Inorg. Chem. **2005**, *44*, 489–495

Inorganic Chemistry
Article

Catalysis by Methyltrioxorhenium(VII): Reduction of Hydronium Ions by Europium(II) and Reduction of Perchlorate Ions by Europium(II) and Chromium(II)

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Received September 22, 2004

The title reactions occur stepwise, the first and fastest being $MeReO_3 + Eu^{2+} \rightarrow Re(VI) + Eu^{3+}$ ($k_{298} = 2.7 \times 10^4$ L mol^{-1} s^{-1}), followed by rapid reduction of Re(VI) by Eu^{2+} to $MeReO_2$. The latter species is reduced by a third Eu^{2+} to Re(IV), a metastable species characterized by an intense charge transfer band, $\epsilon_{410} = 910$ L mol^{-1} cm^{-1} at pH 1; the rate constant for its formation is 61.3 L mol^{-1} s^{-1}, independent of [H^+]. Yet another reduction step occurs, during which hydrogen is evolved at a rate $v = k[\mathrm{Re(IV)}][\mathrm{Eu}^{2+}][\mathrm{H}^+]^{-1}$, with $k = 2.56$ s^{-1} at $\mu = 0.33$ mol L^{-1}. The 410 nm Re(IV) species bears no ionic charge on the basis of the kinetic salt effect. We attribute hydrogen evolution to a reaction between H–Re^{V}O and H_3O^+, where the hydrido complex arises from the unimolecular rearrangement of Re^{III}–OH in a reaction that cannot be detected directly. Chromium(II) ions do not evolve H_2, despite $E°_{Cr} \sim E°_{Eu}$. We attribute this lack of reactivity to the Re(IV) intermediate being captured as $[Re^{IV}–O–Cr^{III}]^{2+}$, with both metals having substitutionally inert d^3 electronic configurations. Hydrogen evolution occurs in chloride or triflate media; with perchlorate present, $MeReO_2$ reduces perchlorate to chloride, as reported previously [Abu-Omar, M. M.; Espenson, J. H. *Inorg. Chem.* **1995**, *34*, 6239–6240].

Introduction

Many metal ions that lie below H_3O^+/H_2 in the electrochemical series survive for lengthy periods in acidic solution because of substantial kinetic barriers. Among them are hydrated Cr^{2+}, Eu^{2+}, and V^{2+} ions which remain indefinitely unchanged provided the solutions are acidic and oxygen is rigorously excluded, despite the fact that these species are thermodynamically unstable toward the formation of M(III) and dihydrogen, shown as eq 1.

$$2M^{2+} + 2H^+ \rightarrow 2M^{3+} + H_2 \tag{1}$$

The driving forces for these reactions are $\Delta E° = 0.415$, 0.380, and 0.230 V for Cr^{2+}, Eu^{2+}, and V^{2+} respectively.[1,2] Because the reactions are spontaneous, a kinetic barrier is responsible for the lack of reactivity. These metal ions are strong single-electron reductants, so the chemistry of dihydrogen formation would entail intermediate formation of $H_{aq}^{\bullet}$, which is not thermodynamically feasible, $E°$ for $H^+/H^{\bullet}$ being -2.3 V.[3,4] Although V^{2+} ion can undergo a two electron change to produce VO^{2+}, the reduction potential for VO^{2+}/V^{2+} is 0.08 V, which means reaction 2 is thermodynamically unfavorable.

$$V^{2+} + H_2O \rightarrow VO^{2+} + H_2 \tag{2}$$

Thus, any actual process for proton reduction must avoid the intermediacy of hydrogen atoms. Hydrogen evolution reactions from a metal or a metal complex have one common feature, an intermediate hydridometal species. Its formation will lower the energy barrier for the production of H_2 as it can react directly with H_3O^+ and avoid the formation of atomic hydrogen. Thus, hydrogen gas can be generated directly by a bimolecular reaction pathway[5,6] or by a proton−hydride reaction pathway.[6,7]

What we believe was the first example of a homogeneously catalyzed, nonphotochemical process for proton

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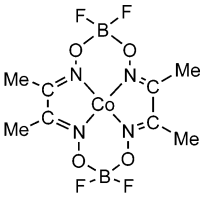
10.1021/ic048669k CCC: $30.25

reduction was reported in 1986. Molecular hydrogen is evolved rapidly from acidic solutions of chromium(II), europium(II), or vanadium(II) ions in the presence of trace concentrations of a catalyst, the cobalt(II) macrocycle Co(dmgBF$_2$)$_2$, **1**.[8] Further, in 1988, Gould et al. noted that ReO_4^- catalyzes what was presumed to be the reduction of H_3O^+ to H_2 by vitamin B_{12s}, cobalt(I)alamin, the cobalt(I) form of B_{12}.[9] Further studies were not carried out because of the difficulties in measuring the yield of H_2 and in determining the oxidation state of the rhenium species involved during the reaction process.[9]

Recently, we observed that upon mixing $MeReO_3$ (MTO) with Eu^{2+} in acidic aqueous solution H_2 is evolved fairly rapidly when perchlorate ions are absent. Even though most of our experiments have been carried out in chloride media, triflate solutions also evolve H_2. It is also important to note that H_2 is not evolved when Cr^{2+} is used instead of Eu^{2+}. Because these observations are unprecedented, we have undertaken a study of the Eu^{2+} reaction to understand, principally by stoichiometry and kinetics, the mechanism of catalyzed hydrogen formation and also the reasons why Cr^{2+} does not behave in the same way.



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The $Eu^{2+}-H^+$ reaction occurs in several steps. The kinetics of three of the steps could be measured by different methods, although to do so required the use of different absolute and relative concentrations of Eu^{2+} and $MeReO_3$.

In the course of this study, we also found that when perchlorate ions are present in the solution, they are reduced to chloride ions before H_2 can be formed. Perchlorate has a powerful thermodynamic tendency for reduction in dilute aqueous solution, although reduction is often very slow. In this study, Eu^{2+}_{aq} or Cr^{2+}_{aq} were used to reduce $MeReO_3$ to $MeReO_2(H_2O)_n$ ($n = 2$, presumably, because $MeReO_2(PAr_3)_2$ has been isolated and characterized[10]), which then rapidly reduces perchlorate ions.

The chemistry of $MeReO_3$ has been extensively reviewed, particularly in the context of its use as a catalyst for reactions of hydrogen peroxide.[11−15]

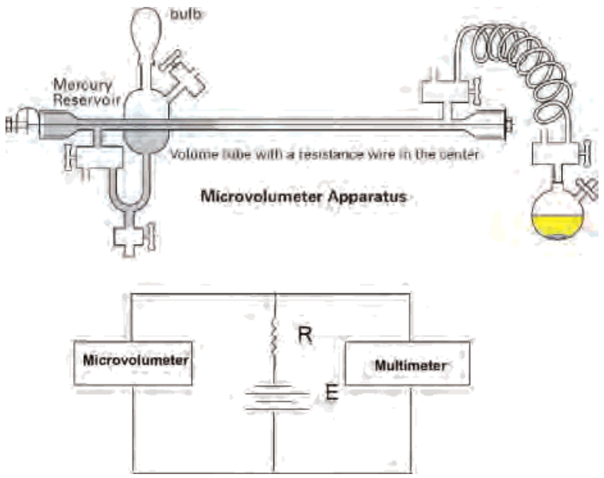

Figure 1. A recording gas microvolumeter system for hydrogen evolution. Top: the microvolumeter apparatus. Bottom: the circuit diagram. R, resistance; E, battery.

Experimental Section

Materials. High-purity water was obtained by passing laboratory distilled water through a Millipore-Q water purification system. Methyltrioxorhenium(VII), CH_3ReO_3 or MTO, was synthesized from sodium perrhenate and tetramethyltin (Strem).[16] Europium(III) solutions were made by dissolving europium(III) oxide (99.97%) in hydrochloric acid or triflic acid. Solutions of europium(II) were prepared from europium(III) solutions either by reduction with amalgamated zinc or by electrochemical reduction at a mercury cathode. Europium(II) solutions were stored in 25 mL Pyrex bottles under a positive pressure of argon. The concentrations of europium(II) were measured by spectrophotometry at 321 nm, where its molar absorptivity is 587 L mol^{-1} cm^{-1}. The acid concentration of electrochemically prepared Eu(II) solutions was titrated by sodium hydroxide after the solution had been passed through a column of Dowex 50W-X8 H^+ cation-exchange resin and rinsed with purified water.

Chromium(II) solutions were prepared by reduction of aqueous chromium(III) chloride with amalgamated zinc. Chromium(III) was determined spectrophotometrically at 408 nm, $\epsilon = 15.8$ L mol^{-1} cm^{-1}.[17] Most other chemicals were reagent grade and obtained commercially: hydrochloric acid, triflic acid, lithium chloride (used to maintain ionic strength), and sodium perchlorate. The acid concentration was analyzed by titration with sodium hydroxide to a phenolphthalein endpoint.

Instrumentation. UV−vis spectra and kinetic data were obtained with Shimadzu model 3101 and OLIS RSM stopped-flow spectrophotometers. Temperature was controlled at 25.0 ± 0.2 °C by circulating thermostated water in the stopped flow instrument and by an electronic (Peltier) cell holder in the spectrophotometer. Hydrogen was identified by gas chromatography. A Gow-Mac GC 350 chromatograph with a thermal conductivity detector was used with argon as the carrier gas and molecular sieve 13x as the stationary phase.

The rate of H_2 formation was determined volumetrically with a recording microvolumeter apparatus, modified from the one previously reported, as diagrammed in Figure 1.[18] The top part represents the glass apparatus in which mercury in the glass capillary tube is

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Figure 2. Visual changes in acidic solution, from left to right: 12 mmol L^{-1} Eu^{2+}; 12 mmol L^{-1} Eu^{2+} with 0.3 mmol L^{-1} $MeReO_3$ after 1 min; 30 min later, showing hydrogen evolution; 12 mmol L^{-1} Cr^{2+}; 12 mmol L^{-1} Cr^{2+} with 0.3 mmol L^{-1} $MeReO_3$ after 1 min; 1 h later. All solutions contain 120 mmol L^{-1} HCl.

pushed into the reservoir as the evolved hydrogen enters through the three-way stopcock at the right. A 30-gauge Nichrome-80 resistance wire passes concentrically through the length of the volumeter tube. A simple circuit is applied to the wire, which is shown in the bottom of the diagram. As the mercury moves through the glass tube, the length of unshorted wire changes in proportion to the change of the gas volume. Thus, the voltage changes linearly with the volume of the gas, which is recorded by a HP 3457A multimeter. A VICI Pressure-Lok gas syringe was used to calibrate the volume against voltage, Figure S-1. In order to get accurate volume readings, the dead volumes in the reaction vessel and the connecting tubing were made as small as possible. A certain “inertia” toward initiating the movement of the mercury was noted. Thus, the evolved H_2 did not appear immediately at the onset of the reaction. The same phenomenon was noted when gas was injected to calibrate the apparatus.

Chloride ion concentrations from the reduction of perchlorate were determined quantitatively by ion chromatography using potentiometry.[19] In the experiments, a Weiss Research CL3005 combination chloride ion selective electrode and a Hanna Instruments HI 1131 combination pH electrode were connected to a Hanna Instruments pH302 pH-meter. The electrodes were calibrated before use with standard NaCl solutions and standard buffers, respectively.

Results

Hydrogen Evolution from Acidic Europium(II) Solutions Containing $MeReO_3$. When 0.3 mmol L^{-1} $MeReO_3$ and 12 mmol L^{-1} Eu^{2+} solutions were mixed in anaerobic 120 mmol L^{-1} HCl, a yellow color was immediately seen. Following that, copious bubbles were generated, increasing over 30−60 min. However, when Cr^{2+} was used instead, we only observed a color change from pale blue to yellow-green, and no bubbles formed over 10 h. The phenomena are depicted in Figure 2.

Immediately upon mixing solutions of $MeReO_3$ and excess Eu^{2+}, two species are evident in the UV−vis spectrum, Eu^{2+} and one we call L410, named for the yellow intermediate with a maximum absorbance at 410 nm, with the spectrum shown in Figure 3. The peak at 321 nm of Eu^{2+} immediately begins to decrease in intensity while the L410 band remains stable until near the very end of the hydrogen evolution period, Figure 4.

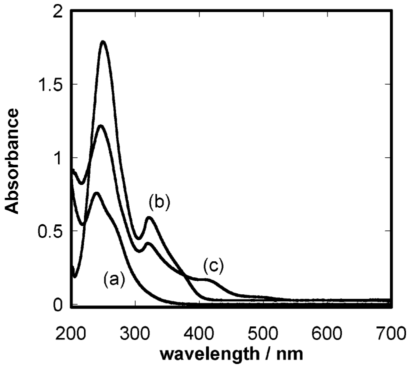

Figure 3. Spectral changes illustrating the formation of L410 from the reaction between $MeReO_3$ and Eu^{2+} in acid: (a) 0.4 mmol L^{-1} $MeReO_3$; (b) 1 mmol L^{-1} Eu^{2+}; (c) 0.2 mmol L^{-1} $MeReO_3$ with 1 mmol L^{-1} Eu^{2+} at 0.14 mol L^{-1} H^+.

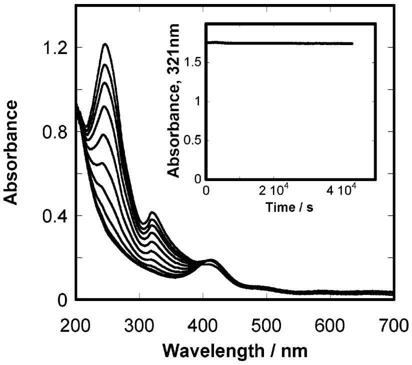

Figure 4. Absorbance decreases at 2 min time intervals during the reaction of 0.93 mmol L^{-1} Eu^{2+} with 0.2 mmol L^{-1} $MeReO_3$ at 0.14 mol L^{-1} H^+. Inset: A control experiment with 3.2 mmol L^{-1} Eu^{2+} in acidic solution for 12 h, showing the stable absorbance in the absence of $MeReO_3$.

Table 1. Quantitative Measurements of Hydrogen Evolution by a Microvolumeter Apparatus

$[Eu^{2+}]^a$	$[MTO]^a$	*E*/mV	V_{H_2}/mL^b	% H_2^c
6	0.2	1.196	1.434	97.5
6	0.2	1.131	1.330	90.3
6	0.2	1.121	1.314	89.3
6	0.2	1.183	1.413	96.0
5	0.2	0.958	1.053	85.8
4	0.2	0.852	0.883	90.0
4	0.2	0.848	0.877	89.5

[a] Units: mmol L^{-1}. [b] From a 20 mL reaction vessel. [c] Calculated on the basis of eq 3, with limiting Eu^{2+}, from the amount of H_2 measured.

As a control experiment, an acidic Eu^{2+} solution was sealed in a cuvette; no bubbles were observed for 12 h, and the absorbance of Eu^{2+} remained unchanged, as shown in the inset to Figure 4. But with $MeReO_3$ in the solution and 0.2 mol L^{-1} H^+, the reaction finished in ca. 20 min. The bubbles evolved were shown to be H_2 by GC. The buildup of H_2 gas was measured quantitatively by the microvolumeter apparatus. Quantitative measurements showed that the yield of H_2 is generally about 90%, Table 1. The yield was calculated under the assumption that eq 3 represents the correct stoichiometry. Note that Eu^{2+} is the limiting reagent, because excess HCl was used and MTO is a catalyst. The shortfall from 100% is taken to reflect the previously

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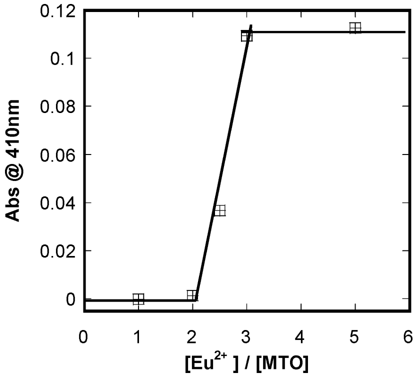

Figure 5. Spectrophotometric titration of $MeReO_3$ with Eu^{2+}. Conditions: 0.2 mmol L^{-1} $MeReO_3$, 0.60 mol L^{-1} H^+, 1-cm cell at 25 °C. The endpoint corresponds to a reactant ratio 3:1 $[Eu^{2+}]/[MeReO_3]$.

mentioned inertia in moving mercury at the start to obtain the first voltammetric response.

$$2Eu^{2+} + 2H^+ \xrightarrow{MeReO_3} 2Eu^{3+} + H_2 \qquad (3)$$

Formation of the Intermediate L410. Figures 5 and S-2 present the results of a spectrophotometric titration of $MeReO_3$ by Eu^{2+}. With <2 equiv Eu^{2+}, no L410 was formed. This shows that the first two reduction steps occur more rapidly than the next. The Re(VI) species never accumulates; $MeRe^{V}O_2$ is known not to absorb at 410 nm.[20] $MeReO_2$ is formed irreversibly because $E°$ for $MeReO_3 + 2e^- + 2H^+ = MeReO_2 + H_2O$ is −0.05 V. With one additional Eu^{2+}, the L410 peak appeared, and the titration arrived at the endpoint. Thus, the spectrophotometric titration yields a ratio $[Eu^{2+}]/[MeReO_3]$ of 3 to form L410, consistent with the stoichiometry of eq 4.

$$MeReO_3 + 3\,Eu^{2+} + 2H^+ = L410 + 3\,Eu^{3+} + H_2O \quad (4)$$

Because Eu^{2+} is a one-electron reducing agent, the overall 3:1 stoichiometry in the L410 formation strongly suggests that L410 is a Re(IV) species. We formulate the sequence of reactions between $MeReO_3$ and Eu^{2+} as follows.

$$MeReO_3 + Eu^{2+} \rightarrow Re^{VI} + Eu^{3+} \quad (k_1) \qquad (5)$$

$$Re^{VI} + Eu^{2+} + 2H^+ \rightarrow MeReO_2 + Eu^{3+} + H_2O \quad (\mathit{fast}) \quad (6)$$

$$MeReO_2 + Eu^{2+} \rightarrow L410 + Eu^{3+} \quad (k_3) \qquad (7)$$

In these reactions, $MeReO_3$ undergoes sequential one-electron changes in which the oxidation state of rhenium changes from VII to IV. We assume the first two steps, eqs 5−6, are very fast because of the large driving force between Eu^{2+} and $MeReO_3$. Stopped-flow experiments were carried out to follow the progress of reaction 5. The concentrations needed to be $MeReO_3 \gg Eu^{2+}$ to avoid reduction beyond $MeReO_2$. This was technically difficult because Eu^{2+} is so easily oxidized by O_2, the last traces of which are difficult to exclude from the instrument. Nonetheless, two determinations with 0.4 mmol L^{-1} Eu^{2+} and excess $MeReO_3$ were successful. The reaction reached completion in 0.1 s with a second-order constant k_1 of 2.7 × 10^4 L mol^{-1} s^{-1}; see Figures S-3 and S-4.

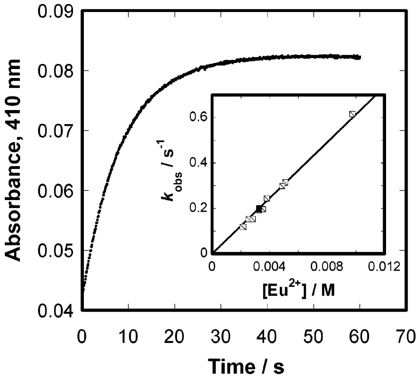

Figure 6. A typical kinetic trace for L410 formation monitored at 410 nm, with 0.2 mmol L^{-1} $MeReO_3$, 2.12 mmol L^{-1} Eu^{2+} in 0.6 mol L^{-1} H^+ at 25 °C. The plot is fitted to first-order kinetics, giving $k_{obs} = 0.118\ s^{-1}$. Inset: linear variation of k_{obs} with $[Eu^{2+}]$.

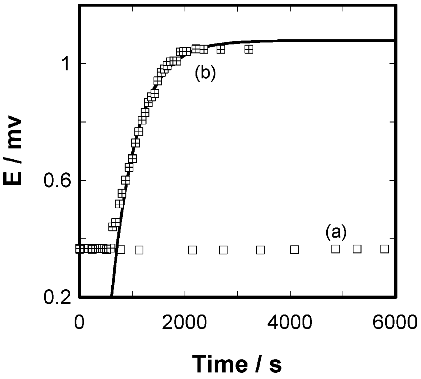

Figure 7. Experiments showing hydrogen evolution from Eu^{2+} acidic solution catalyzed by $MeReO_3$. Conditions: 12.8 mmol L^{-1} Eu^{2+}, 0.22 mol L^{-1} H^+, and $\mu = 0.29$ mol L^{-1}. (a) The control experiment without $MeReO_3$. (b) Experiment with 0.193 mmol L^{-1} $MeReO_3$. The time lag in hydrogen evolution is the "inertia" in moving the Hg plug at the beginning.

The rate-controlling step for L410 formation is given in eq 7. This reaction was followed by monitoring the increase in the absorbance of this species at 410 nm, shown in Figure 6. The reaction obeyed first-order kinetics in the presence of excess Eu^{2+}; see Figures S-5 and S-6. The second-order rate constant k_3 is 61.3 ± 0.2 L mol^{-1} s^{-1} at 25 °C. In addition, variation of acid concentration did not alter k_3. The kinetic data are listed in Table S-1.

Determination of the Rate Law for Hydrogen Evolution. The hydrogen gas was collected by the microvolumeter apparatus, and a full time course kinetic method was used to study the dependence of the rate on the concentrations of the species in the rate law. All the experiments were studied with excess acid and a limiting concentration of Eu^{2+}. Figure 7 gives a typical kinetic trace of gas buildup with $MeReO_3$ as catalyst. When 0.193 mmol L^{-1} $MeReO_3$ reacted with 12.8 mmol L^{-1} Eu^{2+} in 0.22 mol L^{-1} anaerobic HCl, the reaction followed first-order kinetics. The kinetic data are summarized in Tables S-2 and S-3. The reaction is first-order with respect to both [Re] and $[Eu^{2+}]$.

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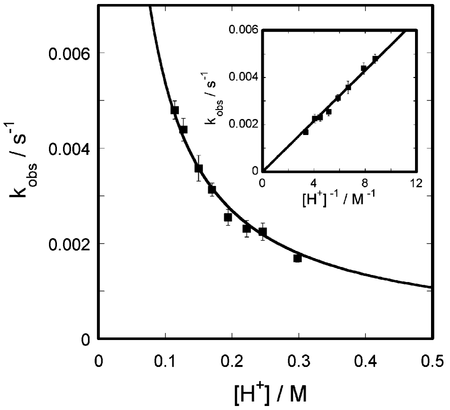

Figure 8. The variation of k_{obs} with [H$^+$] for hydrogen evolution from acidic Eu^{2+} solution by MeReO$_3$ as catalyst. Conditions: 0.21 mmol L^{-1} MeReO$_3$, 6−9 mmol L^{-1} Eu^{2+} at $\mu = 0.33$ mol L^{-1} and 25 °C. The curve through the points is the least-squares fit to $k_{obs} = a \times [H^+]^{-1}$. Inset: plot of k_{obs} vs [H$^+$]$^{-1}$.

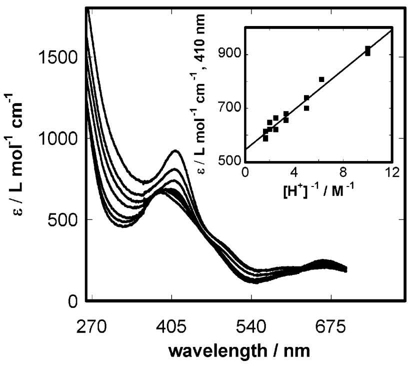

Figure 9. The change in the absorption spectrum of L410 with acid concentration. Reading downward at 410 nm, [H$^+$] is 0.10, 0.16, 0.20, 0.30, 0.40, 0.50, and 0.60 mol L^{-1}. Inset: plot of $\bar{\epsilon}_{410}$ versus [H$^+$]$^{-1}$.

In addition, at a constant ionic strength of 0.33 mol L^{-1}, the reaction was retarded by raising the concentration of acid, Table S-3. Figure 8 shows that k_{obs} is inversely dependent on [H$^+$]. From these kinetic results, the rate law can be expressed by eq 8, with $k_8 = 2.56$ s^{-1} at $\mu = 0.33$ mol L^{-1}.

$$v = k_8 \frac{[\mathrm{Re}][\mathrm{Eu}^{2+}]}{[\mathrm{H}^+]} \tag{8}$$

Investigation of the Acid Dissociation Constant for L410. As described above, the rate of hydrogen formation is inhibited by acid concentration. In addition, the UV−vis spectrum of L410 changes with different acid concentrations. This indicates that there is a protonation step before the rate-controlling hydrogen evolution step, and implicates two Re(IV) species that absorb at 410 nm, partners in an acid−base equilibrium. The acid form is a neutral Re(IV) species, L410H, and its conjugate base is a Re(IV) anion, L410A$^-$. The equilibrium can be expressed by L410H = H$^+$ + L410A$^-$ (K_a).

To determine K_a, we studied the acid effect on the spectrum of L410. Figure 9 shows the UV−vis spectrum of L410 at different pH values. The absorbance at 410 nm decreases with increasing acid concentration. If ϵ_{AH} and ϵ_A designate the respective molar absorptivities of L410H and L410A$^-$ at 410 nm, the average molar absorptivity $\bar{\epsilon}$ at any pH should obey eq 9:

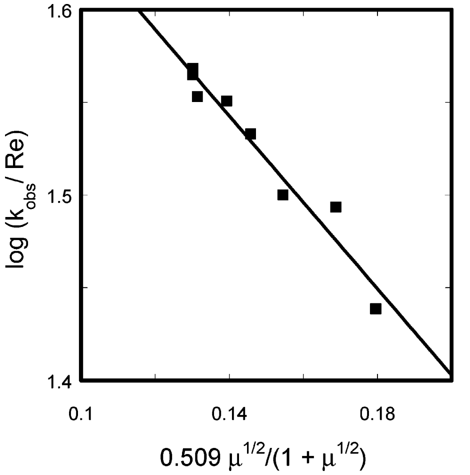

Figure 10. The effect of variable ionic strength on the rate constants for the hydrogen evolution, as plotted according to the Bronsted−Debye−Hückel equation.

$$\bar{\epsilon} = \frac{\epsilon_{AH}[\mathrm{H}^+] + K_a \cdot \epsilon_A}{K_a + [\mathrm{H}^+]} \tag{9}$$

Only when $K_a \ll [\mathrm{H}^+]$ is $\bar{\epsilon}$ linearly dependent on [H$^+$]$^{-1}$, in agreement with the experimental results shown in the inset to Figure 9. Thus, K_a is much smaller than 0.1, and ϵ_{AH} is about 550 L mol^{-1} cm^{-1}. Since K_a falls well below the range of acid concentrations examined, rhenium(IV) exists almost completely in its protonated form L410H throughout this range of [H$^+$]. It is clear therefore that in eq 8 $k_8 = k_4K_a$, where k_4 represents the second-order rate constant for the reaction between L410A$^-$ and Eu^{2+}.

Variation of Ionic Strength for Hydrogen Formation. Kinetic salt effects on hydrogen evolution were examined in the ionic strength range 0.118−0.297 mol L^{-1} by adjusting the LiCl concentration. In these experiments, the acid concentration was kept constant at 0.10 mol L^{-1} with variable concentrations of 2.16−3.54 × 10^{-4} mol L^{-1} MeReO$_3$ and 5.00−5.66 × 10^{-3} mol L^{-1} Eu^{2+}. The results are summarized in Table S-4. On the basis of the rate dependence studies, the pseudo-first-order rate constant is independent of Eu^{2+} and first-order with respect to MeReO$_3$. Because MeReO$_3$ is a catalyst, its concentration remains constant; therefore, the second-order constant $k_{obs}/[\mathrm{Re}]_T$ is the form that normalizes the data to unit catalyst concentration. The plot of log($k_{obs}/[\mathrm{Re}]_T$) against $0.509\mu^{1/2}/(1 + \mu^{1/2})$, which is the form suggested by the Bronsted−Debye−Hückel equation, is presented in Figure 10, which shows the retarding effect of higher ionic strength; its slope is −2.3 ± 0.2.

The Failure of Cr^{2+} To Generate H$_2$. Cr^{2+} does not evolve H$_2$ with MTO as the attempted catalyst. Experiments were carried out with Cr^{2+} and Eu^{2+} used together. The order of addition of the two was varied. In both cases, hydrogen evolution occurs much more slowly, and thus imprecisely, especially when Cr^{2+} is the first metal ion added. The data are shown in Figure 11.

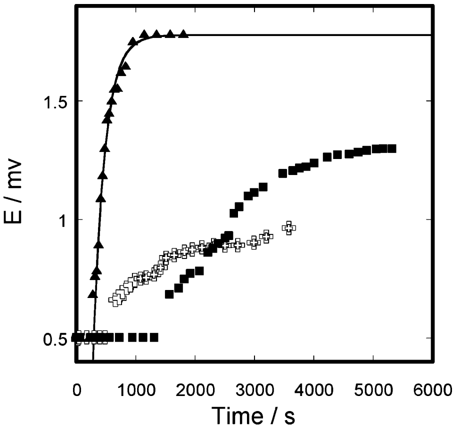

Figure 11. Plots of hydrogen evolution with both Cr^{2+}_{aq} and Eu^{2+}. Conditions: $[H^+] = 0.11$M, $\mu = 0.3$ M, 25 °C. Case 1 (○): 3.3 mM Eu^{2+} mixed with 0.19 mM MTO, and then 3 mM Cr^{2+}. Case 2 (■): 3 mM Cr^{2+} mixed with 0.19 mM MTO, and then 3.3 mM Eu^{2+}. Case 3 (▲): a comparison experiment, 3.3 mM Eu^{2+} mixed with 0.19 mM MTO, and then another 3.3 mM Eu^{2+}. Data from case 3 are fit to first-order kinetics, ignoring the time lag.

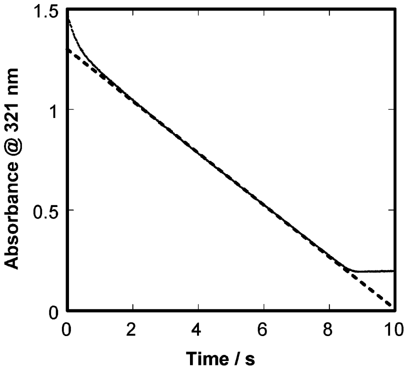

Figure 12. A typical kinetic trace for perchlorate reduction. Conditions: 1.55 mmol L^{-1} Eu^{2+}, 30 mmol L^{-1} ClO_4^-, and 0.10 mmol L^{-1} $MeReO_3$, added last at 0.55 mol L^{-1} H^+ and $\mu = 0.8$ mol L^{-1} at 25 °C.

Stoichiometry of Perchlorate Reduction. Measurement of chloride ion concentration in acidic solutions showed that Cl^-_{aq} was formed quantitatively by the reaction of Eu^{2+}, $MeReO_3$, and sodium perchlorate in HOTf (trifluoromethanesulfonic acid). The same results were found for reactions of $MeReO_3$ and Cr^{2+} in perchloric acid solution. These stoichiometric determinations (Table S5) established that the overall stoichiometry to be 8.1(±0.6):1 Eu^{2+} (or Cr^{2+}) per Cl^- as expected from eq 10.

$$8Eu^{2+}/Cr^{2+} + ClO_4^- + 8H^+ \xrightarrow{MeReO_3} 8Eu^{3+}/Cr^{3+} + Cl^- + 4H_2O \quad (10)$$

Kinetics of Perchlorate Reduction. A repetitive scan stopped-flow experiment was performed with 1.55 mmol L^{-1} Eu^{2+}, 0.1 mmol L^{-1} $MeReO_3$, 30 mmol L^{-1} ClO_4^-, and 550 mmol L^{-1} HCl at 25 °C with $\mu = 0.8$ mol L^{-1}; see Figures 12, S-7, and S-8. Some initial curvature is apparent, which by the deliberate introduction of some O_2 was traced to residual oxygen in the instrument system. The graph of Eu^{2+} versus time with deliberate O_2 is presented in Figure S12.

After the initial curvature in Figure 12, the absorbance readings lay on a straight line until all the Eu^{2+} was consumed. The data were fitted to a linear equation and the pseudo-zero-order rate constant k_{obs} is 1.10×10^{-4} mol L^{-1} s^{-1}. The same method was applied to the kinetic studies with varying concentrations of the three reactants. The data are summarized in Table S-6. The reaction rates are independent of $[Eu^{2+}]$ and directly proportional to $[Re]_T$ and $[ClO_4^-]$, as shown in Figures S-9 and S-10. This implies the rate law given in eq 11, with $k_{11} = 43.2 \pm 0.7$ L mol^{-1} s^{-1} at 25 °C.

$$-\frac{d[Eu^{2+}]}{dt} = k_{11}[Re]_T[ClO_4^-] \quad (11)$$

The kinetics is drastically altered by the order of mixing of M^{2+} (M = Eu or Cr), $MeReO_3$, and ClO_4^-. When $MeReO_3$ was the last reagent added, perchlorate reduction is complete within 10 s. On the other hand, When perchlorate ions are the last species added, the reaction is much slower, and takes 100 s or longer, as depicted in Figure S-11.

Discussion

Mechanism of Hydrogen Evolution. In two separately measured kinetic steps, $MeReO_3$ was reduced by Eu^{2+} to the Re(IV) species L410

$$MeReO_3 \xrightarrow[k_1]{2Eu^{2+}} MeReO_2 \xrightarrow[k_3]{Eu^{2+}} L410 \quad (12)$$

with $k_1 = 2.7 \times 10^4$ L mol^{-1} s^{-1} and $k_3 = 61.3$ L mol^{-1} s^{-1} in aqueous solution at 25 °C. Evolution of hydrogen occurs at a rate $k_8[L410H][Eu^{2+}][H^+]^{-1}$, $k_8 = k_4K_a = 2.56$ s^{-1} at $\mu = 0.33$ mol L^{-1}, implicating the reactant as the anionic species of Re(IV), $L410A^-$, the minority Re(IV) species.

The effect of ionic strength on k_4 was used to determine the charge on the predominant Re(IV) species, L410H. According to the equation $\log k = \log k° + 2Az_Az_B \times [\mu^{1/2}/(1 + \mu^{1/2})]$, the salt effect on the reaction between Eu^{2+} and $L410A^-$ will agree only if, as postulated, the active form of rhenium is the minority conjugate base with an ionic charge of −1. An approach that may be preferable (because it employs the same concept as a net chemical equation) is that of the *net activation process*, defined[21] as the reaction in which the transition state is formed from the *predominant* species. In the case at hand, it is

$$L410H + Eu^{2+} = [\ ^{+}]^{\ddagger} + H^+ \quad (13)$$

for which $\Delta(z^2)^{\ddagger} = 1^2 + 1^2 - 2^2 = -2$, under the presumption that L410H is uncharged. The Bronsted−Debye−Hückel equation states the following: $\log k = \log k° + \Delta(z^2)^{\ddagger} \times A[\mu^{1/2}/(1 + \mu^{1/2})]$, where $A = 0.509$. Because this value of $\Delta(z^2)^{\ddagger}$ matches the slope of Figure 10, −2.3, the data confirm that L410H is uncharged.

With these features in mind, along with our presumption that H_2 formation will arise from the reaction between H^+ and a $H{-}Re^{V}O$ species, we can suggest a chemical mechanism. The version shown in Scheme 1 agrees with all the experimental data. Coordinated solvent molecules are not shown for sake of simplicity. Three fast reactions are intro-

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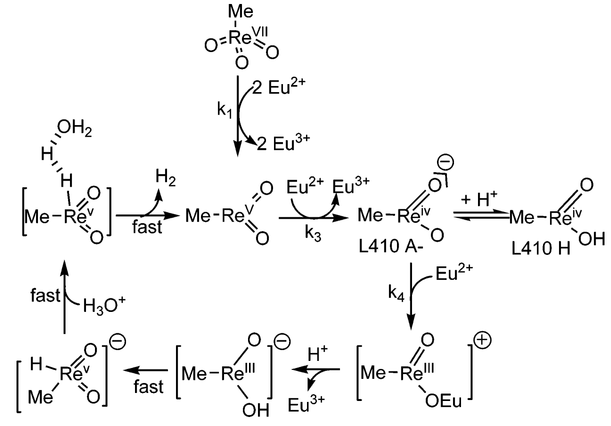
(21) Daugherty, N. A.; Newton, T. W. *J. Phys. Chem.* **1964**, *68*, 612.

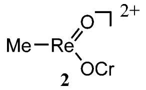
Scheme 1. Mechanism Proposed for Hydrogen Evolution



duced in the last part of the scheme. The most interesting of them is the unimolecular conversion of $Re^{III}OH$ into $H-Re^{V}O$, which is unfortunately not amenable to direct study.

Failure of Cr^{2+} To Evolve Hydrogen. Mixing 0.3 mmol L^{-1} $MeReO_3$ and 12 mmol L^{-1} Cr^{2+} generates an immediate intense yellow-green color; see Figure 2. This species also has an absorption maximum at 410 nm, and we designate it as L410(Cr). A spectrophotometric titration showed that L410Cr formation required a 3:1 consumption ratio of Cr^{2+} to $MeReO_3$, just as for Eu^{2+}. Clearly, L410(Cr) is also a rhenium(IV) species. The species L410(Cr) has a different molar absorptivity from L410H from Eu^{2+} reduction. At 0.1 mol L^{-1} acid concentration, the respective molar absorptivities at 410 nm of L410H and L410(Cr) are 910 and 1200 L mol^{-1} cm^{-1}.

Hydrogen was, however, not evolved over 10 h, during which time L410(Cr) persists unchanged. Because the reactions in Scheme 1 beyond L410 formation are based on rhenium, the cause for the lack of H_2 formation must lie elsewhere. Consider the structural formula of **2**, which we suggest may be the structure of L410(Cr) as it is immediately formed. This assumes that the k_4 step proceeds by an inner-sphere mechanism.



2

Species L410(Cr), as **2**, represents a derivative of Re(IV) and Cr(III) after electron transfer. Both metals in these oxidation states will have d^3 electronic configurations, and as such will be slow to hydrolyze at either the $Re^{IV}-O$ or $Cr^{III}-O$ bonds. One need only postulate that the next needed reaction, between L410(Cr) and Cr^{2+}, is slow (perhaps owing to electrostatic repulsion) to understand why the reaction proceeds no further.

Perchlorate Reduction. Perchlorate has a powerful thermodynamic tendency for reduction in dilute aqueous solution: $E°(ClO_4^-/ClO_3^-) = 1.19$ V. Although this reduction is thermodynamically favorable, it is often very slow. To our knowledge, the only exception to sluggish reduction of perchlorate is the fast reaction provided by a system containing MTO and H_3PO_2.[20] These components react ($k_{298} = 0.028$ L mol^{-1} s^{-1})[20] to form $MeReO_2(H_2O)_n$ ($n = 2$, presumably, because $MeReO_2(PAr_3)_2$ has been isolated and characterized[10]) (MDO), following which it reduces ClO_4^- rapidly, $k_{298} = 7.3$ L mol^{-1} s^{-1} at 25 °C, which is by far the highest rate constant (see Table S-7) recorded for perchlorate reduction.[20]

We recall the case of the reaction between H_3PO_2 and $MeReO_3$, which generates H_3PO_3 and $MeReO_2$ ($k = 0.028$ L mol^{-1} s^{-1}).[20] The subsequent reaction between $MeReO_2$ and ClO_4^- results in reduction of perchlorate to chloride ions in four steps. The first of these is rate-controlling, with $k_{14} = 7.3$ L mol^{-1} s^{-1} at 25 °C:

$$MeReO_2 + ClO_4^- \rightarrow MeReO_3 + ClO_3^- \qquad (14)$$

The difference in the present case is that Eu^{2+} or Cr^{2+} ions serve as the initial reducing agent in reactions that are much faster then eq 14. We find $k_{14} = k_{11}/4 = 5.3 \pm 0.1$ L mol^{-1} s^{-1} at 25 °C, which agrees with the previous value. It had been shown in the earlier work[22] that further reduction of ClO_3^- occurs more rapidly, $k_{15} = 3.8 \times 10^4$ L mol^{-1} s^{-1}:

$$MeReO_2 + ClO_3^- \rightarrow MeReO_3 + ClO_2^- \qquad (15)$$

Perchlorate reduction occurs much more slowly when Eu^{2+} and $MeReO_3$ are mixed prior to the addition of ClO_4^-, Figure S-11. This is because the needed $MeReO_2$ has been converted to L410, which is not active toward perchlorate reduction.

Acknowledgment. This research was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract W-7405-Eng-82 with Iowa State University of Science and Technology. We are grateful to Masoud Nabavizadeh and Patrick Huston for exploring the initial interactions between M^{2+} and $MeReO_3$, to Professor Henry Taube for helpful discussion and comments, and to Professor Edwin S. Gould for calling our attention to the citation in ref 9.

Supporting Information Available: Tables and plots of kinetic data to illustrate agreement to selected mathematical forms and to evaluate numerical parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

IC048669K

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[22] Abu-Omar, M. M.; Appelman, E. H.; Espenson, J. H. *Inorg. Chem.* **1996**, *35*, 7751−7757.