

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

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

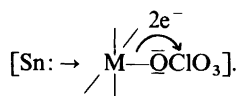
Studies of the reduction of inert oxo-nonmetallates catalyzed by oxo-metallates are extended to the systems Nb(V)–ClO<sub>4</sub><sup>-</sup> and Re(VII)–NO<sub>3</sub><sup>-</sup> using Sn(II) as the reducing agent. Rate laws found are:

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

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

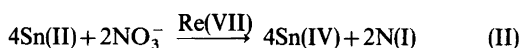
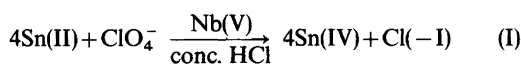
$$\text{Rate} = \frac{k''[\text{Re(V)}][\text{NO}_3^-]^2[\text{Sn(II)}]}{[\text{Sn(II)}](1+k''[\text{Sn(II)}])} \text{ at high } [\text{Sn(II)}]$$

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:



Inert species of oxidized non-metals such as ClO<sub>4</sub><sup>-</sup>,<sup>1,2</sup> NO<sub>3</sub><sup>-</sup>,<sup>3,4</sup> NH<sub>3</sub>OH<sup>+</sup>,<sup>5</sup> H<sub>2</sub>O<sub>2</sub>,<sup>6</sup> and N<sub>2</sub><sup>7</sup> are labilized for reduction by oxo-metallates such as MoO<sub>4</sub><sup>2-</sup>,<sup>1,3-8</sup> in dilute H<sub>2</sub>SO<sub>4</sub> or HCl and WO<sub>4</sub><sup>2-</sup> in conc. HCl.<sup>2</sup> This study extends the knowledge of catalytic phenomena to niobium(V) which is isoelectronic with molybdenum(VI) and on the diagonal of the periodic table with tungsten,

and to rhenium(VII) which is isoelectronic 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.



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.



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

Imposition of a redox chemistry of the oxo-metallate may yield very complicated (and informative) modifications of the rate law given by eqn. (1).

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## NIOBATE CATALYSIS OF THE REDUCTION OF PERCHLORATE

*Experimental.* All the catalytic processes being considered require acid conditions. Niobium(V) as  $\text{Na}_3\text{NbO}_4$  is soluble in water but in dilute acid precipitates quantitatively as the hydrous oxide,  $\text{Nb}_2\text{O}_5$ . However, it is quite soluble in concentrated  $\text{HCl}$ .  $\text{Na}_3\text{NbO}_4$  was dissolved in  $\text{H}_2\text{O}$ , then acidified to give a 0.05 M  $\text{Nb(V)}$  solution in 11.75 M  $\text{HCl}$ . Most attempts to prepare such solutions gave evidence of colloidal  $\text{Nb}_2\text{O}_5$ . Precise reproducibility of kinetic results using different preparations of  $\text{Nb(V)}$  in  $\text{HCl}$  was not possible, but the form of the rate law is consistent and comparisons with  $\text{W(VI)}$  catalyses are interesting and valid. Clear crystals of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  were dissolved in 12.3 M  $\text{HCl}$  to give solutions 11.75 M in  $\text{H}^+$ .

$[\text{Sn(II)}]$  was monitored by quenching the reaction in solutions of ferric ammonium sulfate and titrating with standard  $\text{KMnO}_4$  solution.  $[\text{Cl}^-]$  was sufficiently lowered so that fading end-points were not a problem.

In the absence of  $\text{Nb(V)}$ , 0.1 M  $\text{Sn(II)}$  in the presence of 0.25 M  $\text{HClO}_4$  in 11.50 M  $\text{HCl}$  retained its titer over a 60 h period.  $\text{MoO}_4^{2-}$  is reduced to inert  $\text{MoCl}_6^{3-}$  and does not catalyze  $\text{ClO}_4^-$  reduction in conc.  $\text{HCl}$ . No  $\text{WO}_4^{2-}$  was detected in the niobate used. The catalysis observed was an order of magnitude greater than that for tungstate<sup>2</sup> and could not, therefore, be due to impurities of either  $\text{MoO}_4^{2-}$  or  $\text{WO}_4^{2-}$ .

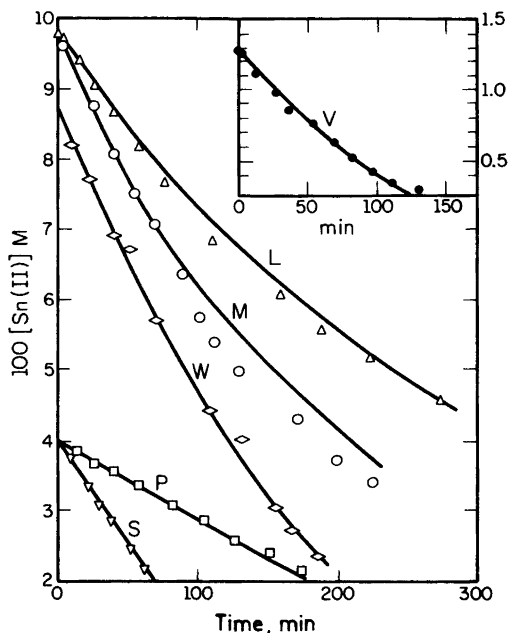
Strict control of  $[\text{H}^+]$  and  $[\text{Cl}^-]$  was necessary since reaction rates were very susceptible to changes in their concentrations. Consistent kinetics were observed if  $[\text{Sn(II)}]$  and  $[\text{ClO}_4^-]$  were 0.1 M or less.  $[\text{Sn(IV)}]_0 > 0.06$  M slowed reaction rates, probably by removing  $\text{Cl}^-$  as  $\text{SnCl}_6^{2-}$ .  $[\text{ClO}_4^-] > 0.2$  M also gave lower reaction rates than expected, probably by causing volatilization of  $\text{HCl}$ . (Mixing 12 M solutions of  $\text{HCl}$  and  $\text{HClO}_4$  causes violent boiling due to dramatic increase of the activity of  $\text{HCl}$ .) 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

$$\begin{aligned} 0.1 \text{ M} &\geq [\text{Sn(II)}]_0 \geq 0.008 \text{ M} \\ 0.1 \text{ M} &\geq [\text{ClO}_4^-]_0 \geq 0.02 \text{ M} \\ 0.0025 \text{ M} &\geq [\text{Nb(V)}] \geq 0.0002 \text{ M} \end{aligned}$$

### Concentrations throughout a run

$$\begin{aligned} 0.1 \text{ M} &\geq [\text{Sn(II)}] \geq 0.001 \text{ M} \\ 0.1 \text{ M} &\geq [\text{ClO}_4^-] \geq 0.005 \text{ M} \end{aligned}$$



*Fig. 1.* Curves for  $[\text{Sn(II)}]$  vs. time calculated from eqn. (4) compared with observed data points for runs with  $[\text{Sn(IV)}]_0 = 0$  and  $[\text{ClO}_4^-]_0 \leq 0.1$  M. The ordinate for run W is  $10^3[\text{Sn(II)}]$  and for run V, in the insert, it is 0 to 0.015 M. Various types of run are plotted.  $[\text{Sn(II)}]_0 < 0.01$  M, V and W;  $[\text{Sn(II)}]_0 \sim 4[\text{ClO}_4^-]_0$ , M and L;  $[\text{Sn(II)}]_0 = 0.04$  M,  $[\text{ClO}_4^-]_0 \sim 0.1$  M, S and P. Curves were calculated from the integrated form of the rate law appropriate to each run. Note: Runs L and M are most susceptible to magnification of error as a run proceeds.

*Results.* Initial rates of reaction were obtained with considerable accuracy since  $[\text{Sn(II)}]$  vs.  $t$  gave a straight line for several points when  $[\text{Sn(II)}]_0 \approx 0.1$  M (see Fig. 1). At low  $[\text{Sn(II)}]$ , reactions deviated from zero order toward first order in  $[\text{Sn(II)}]$  and approximated first order at the lowest  $[\text{Sn(II)}]$  employed. Reactions were first order in  $\text{Nb(V)}$  and in  $\text{ClO}_4^-$  for  $[\text{ClO}_4^-] \leq 0.1$  M. Most runs recorded in Fig. 1 fit the rate law

$$-\frac{d[\text{Sn(II)}]}{dt} = \frac{800[\text{Nb(V)}][\text{ClO}_4^-][\text{Sn(II)}]}{1 + 92[\text{Sn(II)}]} \quad (2)$$

From eqn. (1), constants may be estimated:  $4k_1 = 8.7 \text{ M}^{-1} \text{ min}^{-1}$ ,  $k_2/k_{-1} = 92$ . Using these constants,  $[\text{Sn(II)}]$  vs.  $t$  was calculated for each run, giving curves recorded in Fig. 1. The lines are

Table 1. Sn(II) Reduction of  $\text{ClO}_4^-$ .

Run	$[\text{Sn(II)}]_0$	$10^4[\text{Nb(V)}]$	$[\text{ClO}_4^-]_0$	$10^4$ Init. Rate $\text{M min}^{-1}$	$4K_1k_2^a$ $\text{M}^{-2} \text{min}^{-1}$
L	0.098	12.5	0.028	2.78	810
M	0.099	25	0.024	4.47	760
Q	0.100	25	0.025	3.6	670
Y	0.109	30	0.0237	4.0	825
N	0.10	5	0.234	9.0	780
R	0.10	2.5	0.234	3.67	640
T	0.10	2.5	0.234	3.77	650
X	0.10	2.0	0.237	2.5	540
P	0.04	5.0	0.0934	3.20	800
S	0.04	2.0	0.0934	1.23	770
V	0.013	2.5	0.100	1.28	867
W	0.010	2.5	0.059	0.60	780
K <sup>b</sup>	0.070	5.0	0.2336	3.17	290 <sup>b</sup>

<sup>a</sup> Assume  $k_2/k_{-1}=92$ ;  $K_1=k_1/k_{-1}$ . Values from initial rates. Fig. 1 shows fit of plots of complete runs for  $4K_1k_2=800$ . Runs with low values for  $4K_1k_2$  otherwise fit the general rate law. The values of  $k_1$  are probably lowered by media changes in which activities of  $\text{H}^+$  or  $\text{Cl}^-$  are lowered. <sup>b</sup>  $[\text{Sn(IV)}]=0.225 \text{ M}$ .

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  $[\text{ClO}_4^-]$  and  $[\text{Sn(II)}]$  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  $[\text{Sn(II)}]$  about 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  $k_2/k_{-1}$  and lower values for  $4K_1k_2$ .  $[\text{ClO}_4^-]>0.2$  and  $[\text{Sn(IV)}]_0>0.05$  appear to effect inhibition of reaction not consistent with changes occurring during runs in which  $[\text{ClO}_4^-]<0.1$  and  $[\text{Sn(IV)}]$  increase as Sn(II) is consumed. Vaporization of HCl on addition of 12 M  $\text{HClO}_4$  and formation of  $\text{SnCl}_6^{2-}$  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



#### PERRHENATE CATALYZED REDUCTION OF NITRATE

Tribalat<sup>9</sup> 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  $\text{N}_2\text{O}$  (or  $\text{H}_2\text{N}_2\text{O}_2$ ). 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 studies<sup>10-12</sup> indicate that Sn(II) reduces Re(VII) to Re(V) rapidly during a potentiometric titration, and thence 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  $25.0 \pm 0.1$  °C. Aliquot samples were removed from time to time and quenched in standard iodine solution containing potassium iodide. Excess iodine was titrated with  $\text{S}_2\text{O}_3^{2-}$  or measured spectrophotometrically as  $\text{I}_3^-$ . The ionic strength was maintained at 3.0 using 3 M HCl and 3 M  $\text{HNO}_3$ .

*Results.* Reactions with  $[\text{ReO}_4^-]>10^{-4}$  were too fast to measure using our techniques, so  $[\text{ReO}_4^-]$  was held at  $10^{-5}$  to  $10^{-6}$  M level. A drastic fall-off in rates was observed if  $[\text{NO}_3^-]$  was decreased below 0.6 M. With  $[\text{NO}_3^-]>0.8 \text{ M}$ , two limiting rate laws are obtained. At high  $[\text{Sn(II)}]$  ( $>0.02 \text{ M}$ )

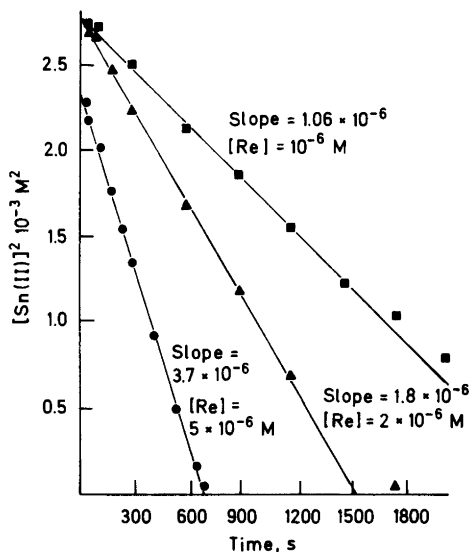


Fig. 2. Inverse first order  $[\text{Sn(II)}]$  dependence at high  $[\text{Sn(II)}]$ . ■, 1.38 M  $\text{NO}_3^-$  ( $k' = 0.56$ ); ▲, 1.35 M  $\text{NO}_3^-$  ( $k' = 0.50$ ); ●, 1.27 M  $\text{NO}_3^-$  ( $k' = 0.46$ ).

$$-\frac{d[\text{Sn(II)}]}{dt} = \frac{k'[\text{NO}_3^-]^2[\text{Re}]}{[\text{Sn(II)}]} \quad (3)$$

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

At low  $[\text{Sn(II)}]$

$$-\frac{d[\text{Sn(II)}]}{dt} = k''[\text{NO}_3^-][\text{Re}][\text{Sn(II)}] \quad (4)$$

Plots of  $\log[\text{Sn(II)}]$  give straight lines proportional to  $[\text{NO}_3^-]$  and  $[\text{Re}]$ . (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 perrhenate primarily to Re(V). The present authors, however, observed that the reaction is measurably slow if titrations are performed with  $10^{-3} \text{ M}$  reagents. It is judged that this reaction is of comparable rate to the catalyses at higher  $[\text{NO}_3^-]$  and  $[\text{Sn(II)}]$  when  $[\text{ReO}_4^-] \sim 10^{-6} \text{ M}$ . Re(V) is oxidized to Re(VII) by nitrate. Re(V) disproportionates slowly and irreversibly to give inert  $\text{ReCl}_6^{2-}$  and  $\text{ReO}_4^-$ .

The drastic decrease in catalysis at low nitrate concentration is attributed to the failure of nitrate

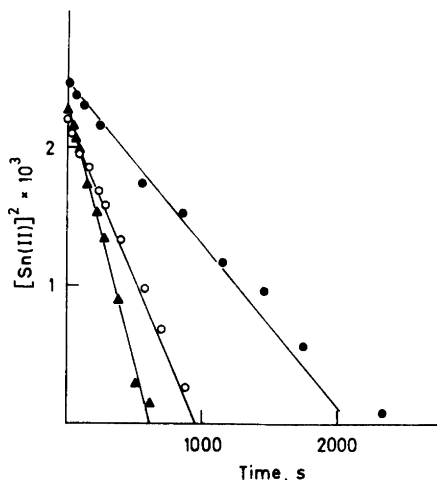


Fig. 3. Inverse first order  $[\text{Sn(II)}]$  dependence at high  $[\text{Sn(II)}]$ .  $[\text{Re}] = 5 \times 10^{-6} \text{ M}$ . ●,  $[\text{NO}_3^-] = 0.67 \text{ M}$ , Slope =  $1.15 \times 10^{-6}$ ,  $k = 0.51$ ; ○,  $[\text{NO}_3^-] = 1.02 \text{ M}$ , Slope =  $2.53 \times 10^{-6}$ ,  $k =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

oxidation of Re(V) to compete with disproportionation. The inverse first order in Sn(II) at high  $[\text{Sn(II)}]$  is attributed to the predominance of

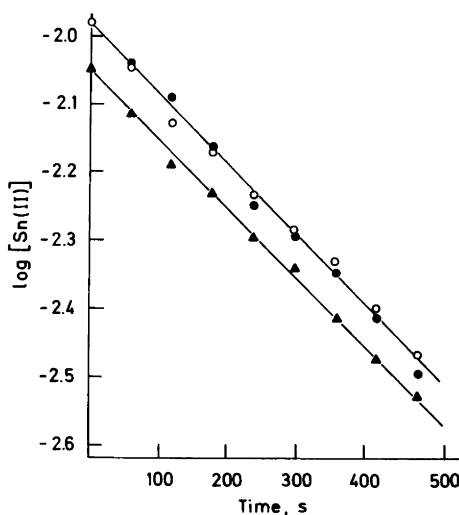
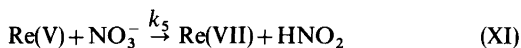
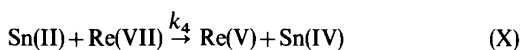
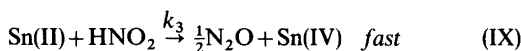
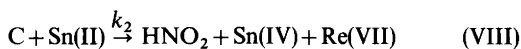


Fig. 4. First order  $[\text{Sn(II)}]$  dependence at low  $[\text{Sn(II)}]$ . ●,  $[\text{NO}_3^-] = 0.679 \text{ M}$ ,  $[\text{ReO}_4^-] = 10^{-6} \text{ M}$ ; ○,  $[\text{NO}_3^-] = 1.13 \text{ M}$ ,  $[\text{ReO}_4^-] = 6 \times 10^{-7} \text{ M}$ ; ▲,  $[\text{NO}_3^-] = 1.69 \text{ M}$ ,  $[\text{ReO}_4^-] = 4 \times 10^{-7} \text{ M}$ ; 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  $\text{NO}_3^-$ . It is concluded that  $\text{ReO}_4^-$  is the catalytic species, that it forms a weak complex with  $\text{NO}_3^-$  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.



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:

$$-\frac{d[\text{Sn(II)}]}{dt} = \frac{k_1 k_2 [\text{Sn(II)}][\text{NO}_3^-][\text{Re(VII)}]}{k_{-1} + k_2 [\text{Sn(II)}]} \quad (5)$$

$$\frac{[\text{Re(VII)}]}{[\text{Re(V)}]} = \frac{k_5 [\text{NO}_3^-]}{k_4 [\text{Sn(II)}]}$$

$$-\frac{d[\text{Sn(II)}]}{dt} = \frac{k_1 k_2 k_5 [\text{NO}_3^-]^2 [\text{Re(V)}]}{k_{-1} k_4 + k_2 k_4 [\text{Sn(II)}]} \quad (6)$$

When  $[\text{Sn(II)}] > 0.03 \text{ M}$ , most of the rhenium is present as Re(V), and equation (6) reduces to eqn. (3). When  $[\text{Sn(II)}] < 0.01 \text{ M}$ , 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.<sup>2</sup> 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 disproportionates rapidly in similar systems in hydrochloric acid and may differ as well in other properties. Perhaps the inertia of  $\text{ReOCl}_5^{2-}$  does not allow both coordination with  $\text{NO}_3^-$  and nucleophilic attack by  $\text{SnCl}_3^-$  to occur. Mo(IV) is undoubtedly less firmly coordinated to  $\text{O}^{2-}$  and  $\text{Cl}^-$  and may interact more readily with the inert 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

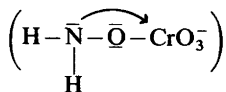
*Nb(V) and W(VI) as catalysts.* We may directly compare niobate catalysis with tungstate catalysis of the reduction of  $\text{HClO}_4$  in conc. hydrochloric acid. The rate of formation of the  $(\text{Nb(V)ClO}_4)$  complex ( $k_1 = 2.2 \text{ M}^{-1} \text{ min}^{-1}$ ) is thirteen times as large as that for the  $(\text{W(VI)ClO}_4)$  complex ( $k_1 = 0.17 \text{ M}^{-1} \text{ min}^{-1}$ ). The ratio  $k_2/k_{-1}$  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  $\text{SnCl}_2$  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)<sup>9</sup> and Mo(IV)<sup>14</sup> respectively under the conditions for catalytic reduction of  $\text{NO}_3^-$  and  $\text{ClO}_4^-$ .

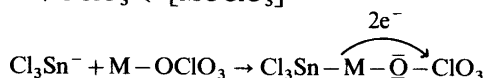
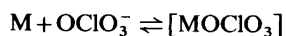
Re(V) and Mo(IV) each disproportionate. Mo(IV) disproportionates rapidly<sup>14</sup> and also serves as a catalyst for oxo-anion reduction. Re(V) is more stable and non-catalytic, but may be oxidized directly by nitrate or reduced to Re(IV) by SnCl<sub>2</sub>. The kinetics of catalysis indicate that 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<sub>4</sub><sup>-</sup> in a (Mo(VI)ClO<sub>4</sub>) complex<sup>1</sup> makes catalysis by Mo(VI) unobservable. Since ReOCl<sub>2</sub><sup>3-</sup> is directly oxidized by NO<sub>3</sub><sup>-</sup>, it is reasonable that electrons transferred to (Re(VII)-NO<sub>3</sub>) should yield reduced nitrogen directly according to reaction VIII in our mechanism.

*The role of oxo-metallates in reduction of oxo-anions.* Positive centers of fully oxidized non-metals such as Cl(VII) in ClO<sub>4</sub><sup>-</sup> and N(V) in NO<sub>3</sub><sup>-</sup> are protected by O<sup>2-</sup> and π-electron clouds from nucleophilic attack by species such as SnCl<sub>3</sub><sup>-</sup> (the most reactive SnCl<sub>n</sub><sup>2-n</sup> complex).<sup>5</sup> No direct reaction of Sn(II) with NO<sub>3</sub><sup>-</sup> or ClO<sub>4</sub><sup>-</sup> is observed at room temperature in dilute aqueous acid solutions. The results of these and previous studies<sup>15</sup> suggest that the *oxo-metallates form complexes having electron transfer pathways between Sn(II) and oxo-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 oxo-nonmetallates such as HPO<sub>3</sub><sup>2-</sup>, NH<sub>2</sub>OH, etc.<sup>16</sup> In two-electron Cr(VI) oxidations, electrons are transferred through an O-bridge in a chromate ester.



In these catalytic systems the labile oxo-metallates form weak O-bridged complexes to inert non-metallates. 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.



The activated state involves direct 2e<sup>-</sup> 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.

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Received July 15, 1978.