Ligand-Assisted Reduction of Osmium Tetroxide with Molecular Hydrogen via a [3+2] Mechanism
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Abstract: Osmium tetroxide is reduced by molecular hydrogen in the presence of ligands in both polar and nonpolar solvents. In CHCl₃ containing pyridine (py) or 1,10-phenanthroline (phen), OsO₄ is reduced by H₂ to the known Os(VI) dimers L₂Os(O)(O)₂Os(O)₂L₂ (L₂ = py₂, phen). However, in the absence of ligands in CHCl₃ and other nonpolar solvents, OsO₄ is unreactive toward H₂ over a week at ambient temperatures. In basic aqueous media, H₂ reduces OsO₄(OH)₆os₂⁻ (n = 0, 1, 2) to the isolable Os(VI) complex, OsO₄(OH)₄²⁻, at rates close to that found in py/CHCl₃. Depending on the pH, the aqueous reactions are exergonic by ΔG = −20 to −27 kcal mol⁻¹, based on electrochemical data. The second-order rate constants for the aqueous reactions are larger as the number of coordinated hydroxide ligands increases, k₁O₄ = 1.6(2) x 10⁻² M⁻¹ s⁻¹ < k₂O₄(OH) = 3.8(4) x 10⁻² M⁻¹ s⁻¹ < k₂O₄(OH)₂ = 3.8(4) x 10⁻¹ M⁻¹ s⁻¹. The observation of primary deuterium kinetic isotope effects, k₁H₂/k₁D₂ = 3.1(3) for OsO₄ and 3.6(4) for OsO₄(OH)⁻, indicates that the rate-determining step in each case involves H—H bond cleavage. Density functional calculations and thermochemical arguments favor a concerted [3+2] addition of H₂ across two oxo groups of OsO₄(L)₂, and argue against H* or H⁻ abstraction from H₂ or [2+2] addition of H₂ across one Os=O bond. The [3+2] mechanism is analogous to that of alkene addition to OsO₄(L)₂ to form diolates, for which acceleration by added ligands has been extensively documented. The observation that ligands also accelerate H₂ addition to OsO₄(L)₂ highlights the analogy between these two reactions.

Introduction
The activation of molecular hydrogen (dihydrogen) by transition metal compounds is a fundamental reaction in both homogeneous and heterogeneous chemistry. The most common and most studied examples involve oxidative addition of H₂ to low-valent metal centers or H₂ addition to a metal surface (Scheme 1a). H₂ is also widely used as a reductant for high-valent metal oxides, for instance, in the activation of precalcatalysts. One of the few heteroatomic H₂ (syn gas) to methanol. H₂ is thought to add across a Zn—O bond in a [2+2] mechanism to give a ZnH—OH fragment. This [2+2] mechanism (Scheme 1b) has been termed σ-bond metathesis when the original M—X bond is cleaved. Homogeneous examples of [2+2] reactions of H₂ include additions to the multiple bonds in Cp*₂Ti(=O)py.

Scheme 1. Pathways for Concerted Addition of H₂ to a Metal Complex
(a) L₃M + H₂ → L₃M—H oxidation addition
(b) L₃M—Z + H₂ → [L₃M—H]++ → L₃M—H [2+2] addition
(c) L₃M—Z + H₂ → [L₃M—H]++ → L₃M—H [3+2] addition

Cp*₂Ti═S, Cp*₂Ti═NR, and (tBu₅SiNH)₂(THF)Zr═NSi₅Bu₃, and to ruthenium amides (Ru═NHR) to give RuH₂NR₂. Both the oxidative addition and the [2+2] pathways can involve metal—dihydrogen complexes.


There are only a small number of studies of homogeneous hydrogenations of metal oxo compounds. The H₂ reduction of permanganate solutions to solid manganese dioxide has received the most attention, starting as far back as 1911. A mechanistic study in aqueous solutions by Webster and Halpern in 1957 concluded that Mn(V) was a likely intermediate.

A recent stimulating experimental and computational paper by Collman, Strasser, et al. described hydrogenations of MnO₄⁻ to solid MnO₂ in both H₂O and C₆H₅Cl solvents, and the related reduction of RuO₂ to RuO₂ in CCl₄. They concluded that Mn-(V) is formed by addition of H₂ to two oxo groups via a [3+2] transition state (Scheme 1c). Net H₂ addition to the two imido ligands of Cp*₂U(NHPh)₂ to give Cp*₂U(NHPh)₂ has also been described.

The [3+2] mechanism is an interesting contrast to the oxidative addition and [2+2] pathways in that hydrogen binds only to the ligands X, without M–H bond formation. The [3+2] path should in general be favored by oxidizing metal centers, because the addition of both hydrogens to the ligands results in a formal two-electron reduction of the metal. The [2+2] mechanism does not involve a metal redox change, and oxidative addition, as the name suggests, is a formal oxidation of M.

Collman et al. reported that 1 atm of H₂ does not reduce OsO₄, MeReO₃, or KReO₄ over several days at room temperature in either CCl₄ or H₂O. It is known from both experimental and computational studies, that OsO₄ oxidizes olefins by a [3+2] mechanism and that such oxidations are accelerated by ligation of tertiary amines to the osmium (to form OsO₄(L))₃. We suspected that a [3+2] reaction of OsO₄ with H₂ would similarly be facilitated by ligand binding. We were also led to this hypothesis through our studies of a reactive osmium(VIII) complex with a hydrotris(1-pyrazolyl)borate (Tp) ligand.

We report here that H₂ readily reduces OsO₄(L)₃, and we present kinetic, mechanistic, and computational studies of these reactions. OsO₄(L)₃ complexes are particularly attractive for mechanistic studies because they undergo two-electron reductions to well-characterized osmium(VI) products (reductions of MnO₄⁻ and RuO₂ yield insoluble metal dioxides, MoO₂). The stoichiometric simplicity of the aqueous OsO₄ + H₂ reactions allows the determination of the thermochromic driving force from electrochemical data. Reduction of OsO₄ by H₂ is accelerated by added ligands, in analogy to the [3+2] addition of OsO₄ to alkenes. DFT calculations predict the acceleration of the reaction by osmium ligation, and the calculations indicate that the [3+2] pathway is highly favored.

Results


Solutions of OsO₄ in CHCl₃, CCl₄, and n-hexane are unchanged after a week under 1 atm of H₂ at ambient temperatures, as indicated by a lack of change in the UV–vis spectra (Figure 1A shows 39 overlaid spectra). A control experiment, done under 1 atm of air, also showed no change. These experiments and most of those described below were performed in the apparatus shown in Figure 1B. Solutions were freeze–pump–thaw degassed in the flask prior to H₂ addition and were stirred throughout the reaction. Prior to acquiring each spectrum (ca. every 15 min for the kinetic studies described below), the whole apparatus was shaken to promote equilibration of dissolved and gaseous H₂. Initial experiments showed that this equilibration was slow on the time scale of the reaction for an unstirred solution in a cuvette directly attached to a Teflon stopcock.

In CHCl₃ in the presence of pyridine (24:1), OsO₄ reacts with 1 atm of H₂ over the course of 16 h. The solution, which is initially yellow due to rapid formation of the pyridine adduct OsO₄(py)₄, gradually turns colorless, and a bright golden-brown precipitate is formed. The precipitate was identified as the osmium(VI)-oxo-pyridine dimer Os₂O₆(py)₄ by comparison of its IR and ¹H NMR spectra with those described in the literature and with spectra of an authentic sample. A balanced equation for this reaction is shown in eq 1.

\[
\text{OsO}_4 + 4\text{py} + \text{H}_2 \rightarrow \frac{1}{2}\text{Os}_2\text{O}_6(\text{py})_4 + \text{H}_2\text{O}
\]
the Os$_2$O$_6$(phen)$_2$ product was again confirmed by comparison with an authentic sample.\textsuperscript{17b} In this system, the monomeric osmium(VI) bis(hydroxide) complex OsO$_2$(OH)$_2$(phen) and its dimerization to Os$_2$O$_6$(phen)$_2$ + water have been described.\textsuperscript{17b,18} Most likely, this bis(hydroxide) complex is an intermediate in the reaction (eq 2) but is not observed because its dimerization is faster than the reaction of OsO$_4$(phen) with H$_2$.\textsuperscript{17,18} Reaction 1 probably also involves a bis(hydroxide) intermediate.

![Figure 2](image-url)

**Figure 2.** Spectra of 0.43 mM OsO$_4$ in 0.170 M phosphate buffer as a function of pH from 8.4 to 13.0. Spectra are virtually unchanged from pH 4.3–8.4.

14 (pK$_{a2}$ = 14.4), and under these conditions it spontaneously reduces to osmate, trans-OsV$_4$(OH)$_2$$_2$\textsuperscript{2-}.\textsuperscript{20,24} Osmate is commercially available as the potassium salt and is the dominant osmium(VI) species in aqueous solutions above pH 5.\textsuperscript{20}

We have examined OsO$_4$ in aqueous phosphate buffer (typically 0.17 M). At neutral pH, the predominant species appears to be the unligated tetrahedral OsO$_4$ based on UV–visible spectra. The spectra are similar to those of gas-phase OsO$_4$ and of OsO$_4$ solutions in noncoordinating media such as CCl$_4$ (Figure 1A).\textsuperscript{25} The spectra display structured absorptions indicative of a high-symmetry species with a low density of vibrational states. Spectra of OsO$_4$ in buffered Millipore water (pH = 4.5–9.2) also show vibrational structure, although the individual lines are broader than those in the spectra taken in CCl$_4$.

Raising the pH causes a substantial change in the optical spectrum of OsO$_4$ as OsO$_4$(OH)$^-$ is formed (Figure 2). Analysis of the spectra (Figure S3) shows that one hydroxide binds to OsO$_4$ with K$_s$ = 13 × 10$^{-12}$ M ($\text{pK}_s$ = 11.9). This is close to the literature value of 6.3 × 10$^{-13}$ M measured in the absence of buffer.\textsuperscript{20,24} The extinction coefficients for OsO$_4$ ($\varepsilon_{250}$ = 3020 M$^{-1}$ cm$^{-1}$, $\varepsilon_{325}$ = 370 M$^{-1}$ cm$^{-1}$) and for OsO$_4$(OH)$^-$ ($\varepsilon_{250}$ = 1470 M$^{-1}$ cm$^{-1}$, $\varepsilon_{325}$ = 1950 M$^{-1}$ cm$^{-1}$) in buffered solutions are within the error of the literature values in unbuffered solutions ($\varepsilon_{250}$ = 3100 M$^{-1}$ cm$^{-1}$, $\varepsilon_{325}$ = 380 M$^{-1}$ cm$^{-1}$ and $\varepsilon_{250}$ = 1480 M$^{-1}$ cm$^{-1}$, $\varepsilon_{325}$ = 2000 M$^{-1}$ cm$^{-1}$).\textsuperscript{20,24} These data show that the phosphate buffer is not binding to OsO$_4$.

**B. Reactions of OsO$_4$ with H$_2$ in Water.** Solutions of OsO$_4$ in phosphate buffer at pH $\leq$ 13 show no change by UV–visible spectroscopy over days at ambient temperatures. Upon exposure to 1 atm of H$_2$, these light yellow solutions turn pink. The optical spectra indicate quantitative formation of OsO$_2$(OH)$_2$\textsuperscript{2-} (eq 4), by comparison with literature values\textsuperscript{20,24} and with the spectrum of a commercial sample of K$_2$OsO$_2$(OH)$_4$ at the same pH and buffer concentration.
The kinetics of reactions of OsO₄ with H₂ at various pH values were monitored by optical spectroscopy (Figure 3) using the cell and procedure described above. The volume of the apparatus and the stirring and frequent shaking ensure constant 
[H₂] over the course of the reaction. Reactions were typically run at ~0.40 mM OsO₄ in 0.17 M phosphate buffer, adjusted to the desired pH by addition of NaOH prior to addition of OsO₄.

Global analyses of spectra from 230 to 600 nm over 2–3 half-lives, using SPECFIT, indicate that the reactions follow first-order kinetics (A–B). Varying the OsO₄ concentration by a factor of 2 (from 0.21 to 0.43 mM) at pH 9.22 gave the same pseudo-first-order rate constants, kₚₒᵢᵦ, within experimental error. The kₚₒᵢᵦ values vary linearly with H₂ concentration from 0.36 to 0.82 mM (0.45–1.03 atm), at both pH 9.22 and pH 12.31 (Figure 4). Thus, the reactions are first order in both H₂ and [OsO₄(OH)ₓ𝑛]⁺. The H₂ concentrations were calculated from literature solubility data for the same pH and buffer ionic strength (different buffers have only a minimal effect, ~±5%, on the H₂ solubility). Varying the buffer concentration from 0 to 0.300 M gave only a 12% random variation in the observed rates, indicating that phosphate is not kinetically important.

Eyring analyses of rate constants from 8 to 68 s⁻¹ gave ΔH° = 13.2(2) kcal mol⁻¹ and ΔS° = −22.3(3) cal mol⁻¹ K⁻¹ at pH 9.22 and ΔH° = 12.9(2) kcal mol⁻¹ and ΔS° = −21.9(3) cal mol⁻¹ K⁻¹ at pH 12.31.

The kinetics of OsO₄ reduction have been examined at pH values from 4.3 to 14.6 (Table 1). At pH's other than 9.22 and 12.31, and for the reactions with D₂ gas, measurements were made only at 1 atm of H₂ or D₂, and k₁ was taken to be kₚₒᵢᵦ.

Table 1. Rate Constants for OsO₄(OH)ₓ⁺ Reduction by H₂ or D₂

<table>
<thead>
<tr>
<th>pH</th>
<th>k₁ (M⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.27</td>
<td>2.3(2) × 10⁻³</td>
</tr>
<tr>
<td>4.32</td>
<td>2.4(2) × 10⁻³</td>
</tr>
<tr>
<td>7.00</td>
<td>6.6(8) × 10⁻³</td>
</tr>
<tr>
<td>8.50</td>
<td>1.5(3) × 10⁻²</td>
</tr>
<tr>
<td>9.22</td>
<td>1.6(2) × 10⁻²</td>
</tr>
<tr>
<td>9.22</td>
<td>5.2(7) × 10⁻³ (D₂)</td>
</tr>
<tr>
<td>9.34</td>
<td>1.8(2) × 10⁻²</td>
</tr>
<tr>
<td>10.64</td>
<td>1.7(2) × 10⁻²</td>
</tr>
<tr>
<td>10.75</td>
<td>1.8(3) × 10⁻²</td>
</tr>
<tr>
<td>11.36</td>
<td>2.0(2) × 10⁻²</td>
</tr>
<tr>
<td>11.80</td>
<td>2.3(2) × 10⁻²</td>
</tr>
<tr>
<td>12.10</td>
<td>2.7(3) × 10⁻²</td>
</tr>
<tr>
<td>12.21</td>
<td>3.3(4) × 10⁻²</td>
</tr>
<tr>
<td>12.31</td>
<td>3.5(4) × 10⁻²</td>
</tr>
<tr>
<td>12.31</td>
<td>9.0(8) × 10⁻³ (D₂)</td>
</tr>
<tr>
<td>12.35</td>
<td>3.5(5) × 10⁻²</td>
</tr>
<tr>
<td>12.50</td>
<td>3.8(4) × 10⁻²</td>
</tr>
<tr>
<td>14.60</td>
<td>3.8(4) × 10⁻¹ b</td>
</tr>
</tbody>
</table>

* Total [Os] typically ~0.4 mM (varied at pH 12.31 from 0.21 to 0.68 mM); [H₂] or [D₂] typically ~0.80 mM (at pH 9.22 and 12.31 varied from ~0.34 to ~0.83 mM); phosphate buffer concentration 0–0.3 M (most often 0.17 M). For a complete list of rate constants and conditions, see Table S1.

* 4 M NaOH; k₂ corrected for the decomposition of cis-Os(O₄(OH))²⁺.

Figure 3. Spectra of the reaction of OsO₄ (0.38 mM) in 0.17 M phosphate buffer under 1.03 atm H₂ taken over 34 h.

![Figure 3](image1)

Figure 4. Plot of the pseudo-first-order rate constant, kₚₒᵢᵦ, versus [H₂] at 298 K for reaction of ~0.40 mM [OsO₄] plus excess H₂(g) in 0.17 M phosphate buffer at pH 9.22 (●) and 12.31 (△).

![Figure 4](image2)

Figure 5. (A) Plot of second-order rate constants, k₂, versus pH. Below pH 10, the osmium is predominantly OsO₄. The line represents the best fit to eq 6. The second-order rate constant of 0.38 M⁻¹ s⁻¹ at pH 14.60 is reduced 10 times to fit on the plot. (B) Speciation curve of OsO₄(OH)ₓ⁺⁺⁺. The reactions with D₂ indicate kinetic isotope effects, k₁/D₁, of 3.1(3) at pH 9.22 and 3.7(4) at pH 12.31. In 4 M NaOH (nominally pH 14.6), OsO₄(OH)₂⁻ decomposes to OsO₃(OH)²⁻ with kₚₒᵢᵦ = 1.1(1) × 10⁻⁴ s⁻¹. Upon addition of H₂ (1 atm, 0.8 mM), kₚₒᵢᵦ increases to 4.1(4) × 10⁻⁴ s⁻¹. Assuming that the increase is due to a bimolecular reaction of H₂ with OsVIII, k₂ at this pH is 3.8(4) × 10⁻¹ M⁻¹ s⁻¹.

The bimolecular rate constants increase with rising pH (Figure 5A). For comparison, the speciation of OsO₄ with pH is plotted on the same pH scale in Figure 5B. Between pH 8 and 13, the...
dominant species in solution are OsO$_4$ and OsO$_4$(OH)$^-$, indicating the rate law in eq 6. Using the $K_i$ derived above for OsO$_4$ + 2 H$_2$O ⇌ OsO$_4$(OH)$^-$ + H$_3$O$^+$ yields eq 7. Equation 7 provides a good fit to the rate constants from pH 8.5 to 12.5, as indicated by the line in Figure 5A.

\[
\frac{d[\text{OsO}_4^{\text{VIII}}]}{dt} = k_2[\text{OsO}_4^{\text{VIII}}][H_2] = k_{\text{OsO}_4}[\text{OsO}_4^{\text{VIII}}][H_2] + k_{\text{OsO}_4\text{OH}}[\text{OsO}_4(\text{OH})^-][H_2] \tag{6}
\]

\[
\frac{d[\text{OsO}_4^{\text{VIII}}]}{dt} = [\text{OsO}_4^{\text{VIII}}][H_2]\left\{\frac{k_{\text{OsO}_4}}{1 + K_H[H^+]} + \frac{k_{\text{OsO}_4\text{OH}}}{1 + [H^+]/K_H}\right\} \tag{7}
\]

It should be noted that the rate constants decrease by a factor of 6.5 on decreasing the pH from pH 8.5 and 4.3 (Table 1; not shown in Figure 5). The origin of this rate retardation at lower pH is not known, but may be due to the formation of solid OsO$_2$ shown in Figure 5). The origin of this rate retardation at lower pH is not known, but may be due to the formation of solid OsO$_2$ shown in Figure 5B, at pH 9.22 aqueous Os$_{\text{VIII}}$ is >99% OsO$_4$, so the rate constants, isotope effect, and activation parameters measured at that pH correspond to reactions of OsO$_4$. At pH 12.31, solutions are 28% OsO$_4$ and 72% OsO$_4$(OH)$^-$. After correcting for this speciation, the reaction of OsO$_4$(OH)$^-$ with H$_2$ has $k_{\text{OsO}_4\text{OH}} = 3.8(4) \times 10^{-2}$ M$^{-1}$ s$^{-1}$, an isotope effect $k_{H_2}/k_{D_2} = 3.6(4)$, and activation parameters $\Delta H^\ddagger = 12.8(2)$ kcal mol$^{-1}$ and $\Delta S^\ddagger = -21.8(2)$ cal mol$^{-1}$ K$^{-1}$.

The reaction of H$_2$ with OsO$_4$(OH)$^-$ is roughly 2.4 times as fast as that with OsO$_4$; the activation parameters are the same within experimental error. OsO$_4$(OH)$^-$ reacts with H$_2$ an order of magnitude faster than OsO$_4$(OH)$^-$. The reactions of OsO$_4$, OsO$_4$(OH)$^-$, and OsO$_4$(NH$_3$)$_2$ with H$_2$ have been studied at the B3LYP level of density functional theory (DFT). The details of the methodology used are described at the end of the experimental section. Computed gas-phase reaction energies, enthalpies, and free energies are shown in Table 2.

### Table 2. Calculated Energies (kcal mol$^{-1}$) and Entropies (cal K$^{-1}$ mol$^{-1}$) Relative to OsO$_4$(L) + H$_2^a$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta^\ddagger$</th>
<th>$\Delta H$</th>
<th>$\Delta S$</th>
<th>$\Delta G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OsO$_4$ + H$_2$</td>
<td>58.6</td>
<td>58.7</td>
<td>-23.9</td>
<td>65.9</td>
</tr>
<tr>
<td>HOsO$_4$(OH)</td>
<td>17.0</td>
<td>20.9</td>
<td>-21.8</td>
<td>27.5</td>
</tr>
<tr>
<td>OsO$_4$(OH)$_2$</td>
<td>-41.2</td>
<td>-35.0</td>
<td>-22.2</td>
<td>-28.3</td>
</tr>
<tr>
<td>OsO$_4$(OH)$^-$ + H$_2$</td>
<td>44.5</td>
<td>44.6</td>
<td>-31.7</td>
<td>54.1</td>
</tr>
<tr>
<td>OsOsO$_4$(OH)$_2$(NH$_3$)</td>
<td>10.3</td>
<td>10.6</td>
<td>-29.9</td>
<td>19.5</td>
</tr>
<tr>
<td>OsO$_4$(OH)$_2$</td>
<td>-57.2</td>
<td>-51.1</td>
<td>-26.2</td>
<td>-43.3</td>
</tr>
</tbody>
</table>

$^a$ At 298 K. $^b$ Electronic energies. $^c$ Energies of the most stable conformer (Figure 8); other conformations have different orientations of the H atoms in the two formed hydroxyl groups.$^{29}$

### Scheme 2. Addition of H$_2$ and OH$^-$ to OsO$_4$

All of the reactions are predicted to be exergonic, with gas-phase free energies from $-28.3$ kcal mol$^{-1}$ for OsO$_4$ + H$_2$ → OsO$_4$(OH)$_2$ to $-43.3$ kcal mol$^{-1}$ for OsO$_4$(OH)$^-$ + H$_2$ → OsO$_4$(OH)$_2$. These values are in the range of solution values determined from aqueous electrochemical measurements ($-25$ kcal mol$^{-1}$, see below). Closer agreement should not be expected, because the experimental values refer to the formation of aqueous OsO$_4$(OH)$_2$.27

Gas-phase transition states were located for the addition of H$_2$ to each of the three osmium species by both [2+2] and [3+2] pathways. As discussed below, addition of OH$^-$ and NH$_3$ to OsO$_4$ is predicted to accelerate the reaction with H$_2$ and make both the [2+2] and the [3+2] pathways more favorable, kinetically as well as thermodynamically. However, the [2+2] reaction is computed to be very endergonic for OsO$_4$, OsO$_4$(OH)$^-$, and OsO$_4$(NH$_3$)$_2$, so only the [3+2] reaction is predicted to occur.

### Discussion

Dihydrogen readily reduces OsO$_4$(L)$_n$ species at room temperature. In aqueous solutions, reductions of OsO$_4$ and OsO$_4$(OH)$^-$ both exhibit activation parameters of $\Delta H^\ddagger \approx 13$ kcal mol$^{-1}$ and $\Delta S^\ddagger \approx -22$ cal mol$^{-1}$ K$^{-1}$. Overall conversion of OsO$_4$ and H$_2$ to the product, OsO$_4$(OH)$_2$,$^{27}$, requires the binding of two hydroxide ions, either prior to or after the H$_2$ activation step (Scheme 2). We begin our discussion with the overall thermochemistry of H$_2$ addition, then proceed to mechanistic discussions, based on experimental and computational results.

#### I. Thermochemistry of H$_2$ Addition

The free energy of reaction for aqueous OsO$_4$ and H$_2$ as a function of pH can be derived from the aqueous redox potentials. These are summarized in the partial Pourbaix or E/pH diagram in Figure 6 and in the equations in Scheme 3 (adapted from ref 20c and corrected for the slightly different pK$_f$ values found here). In
Figure 6, the vertical dashed lines indicate the pK\text{a} values that separate the regions where Os\text{VIII}, Os\text{VII}(OH)^{-}, and Os\text{V}(OH)\text{2}^{2-} are the predominant species (Figure 5B), and the horizontal lines describe the redox potentials versus the normal hydrogen electrode (NHE) for the half reactions in eqs 8–10. The uncertainties in \( E \) are estimated to be \( \pm 40 \text{ mV (1 kcal mol}^{-1} \text{)}. \)

Combining these half-reactions with the pH-dependent H\text{2} potential (eq 11) gives \( \Delta G^\circ \) for reactions of H\text{2} with aqueous Os\text{O}\text{4} at any pH (eqs 12–14). In these equations, \( \Delta G^\circ \) is for all species at standard state except for H\text{2}.

The free energy of eq 14, which includes only osmium species and H\text{2} molecules, is 5.6\text{ kcal mol}^{-1}. The unobserved Os(VII) intermediate, [Os\text{O}4(OH)\text{2}^{2-}]\text{aq}, is unstable with respect to disproportionation to Os(VI) and Os(VIII), 31 so BDFE(1) should be greater than BDFE(2). This implies that BDFE(2) is less than 65 kcal mol\text{^{-1}. This value is also a reasonable upper bound for the bond dissociation enthalpy (BDE, the more common measure of bond strength).32 Preliminary calculations indicate that in gas-phase Os\text{O}2(OH)\text{2}(L) and Os\text{O}2(OH)L, the Os–O–H BDEs vary from 50 to 92 kcal mol\text{^{-1}} depending on the oxidation state of the osmium and its ligands.}

II. Reaction Mechanism. The bimolecular kinetics, the negative activation entropies, and the primary K\text{IEs}, \( \frac{k_{H}}{k_{D}} = 3.1(3) \) for Os\text{O}4 and 3.6(4) for Os\text{O}4(OH)^{-}, all indicate a rate-determining step involving cleavage of the H–H bond upon interaction with an Os\text{VIII} species. Similar \( \frac{k_{H}}{k_{D}} \) values were reported for H\text{2} addition to Mn\text{O}4\text{2}^{-}.11

Following Halpern10 and Collman, Strassner, et al.,11 four mechanisms have been considered for the H\text{2} activation, as illustrated for Os\text{O}4(OH)^{-} in Scheme 5. H\text{2} could transfer H\text{2} to the Os\text{VIII} oxidant, forming Os\text{VII} + H\text{2} or Os\text{V} + H\text{2}, respectively (the bottom two paths of Scheme 5). [2+2] addition could form an osmium(VIII) hydroxo-hydrido complex, Os\text{(O)(H)(OH)(L)}, which might then undergo a 1,2-hydride shift to form Os\text{O}2(OH)\text{2}(L), the direct product of [3+2] addition.

Initial H\text{2} transfer is unlikely because of the thermochromy of this step, following (in essence) an argument made by Halpern for permanganate reactions in 1957.10 The H–H bond of 104 kcal mol\text{^{-1}} is much stronger than the O–H bond formed by the Os\text{VIII} species (49–80 kcal mol\text{^{-1}}). H\text{2} atom transfer from H\text{2} is thus endothermic by >24 kcal mol\text{^{-1}}, a much larger value than the observed \( \Delta H^\circ \) of 13 kcal mol\text{^{-1}}.

\[ \text{OsO}_4 + 2e^- + 2\text{H}_2\text{O} \rightleftharpoons \text{OsO}_4(\text{OH})_2^{2-} \quad E = 0.39 \]

\[ \text{OsO}_4(\text{OH})^+ + 2e^- + \text{H}_2\text{O} + \text{H}^+ \rightleftharpoons \text{OsO}_4(\text{OH})_2^{2-} \quad E = 0.74 - 0.0295\text{pH} \]

\[ \text{OsO}_4(\text{OH})_2^{2-} + 2e^- + 2\text{H}^+ \rightleftharpoons \text{OsO}_4(\text{OH})_2^{2-} \quad E = 1.17 - 0.0591\text{pH} \]

\[ \text{H}_2 \rightleftharpoons 2\text{H}^+ + 2e^- \quad E = 0 - 0.0591\text{pH} \]

\[ \text{OsO}_4 + \text{H}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{OsO}_4(\text{OH})_2^{2-} + 2\text{H}^+ \quad \Delta G^\circ = -0.93\text{V} - 22\text{ kcal mol}^{-1} \text{ at pH 9.2} \]

\[ \text{OsO}_4(\text{OH}) + \text{H}_2 + \text{H}_2\text{O} \rightleftharpoons \text{OsO}_4(\text{OH})_2^{2-} + \text{H}^+ \quad \Delta G^\circ = 1.10\text{V} - 25\text{ kcal mol}^{-1} \text{ at pH 12.3} \]

\[ \text{OsO}_4(\text{OH})_2^{2-} + \text{H}_2 \rightleftharpoons \text{OsO}_4(\text{OH})_3^{2-} \quad \Delta G^\circ = 1.17\text{V} - 27\text{ kcal mol}^{-1} \]
Initial hydride transfer to give OsO₃(OH)(L)⁻ and “H⁺” is also unlikely because H₂ addition proceeds at comparable rates in polar and nonpolar solvents. While a direct comparison of the same reactant in solvents of different polarity has not been possible, OsO₄(py) is reduced by H₂ just as rapidly in CHCl₃ or n-hexane as OsO₄(OH)⁻ species are reduced in water. A hydride transfer rate-determining step should be marked by a faster rate in polar solvents because of the charge separation in the transition state. Also, H⁻ transfer should show a base or buffer dependence because a proton would be liberated, but this dependence is not observed.

The [2+2] and [3+2] mechanisms are difficult to distinguish experimentally, as shown by the years of controversy about the pathway for alkene additions to OsO₄(L)n.²³,³⁴ The issue for alkene oxidations has been settled in favor of the [3+2] mechanism by quantum chemical calculations,¹³ particularly because the secondary isotope effects predicted by the calculations for this mechanism were confirmed by experiments.¹³a

We have used DFT calculations to locate gas-phase transition structures for addition of H₂ to OsO₄, OsO₄(OH)⁻, and OsO₄(NH₃), for both [2+2] and [3+2] pathways. The energies, enthalpies, and free energies are given in Table 2, and the enthalpic changes for OsO₄ and OsO₄(OH)⁻ are illustrated in Figure 7. In all three cases, the [2+2] pathway is predicted to be much less favorable than the [3+2] pathway, both kinetically and thermodynamically. For instance, [3+2] addition of H₂ to OsO₄ is calculated to have a barrier of 18.8 kcal mol⁻¹ and to be exothermic by −35.0 kcal mol⁻¹, while [2+2] addition to form Os(O)(H)(OH) is calculated to have ΔH° = 58.7 kcal mol⁻¹ and ΔH° = +20.9 kcal/mol. It should be noted that the energies for the [3+2] products in the tables and figures are for their most stable conformations, with the O−H bonds in a “head-to-tail” orientation (Figure 8). The initially formed “head-to-head” conformers are higher in energy by ΔE = 5.6−7.2 kcal mol⁻¹.²⁹

The calculated [3+2] gas-phase barrier of ΔH° = 18.8 kcal mol⁻¹ for H₂ + OsO₄ is larger than the experimental value of ΔH° = 13.2(2) kcal mol⁻¹, possibly due to the effect of solvent (see below). Better agreement is found for the reaction of H₂ with OsO₄(OH)⁻: ΔH° = 10.6 kcal mol⁻¹ (calculated, gas phase) versus 12.8 kcal mol⁻¹ (experimental, aqueous). Computational results similar to ours for OsO₄ were obtained by Strassner et al. for H₂ addition to permanganate: The [3+2] pathway was computed to be favored over the [2+2] pathway by 46.5 kcal mol⁻¹ in ΔH° and 78.1 kcal mol⁻¹ in ΔH°.¹¹

The calculated [3+2] transition structures for H₂ addition to OsO₄ and OsO₄(OH)⁻ (Figure 8) show concurrent stretching of H−H and Os−O bonds and formation of O−H bonds. The transition structure for H₂ + OsO₄(OH)⁻ has the shorter H−H distance, consistent with this more exoergic reaction having an earlier transition state. The transition structure for H₂ + OsO₄ has C₂ᵥ symmetry, with equal O−H distances, but that for H₂ + OsO₄(OH)⁻ is surprisingly asymmetric, with more than 0.1 Å difference in the length of the forming O−H bonds. The axial

**Figure 7.** Calculated enthalpies (kcal mol⁻¹) at 298 K for H₂ addition to OsO₄ and OsO₄(OH)⁻ by [2+2] and [3+2] mechanisms.

**Figure 8.** Calculated structures for reactants, transition states, and products for H₂ addition to OsO₄ (top) and OsO₄(OH)⁻ (bottom) by [3+2] mechanisms. Bond lengths are given in angstroms, and bond angles are in degrees. Only the most stable conformers of OsO₂(OH)₂ and OsO₂(OH)₃⁻ are shown.
oxygen, which has a longer bond to Os than the equatorial oxygen, has the shorter forming O–H bond in the transition structure.

The very large preference for the [3+2] over the [2+2] mechanism for H₂ addition is due to the [3+2] pathway being both more exoergic and also symmetry-allowed. Orbital symmetry arguments have been advanced to explain the low barriers for [3+2] alkene addition to OsO₄.²⁸ The frontier orbitals of H₂ and ethylene are isogonal, so the orbital symmetry arguments are the same for H₂ addition to OsO₄.

The cyclic [3+2] pathway for addition of H₂ to OsO₄ is consistent with the small primary kinetic isotope effects observed, kD₂/kH₂ = 3.1 and 3.6 for OsO₄ and OsO₄(OH)⁻. These values are much smaller than the semiclassical maximum of kH₂/kD₂ = 20 for breaking an H–H bond.³⁵,³⁶ The DFT calculations give kD₂/kH₂ = 1.3 for H₂/D₂ addition to OsO₄ and kD₂/kH₂ = 1.5 for OsO₄(OH)⁻.³⁷ To the extent that tunneling contributes to the measured reaction rate, our calculations, which do not include tunneling, should underestimate the size of the primary kinetic isotope effect.

III. Ligand Acceleration. Acceleration of the reaction of H₂ with OsO₄ by added ligands is observed experimentally and also predicted computationally. OsO₄ is unreactive with 1 atm of H₂ in chloroform or hexane at room temperature in the absence of a ligand, but reacts with a half-life of 7 h in the presence of pyridine or 1,10-phenanthroline. The effect is less pronounced in aqueous solutions, where a difference of only 3 kcal mol⁻¹ in the ideal rate constant is observed between OsO₄ and OsO₄(OH)⁻.³⁸ Ligand acceleration is also a key feature of the OsO₄-catalyzed dihydroxylation of alkenes, with rate accelerations varying from modest (×3) to dramatic (×1000) depending on the ligand and the alkene.³⁸a,³⁸b Acceleration of these reactions by added ligands is surprising, because OsO₄ is electron-deficient and is reduced by H₂ and alkenes. Therefore, binding of a donor ligand might have been expected to slow both reactions rather than accelerate them.³³ The observation of this surprising effect in our study is a notable parallel between the addition of H₂ and alkenes to OsO₄ and provides indirect support for a common [3+2] mechanism.

Our DFT calculations find that the activation enthalpies for H₂ addition to OsO₄(OH)⁻ and OsO₄(NH)₃ are lower than that for H₂ + OsO₄ by 8.2 and 3.9 kcal mol⁻¹, and the reactions of ligated OsO₄ are computed to be more exothermic by 16.1 and 10.3 kcal mol⁻¹, respectively. The calculated stabilization of the transition state is 51% of the increased ΔH° for OsO₄(OH)⁻ and 38% for OsO₄(NH)₃ (ΔΔH°/ΔΔH° = 0.51, 0.38). The greater exoergicity implies that the ligand binds more tightly to the OsV(IV)O₂(OH)₂ product than to the OsO₄ reactant. Stronger ligand binding is indeed evident by the substantial shortening in the calculated Os–L bond distances in going from OsO₄ to OsO₂(OH)₂L: d(Os–OH) = 2.115 Å in OsO₂(OH)₂ versus 2.038 Å in OsO₂(OH)₂⁻; d(Os–NH) = 2.534 Å in OsO₄(NH)₃ versus 2.153 Å in OsO₂(OH)₂(NH). This shortening of the Os–L bonds is due, at least in part, to preference of Os(V)₆ (and d²-dioxo compounds in general) to adopt octahedral structures, whereas OsO₄ binds ligands only weakly due to steric crowding and the trans effect of the oxo groups.³⁴ However, a detailed quantum-mechanical understanding of the rate acceleration of OsO₄ addition reactions by ligands is certainly desirable.³⁵

Experimentally, H₂ addition to aqueous OsO₄(OH)⁻ is faster than to aqueous OsO₄, but ΔΔH° is only −0.4(3) kcal mol⁻¹, not the 8.2 kcal mol⁻¹ predicted for the gas-phase reaction.³⁸ To explore the effects of solvent on the reactions, polarized continuum model (PCM) calculations,³² based on the gas-phase optimized structures, were performed for CCl₄ (ε = 2.23) and H₂O (ε = 78.39). The activation barrier for [3+2] addition of H₂ to OsO₄ was computed to be 1.4 kcal mol⁻¹ lower in CCl₄ and 3.7 kcal mol⁻¹ lower in water than in the gas phase. Similar solvent effects were calculated for the amine complex OsO₄(NH)₃. For OsO₄(OH)⁻, the calculated solvent effects were smaller: ΔΔH° (kcal mol⁻¹) = −1.4 (CCl₄), −1.8 (H₂O). The decrease in solvent strength with the addition of water to the transition state is due to the smaller change in polarity of the anionic complex on adding H₂. Thus, including PCM solvation reduces the difference in barriers between OsO₄ and OsO₂(OH)⁻ from 8.2 to 6.3 kcal mol⁻¹, closer to but still substantially larger than the experimental difference of less than 1 kcal mol⁻¹. It seems likely that the aqueous solvent stabilizes the transition state for H₂ addition by more than the dielectric effect modeled in the calculations, perhaps by a specific hydrogen-bonding interaction or by coordination of a water molecule in the transition state.³⁸

Conclusions

Dihydrogen readily reduces OsO₄, OsO₄(OH)⁻, and OsO₂(OH)₂⁻ in aqueous solutions, and OsO₄(py) and OsO₄(phen) in organic solvents. The reactions require a few hours at 25 °C under 1 atm H₂. In contrast, OsO₄ in noncoordinating solvents and in the absence of a ligand is unreactive with H₂ at ambient temperatures. In aqueous solutions, larger rate constants are found for the hydroxide-bound species: kₕ/O₄ < kₕ/O₄/OH < kₕ/O₄/OH/OH. This ligand acceleration has been previously observed in the dihydroxylation of alkenes by OsO₄(L)ₓ and exploited in enantioselective catalysis.³³

The O\textsubscript{VIII} compounds are reduced by H\textsubscript{2} to O\textsubscript{V}, for instance, to osmate, Os\textsubscript{2}(OH)\textsubscript{4}\textsuperscript{2-}. In contrast, most previous studies of metal oxides with hydrogen have involved either solid reactants (ZnO) or products (e.g., MnO\textsubscript{2} and RuO\textsubscript{2} from MnO\textsubscript{2} and RuO\textsubscript{2}).\textsuperscript{9-11} The simple stoichiometry of the OsO\textsubscript{4}(L) + H\textsubscript{2} reactions has allowed us to obtain detailed kinetic and thermodynamic data on the aqueous reactions. The thermochemistry is defined by the aqueous electrochemistry versus the normal hydrogen electrode: \(\Delta G^\circ\) varies from \(-20\) to \(-27\) kcal mol\(^{-1}\) depending on the pH. Kinetic studies of the aqueous reactions show primary kinetic isotope effects, \(k_1 k_0 = 3.1(3)\) for OsO\textsubscript{4} and 3.6(4) for OsO\textsubscript{4}(OH)\textsuperscript{2-}, implicating H–H bond cleavage in the rate-determining steps. Both reactions have low enthalpic barriers, with \(\Delta H^\circ = \pm 13\) kcal mol\(^{-1}\) and \(\Delta S^\circ = \mp 22\) cal mol\(^{-1}\) K\(^{-1}\).

DFT calculations show that the H\textsubscript{2} additions to OsO\textsubscript{4}, both unligated and ligated, occur by a concerted \(3+[2]\) mechanism. The \([3+2]\) addition of H\textsubscript{2} is computed to be highly favored over a competing \([2+2]\) pathway. The products of the \([3+2]\) addition reactions are calculated to be much lower in energy than those from the \([2+2]\) addition reactions, and this energetic difference is reflected in the reaction barriers computed for the two pathways. This conclusion follows that reached by Collman, Strassner, et al. for H\textsubscript{2} reductions of MnO\textsubscript{4} and RuO\textsubscript{4}.

The reaction of H\textsubscript{2} with OsO\textsubscript{4} is isolobal with the well-studied OsO\textsubscript{4} + H\textsubscript{2} reactions, with \(\Delta H^\circ\) and \(\Delta S^\circ\) similar to those from the \([2+2]\) addition reactions. Both reactions have low enthalpic barriers, with \(\Delta H^\circ = \pm 13\) kcal mol\(^{-1}\) and \(\Delta S^\circ = \mp 22\) cal mol\(^{-1}\) K\(^{-1}\).

Experimental and Computational Methodology

Materials. Deionized water was passed through ultra-free filters, purchased from Millipore Corp. (Bedford, MA). Chloroform, n-hexane, benzene, methylene chloride, and pyridine were degassed and dried according to standard procedures.\textsuperscript{44} OsO\textsubscript{4} (Strem, 99.95%), KOH (Sigma-Aldrich, 99.99%), NaOH (Aldrich, 99.99%), NaHPO\textsubscript{4} (T. J. Baker, 99.94%), 1,10-phenanthroline (Aldrich, 99%), D\textsubscript{2}O (Cambridge Isotope Laboratories, 99.9%), H\textsubscript{2} (Airgas Inc., 99.9%), and D\textsubscript{2} (Cambridge Isotope Laboratories, 99.9%) were used without further purification.

Instrumentation and Measurements. H\textsubscript{1} NMR spectra were obtained using a Bruker AV-300 spectrometer at ambient temperatures and are referenced to Me\textsubscript{4} Si or a residual solvent peak: \(\delta\) (multiplicity, coupling constant, number of protons, assignment). H\textsubscript{2} solubility measurements were performed on a Bruker DRX-499. Temperature calibration of the NMR probe was accomplished by Van Geet’s method.\textsuperscript{45} IR spectra were obtained as KBr pellets using a Perkin-Elmer 1600 Series FTIR spectrometer at 4 cm\(^{-1}\) resolution. Electronic absorption spectra were acquired with a Hewlett-Packard 8453 diode array UV–visible spectrophotometer in purified solvents and are reported as \(\lambda\)nm (\(\text{m} \text{M}^{-1} \text{cm}^{-1}\)). A Corning pH meter 430 was used for pH measurements and was calibrated using pH 4 and pH 10 buffers.

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was given no constraints. Of the models examined, the best fits were obtained with a simple pseudo-first-order, A→B, model.

**Computational Methodology.** Using Gaussian 98,46 density functional theory (DFT) at the Becke3LYP (B3LYP) level47 was used to optimize the geometries of all the complexes. The effective core potentials (ECPs) of Hay and Wadt with a double-valence basis set (LanL2DZ)48 were used to describe the Os atom,49 while the 6-31+G(d,p) basis set50 was used for all other atoms. Vibrational frequencies were calculated for all stationary points, to verify whether each was a minimum (NIMAG = 0) or a transition state (NIMAG = 1) on the potential energy surface. The wave functions for all calculated species were checked for stability, with respect to the unrestricted (UB3LYP) wave functions. Solvent effects were taken into account by means of polarized continuum model (PCM) calculations42 using the UFF force field option in which hydrogens have individual spheres. These calculations were performed with Gaussian 03.51 Free energies of solvation were calculated for water (ε = 78.39) and carbon tetrachloride (ε = 2.228) as solvents, using the optimized geometries computed for the gas-phase species.

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**Supporting Information Available:** Kinetic, equilibrium, and computational data. This material is available free of charge via the Internet at http://pubs.acs.org.

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