100 \pm 100$ M^{-1} s^{-1}.

$$-d[L^2Co^{2+}]/dt = k_{14}\,[L^2Co^{2+}][Fe^{III}]_T/[H^+] \qquad (14)$$

Calculations of Composite Rate Constants. Ideally, the mechanisms in Schemes 1 and 2 could be confirmed by calculating the overall rate constants from the independently determined values for individual steps. This approach works well for Scheme 2. Each of the contributing rate constants is known with better than 10% accuracy, Table 1, and the composite $k_{I'}k_{P1}/k_{T'}$ is calculated as 285 ± 86 M^{-1} s^{-1}. The agreement with the measured 254 ± 10 M^{-1} s^{-1} is considered excellent.

Not all of the necessary rate constants for the calculation of k_Ik_{P2}/k_T of Scheme 1 are known for L^{1}RhH^{2+}, and only a limit of >8.3 M^{-1} s^{-1} at 0.10 M HClO$_4$ can be calculated. This value is consistent with the measured rate constant of 80.8 M^{-1} s^{-1}. Provided the mechanism in Scheme 1 is correct, one can calculate the unknown rate constant $k_{P2} = (4 \pm 2) \times 10^5$ M^{-1} s^{-1}. This calculation used the values of k_I, k_T and k_Ik_{P2}/k_T, from Table 1.

Calculations based on Scheme 1 for L^{2}RhH^{2+} yield $k_Ik_{P2}/k_T = 4.7 \pm 3.3$ M^{-1} s^{-1} at 0.1 M H$^+$. Given the large error associated with two of the three individual rate constants used in this calculation, Table 1, the agreement with the observed rate constant of 7.0 ± 0.4 M^{-1} s^{-1} is acceptable.

Steric Effects. The overall rate constants for the Fe^{2+}-catalyzed oxidation of L^{1}RhH^{2+} by t-BuOOH is ~11 times larger than the corresponding rate constant for L^{2}RhH^{2+}. The two reactions have a common initiation step, reaction I, and the sole difference between the two systems resides in the ratios k_{P2}/k_T for L^{1}Rh^{2+} and L^{2}Rh^{2+}. While the absolute rate constants for the reactions of the two complexes with t-BuOOH (k_{P2}) and with Fe^{3+} (k_T) are expected to be different, the relative advantage of one oxidant over the other ($k_{P2}/k_T = 4.3$ for $L = L^1$ and 0.37 for $L = L^2$ at 0.10 M H$^+$) was expected to be more constant. For example, the corresponding ratios for LCo^{2+} complexes are 0.013 (L^1) and 0.042 (L^2), Table 1. Thus the increase in driving force as the metal changes from cobalt to rhodium[34] benefits the ratio k_{P2}/k_T much more for L^{1}Rh^{2+} than for L^{2}Rh^{2+}. Steric crowding, which is much more severe for L^{2}Rh^{2+}, may be responsible for the disproportionately smaller increase in the rate of the L^{2}Rh^{2+}/t-BuOOH reaction relative to that of the L^{2}Rh^{2+}/Fe^{3+} reaction.

The rate constants for the reactions of methyl radicals with the two rhodium hydrides in this work ($k_{P1} = 1 \times 10^9$ M^{-1} s^{-1} for L^{1}RhH^{2+} and 1.4×10^8 M^{-1} s^{-1} for L^{2}RhH^{2+}) are among the largest reported for this kind of reaction.[9−15] The magnitude of the rate constants and the reduced rate of L^{2}RhH^{2+} relative to L^{1}RhH^{2+} are both consistent with the reported dominance of steric effects[9−13] in hydrogen atom transfer from metal hydrides. Clearly, the large thermodynamic driving force also plays a role, and the combination of the two effects appears to be responsible for the bimolecular homolytic substitution at L^{1}RhH^{2+}, eq P1, being as fast ($k = 1 \times 10^9$ M^{-1} s^{-1}) as the coupling reaction between methyl radicals and L^{1}Rh^{2+} (0.86×10^9 M^{-1} s^{-1}). The reaction between L^{1}RhH^{2+} and hydrogen atoms, eq 2, should be at least as fast as reaction P1, consistent with our previous estimate of $k_2 > 3 \times 10^8$ M^{-1} s^{-1}.

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[34] Cu^{2+} oxidizes both L^{1}Rh^{2+} and L^{2}Rh^{2+}, which places the reduction potentials for both LRh^{3+}/LRh^{2+} couples at <0.1 V, i.e., more than 0.3−0.5 V below those for the corresponding cobalt complexes ($E°(L^1Co^{3+}/L^1Co^{2+}) = 0.44$ V (Heckman, R. A.; Espenson, J. H. *Inorg. Chem.* **1979**, *18*, 38) and $E°(L^2Co^{3+}/L^2Co^{2+}) = 0.59$ V (Liteplo, M. P.; Endicott, J. F. *Inorg. Chem.* **1971**, *10*, 1420)).