Mechanisms of Niobate and Perrhenate Catalyzed Reduction of Inert Oxo-anions

G. P. HAIGHT, JR.,* ALICE CARROLL SWIFT and RONALD SCOTT

School of Chemical Sciences, University of Illinois, Urbana, Illinois, USA 61801, and Chemistry Department of Swarthmore College, Swarthmore, Pennsylvania, USA

Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

Studies of the reduction of inert oxo-nonmetallates catalyzed by oxo-metallates are extended to the systems Nb(V)–ClO₄⁻ and Re(VII)–NO₃⁻ using Sn(II) as the reducing agent. Rate laws found are:

\[
\text{Rate} = \frac{k'[\text{Nb(V)}][\text{Sn(II)}][\text{ClO}_4^-]}{1 + k'[\text{Sn(II)}]}
\]

and

\[
\text{Rate} = \frac{k'[\text{Re(VII)}][\text{Sn(II)}][\text{NO}_3^-]}{1 + k'[\text{Sn(II)}]} \quad \text{at low [Sn(II)]}
\]

\[
\text{Rate} = \frac{k''[\text{Re(VI)}][\text{NO}_3^-]^2[\text{Sn(II)}]}{[\text{Sn(II)}](1 + k''[\text{Sn(II)}])} \quad \text{at high [Sn(II)]}
\]

A general mechanism for catalysis has been deduced in which labile oxo-metallate (M) coordinates to inert oxo-nonmetallate, providing a pathway for electrons from Sn(II) to oxidized non-metal in the activated state:

[Sn: → \( \text{M-OClO}_3^- \) → 2e⁻].

Inert species of oxidized non-metals such as ClO₄⁻, NO₃⁻, NH₃OH⁺, H₂O₂, and N₂ are labilized for reaction by oxo-metallates such as MoO₂⁻, H₂SO₄ or HCl and WO₂⁻ in conc. HCl. This study extends the knowledge of catalytic phenomena to niobium(V) which is iso electronic with molybdenum(VI) and on the diagonal of the periodic table with tungsten, and to rhenium(VII) which is iso electronic with tungsten(VI) and is on the diagonal of the periodic table with molybdenum. Kinetics and mechanism studies of reactions I and II reveal characteristics of catalytic behavior identifiable with members of periods V and VI and also with the diagonals containing Nb and W as well as Mo and Re.

\[
\begin{align*}
4\text{Sn(II)} + \text{ClO}_4^- & \xrightarrow{\text{conc. HCl}} \text{Nb(V)} + 4\text{Sn(IV)} + 2\text{Cl}^- \quad (I) \\
4\text{Sn(II)} + 2\text{NO}_3^- & \xrightarrow{\text{Re(VII)}} 4\text{Sn(IV)} + 2\text{N}(I) \quad (II)
\end{align*}
\]

A general mechanism for reduction of a complex containing oxo-nonmetallate coordinated to oxo-metallate (M) exhibits variable kinetics which depend on:

1. The relative reactivity of the complex to dissociation or reduction, and
2. The redox chemistry of the oxo-metallate.

Inert oxo-metallates, M, combine with substrate oxo-anions, S, to form reducible complexes, C.

\[
\begin{align*}
\text{M} + S & \xrightarrow{k_1} C \quad \text{ (III)} \\
\text{C} + \text{Sn(II)} & \xrightarrow{k_2} \text{Products} \quad \text{ (IV)}
\end{align*}
\]

\[
\frac{d[\text{Sn(II)}]}{dr} = \frac{4k_1k_2[\text{M}][\text{S}][\text{Sn(II)}]}{k_{-1} + k_2[\text{Sn(II)}]} \quad \text{ (I)}
\]

Imposition of a redox chemistry of the oxo-metallate may yield very complicated (and informative) modifications of the rate law given by eqn. (I).
NIOBATE CATALYSIS OF THE REDUCTION OF PERCHLORATE

Experimental. All the catalytic processes being considered require acid conditions. Niobium(V) as Na₃NbO₄ is soluble in water but in dilute acid precipitates quantitatively as the hydrous oxide, Nb₂O₅. However, it is quite soluble in concentrated HCl. Na₃NbO₄ was dissolved in H₂O, then acidified to give a 0.05 M Nb(V) solution in 11.75 M HCl. Most attempts to prepare such solutions gave evidence of colloidal Nb₂O₅. Precise reproducibility of kinetic results using different preparations of Nb(V) in HCl was not possible, but the form of the rate law is consistent and comparisons with W(VI) catalysts are interesting and valid. Clear crystals of SnCl₂.2H₂O were dissolved in 12.3 M HCl to give solutions 11.75 M in H⁺. 

[Sn(II)] was monitored by quenching the reaction in solutions of ferric ammonium sulfate and titrating with standard KMnO₄ solution. [Cl⁻] was sufficiently lowered so that fading end-points were not a problem.

In the absence of Nb(V), 0.1 M Sn(II) in the presence of 0.25 M HClO₄ in 11.50 M HCl retained its titer over a 60 h period. MoO₄²⁻ is reduced to inert MoCl₃⁻ and does not catalyze ClO₄⁻ reduction in conc. HCl. No WO₄²⁻ was detected in the niobate used. The catalysis observed was an order of magnitude greater than that for tungstate² and could not, therefore, be due to impurities of either MoO₄²⁻ or WO₄²⁻.

Strict control of [H⁺] and [Cl⁻] was necessary since reaction rates were very susceptible to changes in their concentrations. Consistent kinetics were observed if [Sn(II)] and [ClO₄²⁻] were 0.1 M or less. [Sn(IV)]₀ > 0.06 M slowed reaction rates, probably by removing Cl⁻ as SnCl₂⁻. [ClO₄²⁻] > 0.2 M also gave lower reaction rates than expected, probably by causing volatilization of HCl. (Mixing 12 M solutions of HCl and HClO₄ causes violent boiling due to dramatic increase of the activity of HCl.) Under these restrictions, a consistent rate law was found to apply to a series of runs in which the following variations of concentrations were employed:

Initial concentrations
0.1 M ≥ [Sn(II)]₀ ≥ 0.008 M
0.1 M ≥ [ClO₄²⁻]₀ ≥ 0.02 M
0.0025 M ≥ [Nb(V)] ≥ 0.0002 M

Concentrations throughout a run
0.1 M ≥ [Sn(II)] ≥ 0.001 M
0.1 M ≥ [ClO₄²⁻] ≥ 0.005 M

Results. Initial rates of reaction were obtained with considerable accuracy since [Sn(II)] vs. t gave a straight line for several points when [Sn(II)]₀ ≈ 0.1 M (see Fig. 1). At low [Sn(II)], reactions deviated from zero order toward first order in [Sn(II)] and approximated first order at the lowest [Sn(II)] employed. Reactions were first order in Nb(V) and in ClO₄⁻ for [ClO₄⁻] ≤ 0.1 M. Most runs recorded in Fig. 1 fit the rate law

\[- \frac{d[Sn(II)]}{dt} = \frac{800[Nb(V)][ClO₄²⁻][Sn(II)]}{1+92[Sn(II)]} \quad (2)\]

From eqn. (1), constants may be estimated: 4k₁ = 8.7 M⁻¹ min⁻¹, k₂/k₁ = 92. Using these constants, [Sn(II)] vs. t was calculated for each run, giving curves recorded in Fig. 1. The lines are

Table 1. Sn(II) Reduction of ClO₄⁻.

<table>
<thead>
<tr>
<th>Run</th>
<th>[Sn(II)]₀</th>
<th>10⁴[Nb(V)]</th>
<th>[ClO₄⁻]₀</th>
<th>10⁴ Init. Rate M min⁻¹</th>
<th>4K₁k₂ * M⁻² min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>0.098</td>
<td>12.5</td>
<td>0.028</td>
<td>2.78</td>
<td>810</td>
</tr>
<tr>
<td>M</td>
<td>0.099</td>
<td>25</td>
<td>0.024</td>
<td>4.47</td>
<td>760</td>
</tr>
<tr>
<td>Q</td>
<td>0.100</td>
<td>25</td>
<td>0.025</td>
<td>3.6</td>
<td>670</td>
</tr>
<tr>
<td>Y</td>
<td>0.109</td>
<td>30</td>
<td>0.0237</td>
<td>4.0</td>
<td>825</td>
</tr>
<tr>
<td>N</td>
<td>0.10</td>
<td>5</td>
<td>0.234</td>
<td>9.0</td>
<td>780</td>
</tr>
<tr>
<td>R</td>
<td>0.10</td>
<td>2.5</td>
<td>0.234</td>
<td>3.67</td>
<td>640</td>
</tr>
<tr>
<td>T</td>
<td>0.10</td>
<td>2.5</td>
<td>0.234</td>
<td>3.77</td>
<td>650</td>
</tr>
<tr>
<td>X</td>
<td>0.10</td>
<td>2.0</td>
<td>0.237</td>
<td>2.5</td>
<td>540</td>
</tr>
<tr>
<td>P</td>
<td>0.04</td>
<td>5.0</td>
<td>0.0934</td>
<td>3.20</td>
<td>800</td>
</tr>
<tr>
<td>S</td>
<td>0.04</td>
<td>2.0</td>
<td>0.0934</td>
<td>1.23</td>
<td>770</td>
</tr>
<tr>
<td>V</td>
<td>0.013</td>
<td>2.5</td>
<td>0.100</td>
<td>1.28</td>
<td>867</td>
</tr>
<tr>
<td>W</td>
<td>0.010</td>
<td>2.5</td>
<td>0.059</td>
<td>0.60</td>
<td>780</td>
</tr>
<tr>
<td>K</td>
<td>0.070</td>
<td>5.0</td>
<td>0.2336</td>
<td>3.17</td>
<td>290</td>
</tr>
</tbody>
</table>

* Assume k₂/k₋₁ = 92; K₁ = k₁/k₋₁. Values from initial rates. Fig. 1 shows fit of plots of complete runs for 4K₁k₂ = 800. Runs with low values for 4K₁k₂ otherwise fit the general rate law. The values of k₁ are probably lowered by media changes in which activities of H⁺ or Cl⁻ are lowered. * [Sn(IV)] = 0.225 M.

calculated from eqn. (4). The points are from experimental data.

Runs L and M, for which fitting is apparently poor, are most susceptible to error. Both [ClO₄⁻] and [Sn(II)] are changing. Any error in setting initial ratios is quickly magnified as the run proceeds. Small changes in constants would produce a better fit for run L. Run M appears to show a jump in [Sn(II)] halfway through a long run, after a good fit for early points.

Runs recorded in Table 1 but not in Fig. 1 generally fit the form of the rate law with comparable values for k₂/k₋₁ and lower values for 4K₁k₂. [ClO₄⁻] > 0.2 and [Sn(IV)] > 0.05 appear to effect inhibition of reaction not consistent with changes occurring during runs in which [ClO₄⁻] < 0.1 and [Sn(IV)] increase as Sn(II) is consumed. Vaporization of HCl on addition of 12 M HClO₄ and formation of SnCl₂⁻ could change the medium of reaction enough to account for these inhibitions.

The rate law is consistent with the general mechanism given above, which in this case is

\[ \text{Nb(V)} + \text{ClO}_4^- \xrightarrow{k_1} C \quad \text{(V)} \]

\[ \text{C + Sn(II)} \xrightarrow{k_2} \text{Products} \quad \text{(VI)} \]

PERRHENATE CATALYZED REDUCTION OF NITRATE

Tribalat⁹ has studied the titration of nitrate and nitrite with Sn(II) in hydrochloric acid. In the presence of traces of perrhenate ion, potentiometric titrations were possible which indicated that both nitrate and nitrite ions were reduced to N₂O (or H₂N₂O₅). Attempts to carry out reactions with excess Sn(II) failed. Reaction occurs readily if small increments of Sn(II) are added to solutions containing nitrate and perrhenate, but not if nitrate is added to solutions containing Sn(II) and perrhenate. Since other studies¹⁰⁻¹² indicate that Sn(II) reduces Re(VII) to Re(V) rapidly during a potentiometric titration, and hence more slowly to Re(IV), Tribalat concludes that Re(V) is the catalyst. Our studies suggest Re(VII) is the catalyst.

Experimental. Reactions were carried out under nitrogen in flasks thermostated at 25.0±0.1 °C. Aliquot samples were removed from time to time and quenched in standard iodine solution containing potassium iodide. Excess iodine was titrated with S₂O₃²⁻ or measured spectrophotometrically as I₂⁻. The iodine strength was maintained at 3.0 using 3 M HCl and 3 M HNO₃.

Results. Reactions with [ReO₄⁻] > 10⁻⁴ were too fast to measure using our techniques, so [ReO₄⁻] was held at 10⁻⁵ to 10⁻⁶ M level. A drastic fall-off in rates was observed if [NO₃⁻] was decreased below 0.6 M. With [NO₃⁻] > 0.8 M, two limiting rate laws are obtained. At high [Sn(II)] (> 0.02 M)
Fig. 2. Inverse first order [Sn(II)] dependence at high [Sn(II)]. ■, 1.38 M NO$_3^-$ (k' = 0.56); ▲, 1.35 M NO$_3^-$ (k' = 0.50); ●, 1.27 M NO$_3^-$ (k' = 0.46).

\[- \frac{d[\text{Sn(II)}]}{dr} = \frac{k'[\text{NO}_3^-]^2[\text{Re}]}{[\text{Sn(II)}]} \]  

Plots of [Sn(II)]$^2$ vs. time give straight lines whose slopes are proportional to [Re] and to [NO$_3^-$]$^2$ (Figs. 2 and 3).

At low [Sn(II)]

\[- \frac{d[\text{Sn(II)}]}{dr} = k''[\text{NO}_3^-][\text{Re}][\text{Sn(II)}] \]  

Plots of log[Sn(II)] give straight lines proportional to [NO$_3^-$] and [Re]. (Fig. 4). From plots in Figs. 2, 3, and 4, we calculate k' as $0.49 \pm 0.07 \text{ M}^{-1} \text{ s}^{-1}$ and k'' as $3.39 \pm 0.01 \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$.

**Mechanism.** Potentiometric titrations show that Sn(II) reduces permanganate primarily to Re(V). The present authors, however, observed that the reaction is measurably slow if titrations are performed with $10^{-3}$ M reagents. It is judged that this reaction is of comparable rate to the catalyses at higher [NO$_3^-$] and [Sn(II)] when [ReO$_4^{2-}$] $\sim 10^{-6}$ M. Re(V) is oxidized to Re(VII) by nitrate. Re(V) disproportionates slowly and irreversibly to give inert Re$_2$O$_7^{2-}$ and ReO$_4^{2-}$.

The drastic decrease in catalysis at low nitrate concentration is attributed to the failure of nitrate oxidation of Re(V) to compete with disproportionation. The inverse first order in Sn(II) at high [Sn(II)] is attributed to the predominance of

Fig. 3. Inverse first order [Sn(II)] dependence at high [Sn(II)]. [Re] = $5 \times 10^{-6}$ M; ●, [NO$_3^-$] = 0.67 M, Slope = $1.15 \times 10^{-6}$, k = 0.51; ○, [NO$_3^-$] = 1.02 M, Slope = $2.53 \times 10^{-6}$, k = 0.49; ▲, [NO$_3^-$] = 1.27 M, Slope = $3.50 \times 10^{-6}$, k = 0.43; k'' = $0.49 \pm 0.07 \text{ M}^{-1} \text{ s}^{-1}$.

Fig. 4. First order [Sn(II)] dependence at low [Sn(II)]. ●, [NO$_3^-$] = 0.679 M, [ReO$_4^{2-}$] = $10^{-6}$ M; ○, [NO$_3^-$] = 1.13 M, [ReO$_4^{2-}$] = $6 \times 10^{-7}$ M; ▲, [NO$_3^-$] = 1.69 M, [ReO$_4^{2-}$] = $4 \times 10^{-7}$ M; All slopes = 0.001; k'' = $3.39 \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$.

reduction of Re(VII) by Sn(II) over oxidation of Re(V) by NO$_3^-$ . It is concluded that ReO$_4^-$ is the catalytic species, that it forms a weak complex with NO$_3^-$ which is easily reduced by Sn(II). The following possible mechanism is in accord with the kinetics, and the known simple reactions occurring in this system.

\[ \text{Re(VII)} + \text{NO}_3^- \xrightarrow{k_{1\rightarrow}} \text{C} \quad (\text{VII}) \]

\[ \text{C} + \text{Sn(II)} \xrightarrow{k_2} \text{HNO}_2 + \text{Sn(IV)} + \text{Re(VII)} \quad (\text{VIII}) \]

\[ \text{Sn(II)} + \text{HNO}_2 \xrightarrow{k_3} \frac{1}{2} \text{N}_2\text{O} + \text{Sn(IV)} \quad \text{fast} \quad (\text{IX}) \]

\[ \text{Sn(II)} + \text{Re(VII)} \xrightarrow{k_4} \text{Re(V)} + \text{Sn(IV)} \quad (\text{X}) \]

\[ \text{Re(V)} + \text{NO}_3^- \xrightarrow{k_5} \text{Re(VII)} + \text{HNO}_2 \quad (\text{XI}) \]

\[ 3\text{Re(V)} \rightarrow 2\text{Re(IV)} + \text{Re(VII)} \quad (\text{XII}) \]

If reaction XII becomes important, a drastic decrease in catalysis occurs, stopping the reaction. Thus catalysis is observed only so long as Re is maintained as Re(V) + Re(VII) without irreversible reduction to Re(IV).

If reaction VIII is the rate-determining step:

\[ -\frac{d[\text{Sn(II)}]}{dt} = \frac{k_1k_2[\text{Sn(II)}][\text{NO}_3^-][\text{Re(VII)}]}{k_{-1} + k_2[\text{Sn(II)}]} \quad (5) \]

\[ \frac{[\text{Re(VII)}]}{[\text{Re(V)}]} = \frac{k_3[\text{NO}_3^-]}{k_4[\text{Sn(II)}]} \]

\[ -\frac{d[\text{Sn(II)}]}{dt} = \frac{k_1k_2k_5[\text{NO}_3^-]^2[\text{Re(V)}]}{k_{-1}k_4 + k_2k_4[\text{Sn(II)}]} \quad (6) \]

When [Sn(II)] > 0.03 M, most of the rhenium is present as Re(V), and equation (6) reduces to eqn. (3). When [Sn(II)] < 0.01 M, Re(VII) predominates and eqn. (5) reduces to eqn. (4). Thus the two observed rate laws can be derived from the postulated mechanism.

Discussion of the steps in the mechanism. Reactions IX, X, and XII have been observed to proceed quantitatively. Reaction XI is postulated on the basis of qualitative observations. Reactions VII and VIII are postulated to fit the kinetics. Tungstate was found to catalyze the reduction of perchlorate in hydrochloric acid by a similar complex-forming mechanism. Re(VII) and W(VI) might reasonably be expected to behave similarly. The fact that W(VI) is not reduced by Sn(II) in conc. HCl simplifies the mechanism of tungstate catalysis. However, the two mechanisms, insofar as they involve Re(VII) and W(VI), may be considered to be the same.

A possible inconsistency is involved in the rejection of Re(V) as the catalyst, contrary to Tribalat’s conclusions. Re(V) is a d$^2$ species analogous to Mo(IV) which is apparently a powerful catalyst for reduction of oxo-ions. However, Re(V) is more inert than Mo(IV) which disproporionate rapidly in similar systems in hydrochloric acid and may differ as well in other properties. Perhaps the inertia of ReOCl$_3^-$ does not allow both coordination with NO$_3^-$ and nucleophilic attack by SnCl$_3$ to occur. Mo(IV) is undoubtedly less firmly coordinated to O$^{2-}$ and Cl$^-$ and may interact more readily with the weak nitrate ion. In any case, it has not been possible for the authors to find a mechanism involving Re(V) as the active catalyst consistent with the kinetics and other observations.

**DISCUSSION**

**Nb(V) and W(VI) as catalysts.** We may directly compare niobate catalysis with tungstate catalysis of the reduction of HClO$_4$ in conc. hydrochloric acid. The rate of formation of the (Nb(V)ClO$_4$) complex ($k_1 = 2.2 \text{ M}^{-1} \text{ min}^{-1}$) is thirteen times as large as that for the (W(VI)ClO$_4$) complex ($k_5 = 0.17 \text{ M}^{-1} \text{ min}^{-1}$). The ratio $k_5/k_{-1}$ is much smaller for niobate than for tungstate. This is consistent with the niobate complex being the more labile with higher rates of both formation and dissociation. The possibility that reduction of the complex by SnCl$_2$ is much faster for tungstate than for niobate is not ruled out by the data but seems less likely to the authors. The behavior of Nb(V) appears to be completely analogous to that of W(VI). Conditions of reaction, and mechanisms found, correspond, as do many common properties, along diagonals moving from upper left to lower right in the periodic table.

**Rhenium and molybdenum as catalysts.** Both rhenium(VII) and Mo(VI) are reducible to tin(II) to Re(V)$^9$ and Mo(IV)$^{14}$ respectively under the conditions for catalytic reduction of NO$_3^-$ and ClO$_4^-$. 

Re(V) and Mo(IV) each disproportionate. Mo(IV) disproportionates rapidly\(^{14}\) and also serves as a catalyst for o xo-anion reduction. Re(V) is more stable and non-catalytic, but may be oxidized directly by nitrate or reduced to Re(IV) by SnCl\(_2\). The kinetics of catalysis indicate that Re(VII), like tungsten(VI) is the catalyst operating by the general mechanism proposed in the introduction, making this a property of the sixth period elements.

However, Nb(V) is also catalytic. It is possible that Mo(VI) catalysis would be observed if Mo(VI) were not so easily reduced — that reduction of Mo(VI) rather than ClO\(_2^-\) in a (Mo(VI)ClO\(_4^-\)) complex\(^1\) makes catalysis by Mo(VI) unobservable. Since ReOCl\(_3^2^-\) is directly oxidized by NO\(_3^-\), it is reasonable that electrons transferred to (Re(VII)-NO\(_3^-\)) should yield reduced nitrogen directly according to reaction VIII in our mechanism.

The role of o xo-metallates in reduction of oxo-anions. Positive centers of fully oxidized nonmetals such as Cl(VII) in ClO\(_4^-\) and N(V) in NO\(_3^-\) are protected by O\(^2-\) and \(\pi\)-electron clouds from nucleophilic attack by species such as SnCl\(_2^-\) (the most reactive SnCl\(_2^-\) complex).\(^5\) No direct reaction of Sn(II) with NO\(_3^-\) or ClO\(_4^-\) is observed at room temperature in dilute aqueous acid solutions. The results of these and previous studies\(^15\) suggest that the o xo-metallates form complexes having electron transfer pathways between Sn(II) and o xo-nonmetallates. It is further suggested that these catalyses are examples of innersphere two-electron transfers, such as were observed in studies of chromic acid oxidations of o xo-nonmetallates such as HPO\(_3^-\), NH\(_2\)OH, etc.\(^6\) In two-electron Cr(VI) oxidations, electrons are transferred through an O-bridge in a chromate ester.

\[
\begin{align*}
&\text{H} &\text{N} &\text{O} &\text{CrO}_3^- \\
\text{H}
\end{align*}
\]

In these catalytic systems the labile o xo-metallates form weak O-bridged complexes to inert nonmetallates. Nucleophilic attack on the labile metal center by a reducing agent then leads to innersphere two-electron transfer from metal to nonmetal through an O-bridge.

\[
\text{M} + \text{OCIO}_3^- \rightleftharpoons [\text{MOCIO}_3] \\
\text{Cl}_3\text{Sn}^- + \text{M} - \text{OCIO}_3 \rightarrow \text{Cl}_3\text{Sn} - \text{M} - \text{O} - \text{ClO}_3
\]

The activated state involves direct 2e\(^-\) attack on the metal center bridged by O to the nonmetal. M may be Mo(IV), Nb(V), W(VI), or Re(VII). It is quite likely that oxidized metal ions play similar roles in heterogeneous catalyses involving metal oxides.

This work was supported in part by grants from the Climax Molybdenum Company and from the National Institutes of Health, GM-22887.

REFERENCES


Received July 15, 1978.