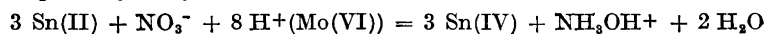# The Mechanism of Reduction of Nitrate

## II. The Kinetics and Mechanism of the Molybdate Catalyzed Reduction of Nitrate by Sn(II) in Acid Solution

G. P. HAIGHT, Jr.* and ALFRED KATZ**

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Molybdate catalyses the reduction of nitrate by Sn(II) in acid solution. In 3.0 M hydrochloric acid the reduction takes place in two steps to hydroxylamine and ammonia. For the reaction

$$3 \text{ Sn(II)} + \text{NO}_3^- + 8 \text{ H}^+(\text{Mo(VI)}) = 3 \text{ Sn(IV)} + \text{NH}_3\text{OH}^+ + 2 \text{ H}_2\text{O}$$

the rate law is:

$$-d[\text{Sn(II)}]/dt = \frac{k'[\text{Sn(II)}][\text{NO}_3^-][\text{Mo}]}{1 + k''[\text{Mo}]^{1/2} + k'''[\text{NO}_3^-]}$$

In 3.0 M sulfuric acid the reaction is much slower and the reduction of nitrate proceeds only to nitrous oxide. For the reaction

$$4 \text{ Sn(II)} + 2 \text{ NO}_3^- + 10 \text{ H}^+ = (\text{Mo(VI)}) 4 \text{ Sn(IV)} + \text{N}_2\text{O} + 5\text{H}_2\text{O}$$
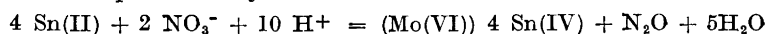
the rate law is:

$$-d[\text{Sn(II)}]/dt = k''''[\text{Mo}]^{1/2}[\text{NO}_3^-]$$

A general mechanism is derived for these and similar reductions catalyzed by molybdate. Comparisons are made with rate constants derived from catalytic polarographic waves previously reported.

The first paper [1] in this series has described the pattern of products obtained in molybdate catalyzed reductions of nitrate effected by stannous ions. This product pattern apparently depends on events occurring after the initial step in the reduction of nitrate. Since the function of molybdate catalyst is apparently wholly that of rendering the robust nitrate ion reducible, it is important to understand the means by which this initial step is accomplished. In this paper the kinetics of the reduction of nitrate in hydrochloric acid to-
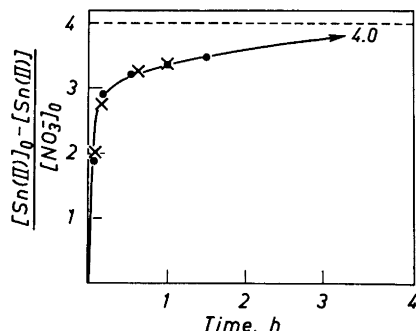
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*Fig. 1.* A plot of the number of moles of Sn(II) consumed per mole of nitrate added *vs.* time demonstrating the sharp change in rate after all the nitrate is converted to hydroxylamine. ● Start with Mo(VI) 2.3 × $10^{-4}$ M. × Start with Mo(V) 2.3 × $10^{-4}$ M. $[Sn(II)]_0 = 0.10$ M. $[NO_3^-]_0 = 0.02$ M. $T = 25°C$.

gether with preliminary results in sulfuric acid are described. Previously, Kolthoff, Sandell, and Moskowitz[2] have employed molybdate to catalyze the reduction of nitrate by ferrous ions at 100°C for analytical purposes. Tribalat[3] has reported on the perrhenate catalyzed reductions of nitrate in which she assumes Re(V) to be the catalytic species. Johnson and Robinson [4] have discussed polarographic waves representing molybdate catalyzed reductions of nitrate. Haight [5] has interpreted these catalytic waves as resulting from the catalytic activity of Mo(IV) produced by the reduction of molybdate. Similar catalytic activity of molybdate toward perchlorate [6-8] and hydroxylamine [9] has already been reported. We shall attempt to relate the present findings to those recorded for other systems. The function of molybdate in rendering nitrate reducible is particularly important in view of its required presence for the enzymatic reduction of nitrates occurring in the biochemistry of plants [10].

## EXPERIMENTAL

The conditions of experiment, preparation of solutions, and methods of chemical analysis are given in the previous paper [1]. All kinetic runs were performed in a thermostat at 25°C. Ion normality was maintained at 3.0.

## RESULTS

*Kinetics of the reaction in 3.0 molar hydrochloric acid.* The rate of reduction of nitrate to hydroxylamine [1] proved to be so much faster than the subsequent reduction of hydroxylamine to ammonia [9] that it proved possible to consider the reaction:

$$\overset{(Mo(VI))}{3\ Sn(II) + NO^- + 8\ H^+ = 3\ Sn(IV) + NH_3OH^+ + 2\ H_2O} \qquad (I)$$
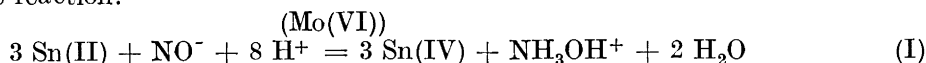
as a separate process. In this study, catalysis was so effective that molybdate concentrations employed were in the range of $2 \times 10^{-9}$ to $6 \times 10^{-5}$ M. At such low concentrations it was not possible to ascertain by colorimetric means which oxidation state of molybdenum was the dominant species present during a run as in previous studies [7-9]. It was impossible to distinguish runs begun

**Fig. 2.** Plots of log [Sn(II)] vs. time for runs containing large excess of nitrate demonstrating 1st order dependence on [Sn(II)]. Slopes are approximately proportional to [Mo(VI)] for constant excess [NO$_3^-$].

| | | |
|---|---|---|
| +, ●, O, ▲ | 0.16 M NO$_3^-$ | |
| × | 0.12 M NO$_3^-$ | |
| + | 0.37 × 10$^{-6}$ M Mo | |
| ● | 1.50 × 10$^{-6}$ M Mo | |
| × | 4.3 × 10$^{-6}$ M Mo | |
| O | 18.7 × 10$^{-6}$ M Mo | |
| ▲ | 37.5 × 10$^{-6}$ M Mo | |
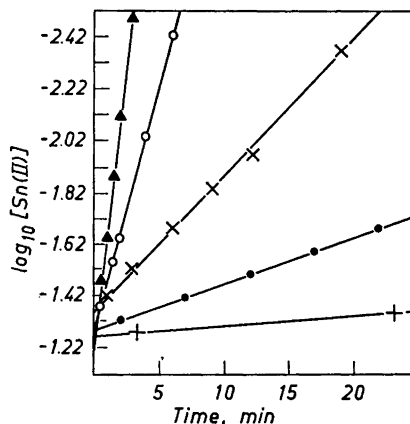
with Mo(VI) from those begun with Mo(V). Steady state conditions are achieved at the start of each run contrary to experience with the reduction of perchlorate [7] and hydroxylamine [9] and also contrary to the experience with nitrate in sulfuric acid to be described. Fig. 1 illustrates the separability of the two steps involved in the reduction of nitrate to ammonia and the indistinguishability of runs started with Mo(VI) and with Mo(V).

In the following discussion, overall chemical reactions will be numbered consecutively with Roman numerals. Mathematical equations will be numbered consecutively with Arabic numerals and will be referred to as "eqn. ( )" in the text. Individual chemical steps used in reaction mechanisms will also be numbered consecutively using Arabic numerals and will be referred to as "reaction ( )" in the text. A (±) indicates a reversible reaction. Rate constants $k_n$ and equilibrium constants $K_n$ will be assigned the same number as the
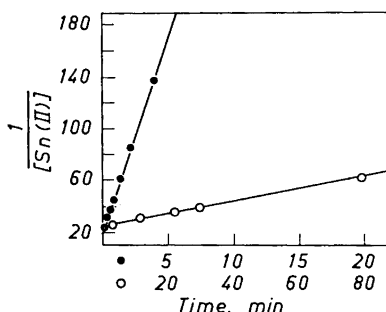


**Fig. 3.** Plots of 1/[Sn(II)] vs. time for runs containing [Sn(II)]$_0$ = 3[NO$_3^-$]$_0$.

| | | |
|---|---|---|
| O | 1.5 × 10$^{-6}$ M Mo |
| ● | 5.26 × 10$^{-5}$ M Mo |
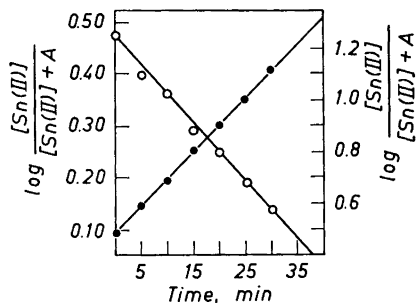


**Fig. 4.** Plots of log [(Sn(II)]/([Sn(II)] +$A$) for runs with neither Sn(II) nor NO$_3^-$ present in high excess.

| | | |
|---|---|---|
| O | $A$ = −0.0112 | left hand ordinate |
| ● | $A$ = +0.1495 | right hand ordinate |

reaction they represent. Empirical constants used in experimental rate laws will be given distinguishing superscripts.

*Determination of the rate law in hydrochloric acid.* For runs containing an excess of nitrate, plots of log [Sn(II)] *vs.* time give straight lines with slopes very nearly proportional to the concentration of molybdenum as shown in Fig. 2. In runs in which [Sn(II)] = 3 [NO$_3^-$] plots of 1/[Sn(II)] *vs.* time gave straight lines as shown in Fig. 3. These combined results suggest a rate law showing first order dependence on all three reagents.

$$-\mathrm{d}[(\mathrm{Sn(II)}]/\mathrm{d}t = k_{\mathrm{obs}}[\mathrm{Sn(II)}][\mathrm{NO_3^-}][\mathrm{Mo}] \qquad (1)$$

Eqn. (1) predicts that for runs in which [Sn(II)] ⧧ 3[NO$_3^-$] plots of log ([Sn(II)]/([Sn(II)] + $A$) *vs.* $t$ should give straight lines. $A$ = 3[NO$_3^-$]−[Sn(II)] and is constant for a given run. Fig. 4 demonstrates the validity of the above prediction.

Calculation of $k_{\mathrm{obs}}$ from the slopes of the lines obtained in plots such as those given in Fig. 2—4 showed that $k_{\mathrm{obs}}$ decreases with increasing molybdenum concentration when nitrate is not present in large excess according to the law:

$$k_{\mathrm{obs}} = k'/(1 + k'''[\mathrm{Mo}]^{\frac{1}{2}}) \qquad (2)$$

This finding is similar to that observed with polarographic catalytic currents which were proportional to the first power of molybdenum concentration if it was below $10^{-5}$ M and proportional to the square root of the molybdenum concentration if it was above $10^{-4}$ M.

It was also found that $k_{\mathrm{obs}}$ decreased with increasing concentrations of nitrate when it was present in great excess according to the law:

$$k_{\mathrm{obs}} = k'/(1 + k''''[\mathrm{NO_3^-}]) \qquad (3)$$

Plots of 1/$k_{\mathrm{obs}}$ *vs.* [Mo]$^{\frac{1}{2}}$ and *vs.* [NO$_3^-$] are shown in Fig. 5. The considerable scatter shown in the plot of 1/$k_{\mathrm{obs}}$ *vs.* [NO$_3^-$] reflects the interdependence of the two correction terms. Points for a given nitrate concentration converge on the line drawn if the effect due to molybdenum inhibition is allowed for. From the slopes and intercepts of the lines in Fig. 5 estimated values of $k'$, $k''$, and $k'''$ may be obtained. By successive approximations the values $k'' = 312$ (l/m)$^{\frac{1}{2}}$ and $k''' = 30$ l/m were obtained. Using these values, $k'$ was calculated for over thirty runs from plots similar to those in Figs. 2, 3, and 4. The value of $k'$ thus obtained is $1.96 \times 10^4$ (l/m)$^{\frac{1}{2}}$sec$^{-1}$ with a mean deviation of ± 0.08.
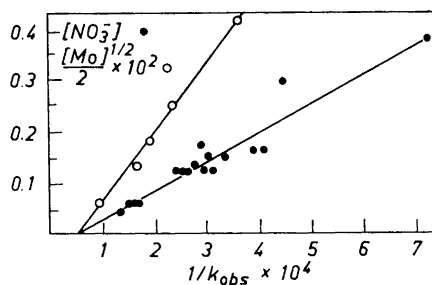


*Fig. 5.* Estimation of inhibition terms in the rate law. A plot of 1/$k_{\mathrm{obs}}$ × 10$^4$ (abscissa) *vs.* 10$^3$[Mo]$^{\frac{1}{2}}$ (open dots), and *vs.* [NO$_3^-$] (closed dots). Intercept gives 1/$k'$. Slopes give $k''/k'$ and $k'''/k'$, respectively.

*Table 1.* Rate constants from individual runs in 3 M HCl. $k'' = 312$. $k''' = 30$.

| Run | $[Sn(II)]_0$ m/l | $[NO_3^-]_0$ m/l | $[Mo]$ $\mu$m/l | Plot vs. t | $k_{obs} \times 10^3$ | $k' \times 10^3$ | Remarks |
|---|---|---|---|---|---|---|---|
| 8 | 0.050 | 0.370 | 25 | $\log[Sn(II)]$ | 1.38 | 18.8 | |
| 9 | 0.048 | 0.159 | 0.002 | » | 2.59 | 15 | only 2 points |
| 11 | 0.048 | 0.150 | 1.5 | » | 3.0 | 17.7 | |
| 12 | 0.048 | 0.128 | 4.26 | » | 3.6 | 19.6 | |
| 13 | 0.048 | 0.160 | 18.7 | » | 2.44 | 17.5 | |
| 14 | 0.048 | 0.159 | 37.5 | » | 2.58 | 20.0 | |
| 17 | 0.048 | 0.286 | 1.43 | » | 2.22 | 22.0 | |
| 25 | 0.048 | 0.150 | 1.5 | » | 3.30 | 19.4 | Same as 11 |
| 31 | 0.040 | 0.122 | 12.2 | » | 3.10 | 17.7 | 5 duplicates |
| 32 | 0.040 | 0.122 | 6.0 | » | 3.34 | 18.3 | 5 duplicates |
| 33 | 0.040 | 0.122 | 0.5 | » | 3.88 | 19.3 | 5 duplicates |
| 34 | 0.040 | 0.122 | 1.0 | » | 3.88 | 19.4 | 4 duplicates |
| 35 | 0.040 | 0.122 | 2.41 | » | 4.10 | 21.2 | 3 duplicates |
| 36 | 0.040 | 0.122 | 2.41 * | » | 4.10 | 21.2 | 3 duplicates |
| 37 | 0.040 | 0.122 | 6.00 * | » | 3.48 | 19.2 | 2 duplicates |
| 38 | 0.033 | 0.122 | 1.00 * | » | 4.15 | 20.8 | |
| 45 | 0.033 | 0.127 | 2.00 | » | 4.00 | 21.0 | 2 duplicates |
| 47 a | 0.031 | 0.174 | 1.57 | » | 3.62 | 23.0 | 25°C |
| 47 b | 0.031 | 0.174 | 1.57 | » | 3.05 | 19.7 | 22°C |
| 39 | 0.0322 | 0.061 | 2.4 | $\log\dfrac{[Sn(II)]}{[Sn(II)]+A}$ | 6.24 | 19.8 | |
| 40 | 0.0279 | 0.0483 | 2.4 | » | 7.03 | 19.6 | |
| 41 | 0.0645 | 0.0177 | 6.0 | » | 10.29 | 18.4 | |
| 42 | 0.0645 | 0.0177 | 11.7 | » | 9.81 | 21.4 | |
| 43 | 0.0627 | 0.0177 | 28.6 | » | 8.19 | 20.6 | |
| 5 | 0.096 | 0.024 | 65.0 | » | 5.78 | 19.7 | |
| 18 | 0.0465 | 0.0158 | 52.6 | $1/[Sn(II)]$ | 5.0 | 17.2 | |
| 26 | 0.0373 | 0.0124 | 1.5 | $1/[Sn(II)]$ | 15.0 | 22.0 | |

* Reaction started with Mo(V).

$A = 3[NO_3^-]_0 - [Sn(II)]_0$

Data describing the initial composition of all runs and the values of $k_{obs}$ and $k'$ obtained for each run are collected in Table 1. The rate law has been found valid for nitrate concentrations between 0.005 and 0.37 M, Sn(II) concentrations between 0.002 and 0.10 M, and molybdate concentrations between $10^{-7}$ and $10^{-4}$ M. (Two points obtained with a run $10^{-9}$ M in molybdenum gave gave $k_{obs}$ predicted by the above constants.) The equation best describing the kinetics of this reaction at 25° in 3.0 M hydrochloric acid is then:

$$\mathrm{d}[Sn(II)]/\mathrm{d}t = \frac{1.96 \times 10^4[Sn(II)][NO_3^-][Mo]}{1 + 312[Mo]^{1/2} + 30[NO_3^-]} \qquad (4)$$

if $t$ is in seconds and concentrations in moles per liter.

*Effects of other species present during runs on the reaction rate.* Hydroxylamine could not be added initially without giving interference through its reduction. but it seems unlikely that this product could otherwise affect the kinetics. Stannic chloride was added to one run causing a 20 % increase in reaction rate but not altering the form of the rate law. This small effect could have resulted

from an increase in hydrogen ion resulting from hydrolysis or a change in the concentration of free chloride ion. We are confident that Sn[IV) does not inhibit the reaction in any case. Substitution of lithium chloride for hydrogen chloride showed that the rate is roughly proportional to the square of the hydrogen ion concentration in the vicinity of 3.0 M. For $[H^+] < 2.0$ M the reaction order in Sn(II) changes introducing complexities which have not been further investigated as yet. Phosphoric acid in addition to 3.0 M hydrochloric acid had no effect on the reaction rate. The effect of substituting sulfuric acid for hydrochloric acid will be discussed separately.

Eqn. (4) has been tested for typical runs as follows: Let

$y$ = the number of transformations in moles per liter of nitrate ion at time $t$.
$a$ = the original concentration of nitrate ion in moles per liter.
$3b$ = the original concentration of Sn(II) in moles per liter.
$A = (1 + 312[Mo]^{1/2})/(1.96 \times 10^4[Mo])$
$B = 0.0015/[Mo]$

$A$ and $B$ are constants for any given run but change from run to run. Eqn. (4) may now be transformed to read:

$$\mathrm{d}t/\mathrm{d}t = \frac{A}{(a-y)(b-y)} + \frac{B}{(b-y)}$$

which integrates to give:

$$t = \frac{A}{(a-b)} \ln \frac{b(a-y)}{a)b-y)} + B \ln \frac{b}{|(b-y)} \tag{5}$$

If $a = b$, eqn. (5) becomes:

$$t = A/(a-y) - A/a + B \ln(a/(a-y))$$

Values of $t$ are calculated for different values of $y$ and compared with observed times. Results of such calculations for typical runs appear in Tables 2—5.

Given the rate law in eqn. (4), it is now possible to test the assumption that reduction of nitrate to hydroxylamine is essentially complete before reduction of hydroxylamine to ammonia becomes significant. The maximum concentration of hydroxylamine will occur when the rate of reduction of hydroxvlamine equals the rate of reduction of nitrate. Thus

$$\mathrm{d}[NO_3^-]/\mathrm{d}t = \mathrm{d}[NH_2OH]/\mathrm{d}t$$

For a run employing low molybdate and low nitrate concentrations we can simply employ the numerators of rate laws given by eqn. (4) and in Ref.[10].

$$2 \times 10^4(a-y)(b-y)[Mo] = 3(0.02(b-y)y[Mo]^{1/2}) \tag{6}$$

where $y$ is the concentration of hydroxylamine. The factor 3 appears due to the assumption that $[Sn(II)] = 3b-3y$. This in fact assumes that virtually no hydroxylamine has been reduced, but the consequences of so assuming are not great as seen below. From eqn. (6) we see that maximum hydroxylamine concentration appears when

$$y/(a-y) = 3.3 \times 10^5 [Mo]^{1/2}$$

*Table 2.* Chronometric integral for run 33 (excess $NO_3^-$) *cf.* Eqn. (5). $a = 0.122$. $b = 0.0112$. $A = 122$. $B = 3000$.

| $t_{obs}$ sec | $a-y$ | $10^3(b-y)$ | $\dfrac{A}{(a-b)}\ln\dfrac{b(a-y)}{a(b-y)}$ | $B\ln[b/(b-y)]$ | $t_{calc}$ sec |
|---|---|---|---|---|---|
| 607 | 0.118 | 9.470 | 147 | 495 | 658 |
| 1 211 | 0.1164 | 8.108 | 308 | 972 | 1 280 |
| 1 803 | 0.1154 | 6.922 | 470 | 1 449 | 1 919 |
| 2 410 | 0.1144 | 5.888 | 640 | 1 923 | 2 563 |
| 3 000 | 0.1136 | 5.052 | 794 | 2 390 | 3 184 |
| 3 600 | 0.1130 | 4.360 | 955 | 2 822 | 3 777 |
| 4 200 | 0.1120 | 3.620 | 1 158 | 3 370 | 4 528 |
| 4 804 | 0.1120 | 3.280 | 1 367 | 3 670 | 5 037 |

*Table 3.* Chronometric integral for run 39 (small excess of $NO_3^-$). $a = 0.0580$. $b = 0.007124$. $A = 31$. $B = 625$. $t = 0$ at first measured point, 5 min after start of run.

| $t_{obs}$ | $a-y$ | $10^3(b-y)$ | $\dfrac{A}{(a-b)}\ln\dfrac{b(a-y)}{a(b-y)}$ | $B\ln[b/(b-y)]$ | $t_{calc}$ |
|---|---|---|---|---|---|
| 300 | 0.0562 | 5.315 | 155 | 182 | 337 |
| 600 | 0.0550 | 4.109 | 297 | 344 | 641 |
| 900 | 0.0542 | 3.346 | 420 | 472 | 892 |
| 1 200 | 0.0534 | 2.520 | 567 | 650 | 1 217 |
| 1 500 | 0.0529 | 1.975 | 715 | 800 | 1 515 |

*Table 4.* Chronometric integral for run 18. (Equivalent Sn(II) and $NO_3^-$). $a = b = 0.0109$. $A = 3.16$. $B = 28.5$. $t = 0$, one minute after start.

| $t_{obs}$ | $a-y$ | $A/(a-y)-A/a$ | $B\ln[a/(a-y)]$ | $t_{calc}$ |
|---|---|---|---|---|
| 60 | 0.00890 | 65 | 13 | 78 |
| 120 | 0.00757 | 126 | 23 | 149 |
| 305 | 0.00543 | 292 | 46 | 338 |
| 600 | 0.00401 | 498 | 63 | 561 |
| 1 200 | 0.00243 | 1 010 | 77 | 1 087 |

This run is particularly sensitive to small initial errors which would cause larger and larger deviations from equivalence as the run progressed.

This means that even at the lowest concentrations of molybdate employed, over 99 % of the nitrate has been converted to hydroxylamine before the rates become equal.

*Determination of the rate law in 3.0 M sulfuric acid.* Only a few runs were made in this medium, but the contrast in the observed kinetics with those observed in hydrochloric acid is so striking that we feel obliged to report our preliminary findings. In the absence of chloride, the reduction of nitrate is extremely slow. In general, we employed one thousand fold more catalyst, yet had to follow reactions for several days to obtain significant change unless a very large excess of nitrate was employed. All the runs employed Mo(VI) as a starting material. Initial periods of faster reaction involving 30 minutes to several hours were observed. Steady state conditions apparently coincided

with the complete conversion of Mo(VI) to Mo(V) which is not a fast process in the absence of chloride. The reaction is slower than the corresponding catalytic reduction of perchlorate under similar conditions. It is inhibited by chloride ions if $[Cl^-]/[Sn(II)] < 2.0$, and then accelerated by higher concentrations of chloride. The reaction stoichiometry is

$$10\ H^+ + 4\ Sn(II) + 2\ NO_3^- = 4\ Sn(IV) + N_2O + 5\ H_2O \qquad (II)^{[1]}$$
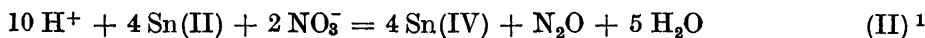
The reaction rate after the steady state is reached is independent of the concentration of Sn(II), directly proportional to the nitrate concentration and to the square root of the molybdenum concentration. The rate law when essentially all the molybdenum is present as Mo(V) is thus found to be:

$$-d[Sn(II)]/dt = k''''[Mo]^{1/2}[NO_3^-] \qquad (7)$$

The integrated form of eqn. (7) can be given as

$$t = A\ \ln(a/(a-y))$$

where $t$ is the time in seconds, $A = 2/k''''[Mo]^{1/2}$, $a$ is the initial concentration of nitrate ion, and $y$ is the number of transformations of nitrate ion in moles per liter. $A$ is contant for a given run, but varies from run to run. Tables 6 to 9 show calculated vs. observed times for points obtained after reaching steady state conditions and using $k'''' = 1.2 \times 10^{-4}$ (l/m)$^{1/2}$sec$^{-1}$.

The reaction in sulfuric acid needs further investigation both to confirm these preliminary results and to explore the complicated effects of chloride ion upon the kinetics and stoichiometry of the reaction.

MECHANISM¦ OF THE MOLYBDATE CATALYZED REDUCTION OF NITRATE

Reductions in hydrochloric acid

The catalytically active oxidation state of molybdenum must be chosen among the stable VI, V, and III states and the unstable IV state. Mo(VI) forms a complex with nitrate [11] and catalyzes reduction of nitrate by ferrous ion at 100°C.[2] Ferrous ion does not reduce Mo(VI). Dimeric Mo(V) is oxidized directly by perchlorate again at 100°C and this reaction is responsible for the catalytic electroreduction of perchlorate studied by Rechnitz [8]. In previous studies of the reduction of perchlorate, nitrate, and hydroxylamine one of the authors has found, using stannous ions instead of ferrous ions, or, using more negative potentials than those used by Rechnitz, that the unstable species, Mo(IV), is catalytically active. In the latter cases catalyses attributed to Mo(IV) are far more effective than those attributed to Mo(V) or Mo(VI). Mo(III) is noncatalytic in polarographic reductions and can thus be ruled out.

Because Mo (VI) is instantly reduced by Sn(II) in hydrochloric acid and because no difference is observed between reactions started with Mo(VI) and Mo(V) we think it unlikely that Mo(VI) is the active species. In 3.0 M hydrochloric acid Mo(V) is the final product of reduction of Mo(VI) with Sn(II). In order to see if reoxidation of Mo(V) by nitrate ions could be involved in the catalysis, several experiments were performed on the direct oxidation of Mo(V). In each case a period of virtually no reaction was followed by a period of rather

*Table 5.* Chronometric integral for run 43 in hydrochloic acid. Sn(II) in excess. $t = 0$ at first recorded point, 4 min after start of the run. $a = 0.00770$. $b = 0.01089$. $A = 4.65$. $B = 52.5$.

| $t_{obs}$ sec | $10^3(a-y)$ m/l | $10^3(b-y)$ m/l | $\dfrac{A}{(a-b)} \ln \dfrac{b(a-y)}{a(b-y)}$ | $B \ln[b/(b-y)]$ | $t_{calc}$ sec |
|---|---|---|---|---|---|
| 60 | 6.80 | 9.975 | 61 | 5 | 66 |
| 240 * | 4.80 | 8.040 | 243 | 16 | 259 |
| 360 | 4.10 | 7.320 | 344 | 19 | 363 |
| 480 * | 3.43 | 6.627 | 464 | 27 | 491 |
| 660 | 2.76 | 5.963 | 621 | 34 | 655 |
| 662 * | 2.72 | 5.920 | 634 | 34 | 668 |
| 960 | 1.91 | 5.107 | 934 | 40 | 974 |
| 960 * | 1.98 | 5.177 | 894 | 39 | 933 |

\* Points from an alternate, identical run.

*Table 6.* Chronometric integral for run 2 in sulfuric acid. $A = 1.884 \times 10^4$. $a = 0.461$ m/l. $[Sn(II)]_0 = 0.125$ m/l. Mo $= 0.0077$. $k'''' = 1.2 \times 10^{-4}$.

| $t_{obs}$ seconds | $(a-y)$ m/l | $A \ln[a/(a-y)] = t_{calc}$ sec. | $-t_{obs}$ | $--t_{calc}$ |
|---|---|---|---|---|
| 90 | 0.4469 | 5 550 | 90 | 5 550 |
| 270 | 0.4441 | 7 050 | 180 | 1 390 |
| 630 | 0.4437 | 7 220 | 360 | 170 |
| 3 510 | 0.4366 | 10 250 | 2 880 | 3 030 |
| 7 230 | 0.4266 | 14 600 | 3 720 | 4 350 |
| 9 600 | 0.4171 | 18 750 | 2 370 | 4 150 |
| 9 990 | 0.4164 | 19 150 | 390 | 400 |
| 15 790 | 0.4051 | 24 400 | 5 800 | 5 280 |

This exploratory run was expected to be over in a few minutes. It shows the initial surge of reaction. Run 5 below shows how greater care eliminates the erratic behavior of later points. Low values of $\Delta t_{obs}$ are due to the initial surge at the start and to inadequate precautions against air oxidation later in the run.

*Table 7.* Chronometric integral for run 5 in sulfuric acid. $t = 0$ after 34 min to allow for initial surge. $A = 1.884 \times 10^5$. $a = 0.4420$ m/l. $[Sn(II)]_0 = 0.0736$ m/l.

| $t_{obs}$ sec. | $(a-y)$ m/l | $A \ln[a/(a-y)] = t_{calc}$. sec. |
|---|---|---|
| 3 540 | 0.4328 | 3 700 |
| 9 190 | 0.4196 | 9 770 |
| 9 850 | 0.4179 | 10 550 |
| 12 480 | 0.4113 | 13 400 |

*Table 8.* Chronometric integral for run 6 in sulfuric acid. $t = 0$ after 168 min to allow for initial surge \*. $A = 2.82 \times 10^5$. $a = 0.4415$. $[Sn(II)]_0 = 0.0720$.

| $t_{obs}$ sec. | $(a-y)$ m/l | $A \ln[a/(a-y)] = t_{calc}$. sec. |
|---|---|---|
| 3 180 | 0.4369 | 3 240 |
| 3 540 | 0.4365 | 3 445 |
| 19 920 | 0.4131 | 19 100 |

\* Note that runs 5 and 6 differ only in [Mo]. Each require the same number of transformations to reach steady state conditions.

*Table 9.* Chronometric integral for run 7 in sulfuric acid. (Equivalent $Sn(II)$ and $NO_3^-$). $t = 0$ after 24 h allowed for steady state *. $A = 2.42 \times 10^5$. $a = 0.0240$ m/l $= [Sn(II)]_0/2$.

| $t_{obs}$ sec. | $(a-y)$ m/l | $A \ln[a/(a-y)] = t_{calc.}$ sec. |
|---|---|---|
| 67 000 | 0.01850 | 63 000 |
| 67 700 | 0.01815 | 67 400 |
| 157 000 | 0.01215 | 160 000 |

* This length of time may not be necessary but was convenient because of the slowness of the reaction.

rapid reaction, indicating that an autocatalytic process was involved. The induction period involving 15 to 30 min convinced us that direct oxidation of Mo(V) by nitrate does not play a significant part in the catalytic process under study. The arguments against the stable states of molybdenum as active catalytic species bring us once again to consider that Mo(IV) is the active catalyst. This conclusion is also consistent with the effectiveness of catalysis in the present case being even greater than in those other cases where Mo(IV) was considered. This conclusion is also interesting in view of the fact that Tribalat [3] found it necessary to assume that Re(V), which is electronically similar to Mo(IV) is the catalytically active state of rhenium in reductions of nitrate by stannous chloride.
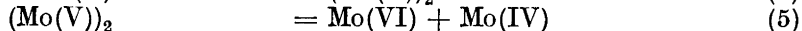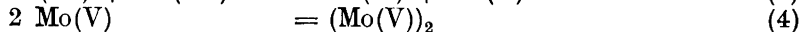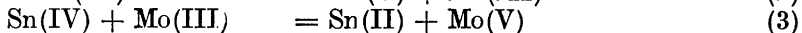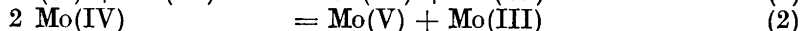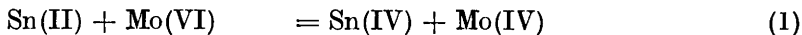
Bergh [12] has recently studied the reactions of Sn(II) and the the various oxidation states of molybdenum in hydrochloric acid. In concentrated hydrochloric acid the stoichiometric reaction:

$$2 \text{ Sn(II)} + 2 \text{ Mo(VI)} = 2 \text{ Sn(IV)} + \text{Mo(V)} + \text{Mo(III)} \qquad (III)$$
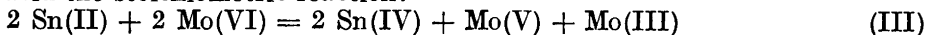
occurs, while in dilute hydrochloric acid the following is observed.

$$\text{Sn(II)} + 2 \text{ Mo(VI)} = \text{Sn(IV)} + (\text{Mo(V)})_2 \qquad (IV)$$
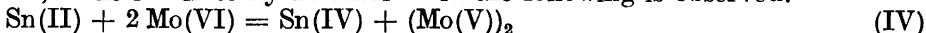
Sacconi and Cini [13] have studied the reversible dimerization of Mo(V) as concentrated hydrochloric acid is diluted. To explain reactions (III) and (IV) and some features of the catalytic reactions believed to involve Mo(IV) we propose the following closed system. These reactions are believed to be taking place in equilibria involving Sn(II), Sn(IV), and the various oxidation states of molybdenum.

| | | |
|---|---|---|
| Sn(II) + Mo(VI) | = Sn(IV) + Mo(IV) | (1) |
| 2 Mo(IV) | = Mo(V) + Mo(III) | (2) |
| Sn(IV) + Mo(III) | = Sn(II) + Mo(V) | (3) |
| 2 Mo(V) | = (Mo(V))₂ | (4) |
| (Mo(V))₂ | = Mo(VI) + Mo(IV) | (5) |

Reactions (1) and (2) together account for reaction (III) in concentrated hydrochloric acid. Reaction (1) accounts for initial surges of fast reaction observed when catalyses are started with Mo(VI) [7,9]. If reactions (1) and (2) occur in dilute acid as well, then (3) and (4) are required for obtaining essentially complete production of (Mo(V))₂. Reaction (5) is proposed both to close the sequence and as a possible initial source of Mo(IV) for catalyses begun with molybdenum in the (V) state. The known reaction of Mo(III) with Mo(VI) is omitted from
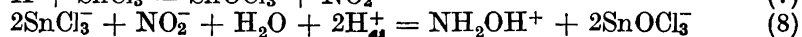
the sequence since its rate is not competitive with the rate of reaction $(1)^{12}$. The kinetics of catalytic reduction of species placed in this system will vary according to the effect of the species on the equilibrium system represented by reactions (1) to (5).

Important features of the kinetics of reaction(I) when compared with other molybdate catalyzed reductions are:

(a.) The disappearance of half powers from the rate law as the molybdenum concentration is decreased to $10^{-6}$ M.

(b.) The absence of initial surges and induction periods for reactions begun with Mo(VI) and Mo(V), respectively.

(c.) The fact that molybdate concentrations are 1/100 to 1/1 000 those required for Sn(II) reductions of perchlorate [7], hydroxylamine [9], and of nitrate in sulfuric acid.

The development of first order dependence on molybdenum concentration when it is very low agrees with observations made on catalytic polarographic currents [5]. The absence of surges and induction periods at the start of reaction (I) indicate that Mo(IV) is present in its steady state concentration from the start whether the reaction is started with Mo(VI) or Mo(V).

A mechanism consistent with the rate law given by eqn. (4) and with the above observations and assumptions can be derived if it is assumed that Mo(IV) forms an active complex with nitrate which is redued by Sn(II).

$$\text{Mo(IV)} + \text{NO}_3^- = \text{X} \qquad\qquad (\pm\ 6)$$
$$\text{X} + \text{SnCl}_3^- = \text{SnOCl}_3^- + \text{NO}_2^- \qquad\qquad (7)$$
$$2\text{SnCl}_3^- + \text{NO}_2^- + \text{H}_2\text{O} + 2\text{H}_{al}^+ = \text{NH}_2\text{OH}^+ + 2\text{SnOCl}_3^- \qquad (8)$$

X is assumed to be an addition complex in equilibrium with Mo(IV) and nitrate ion. $\text{SnCl}_3^-$ is the most abundant and most reactive chloro-tin(II) complex in 3.0 M hydrochloric acid $^{9,14,15}$. Reaction (8) is fast [1] and plays no part in the kinetics except to make the number of transformations of Sn(II) three times the number of transformations of nitrate.
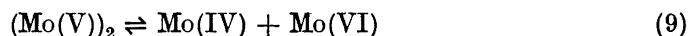
From reactions $(\pm\ 6)$ and (7) we obtain

$$\text{Rate} = K_7 K_6 [\text{Mo(IV)}][\text{Sn(II)}][\text{NO}_3^-] \qquad\qquad (8)$$

Since most of the molybdenum becomes $[\text{Mo(V)}]_2$ in the absence of nitrate we assume $k_1 \gg k_5$ leading to an equation for the steady state in Mo(IV):

$$k_2[\text{Mo(IV)}]^2 = k_5[(\text{Mo(V)})_2] \qquad\qquad (9)$$

It may also be argued that the sequence of reactions (1) to (5) describes simply the equilibrium

$$(\text{Mo(V)})_2 \rightleftharpoons \text{Mo(IV)} + \text{Mo(VI)} \qquad\qquad (9)$$

If $[\text{Mo(IV)}] = [\text{Mo(VI)}]$

$$[(\text{Mo(V)})_2] = k_9[\text{Mo(IV)}]^2 \qquad\qquad (9a)$$

which is equivalent to (9) if $k_9 = k_2/k_5$. This simply says the rate of reformation of $[\text{Mo(V)}]_2$ is the same as the rate of disproportionation of Mo(IV) which is a reasonable assumption.

*Table 10.* Values of rate and equilibrium constants *.

| Values | Source |
|---|---|
| $k' = K_6 k_7 = 2.0 \times 10^4$ | This paper |
| $k'' = 2(k_2/k_5)^{1/2} = 312$ | This paper |
| $k''' = K_6 = 30$ | This paper |
| $k_2 \sim 10^4$ | Polarography, Ref.[5] *** |
| $k_5 \sim 0.4$ | $k''$ and $k_2$ |
| $k_6 \sim 156$ (if $n = 2$) ** | Polarography, Ref.[5] *** |
|     625 (if $n = 4$) ** | |
| $k_{-6} \sim 5$ or $20$ | $k_6/K_6$ |
| $k_7 = 667$ | This paper |

\* All values in this table derived from the present study refer to kinetics in hydrochloric acid. The results in sulfuric acid are not extensive enough for such analysis as yet.

\*\* The quantity $n$ is the number of electrons involved in the electrode process associated with the catalytic current. It has not been determined but 2 and 4 are considered the most likely values.

\*\*\* Constants obtained polarographically involve work in a different medium and therefore only order of magnitude comparisons can be made.

A material balance in molybdenum requires that

$$[\text{Mo(IV)}] + [\text{X}] + 2[(\text{Mo(V)})_2] = [\text{Mo}] \tag{10}$$
$$[\text{Mo(IV)}] + K_6[\text{Mo(IV)}][\text{NO}_3^-] + 2k_2/k_5[\text{Mo(IV)}]^2 = [\text{Mo}]$$

$$[\text{Mo(IV)}] = \frac{2[\text{Mo}]}{1 + K_6[\text{NO}_3^-] + [(1 + K_6[\text{NO}_3^-])^2 + 8k_2/k_5[\text{Mo}]]^{1/2}} \tag{11}$$

If eqn. (11) is substituted in eqn. (8) a rate law is obtained which behaves in just the same way as rate law (4) at high $[\text{NO}_3^-]$ and low $[\text{Mo}]$. Rate law (4) requires that

$$[\text{Mo(IV)}] = \frac{[\text{Mo}]}{1 + K_6[\text{NO}_3^-] + [(2 \ k_2/k_5)[\text{Mo}]]^{1/2}} \tag{11a}$$

where $K_6 = 30$ and $\sqrt{2k_2/k_5} = 312$. Eqn. (11a) is approximately eqn. (11) under conditions where the right hand sides of eqn. (11) and (11a) approximate one another.

Values of rate and equilibrium constants for steps in the mechanism obtained from this and previous studies are summarized in Table 10.

## Mechanism of the reduction of nitrate in sulfuric acid.

Important features of the kinetics of reaction (II) when compared with other molybdate catalyzed reductions are:

(*a*) The reaction is extremely slow. In sulfuric acid the reduction of nitrate is slower than that of perchlorate while the opposite is true in hydrochloric acid.

(*b*) A steady state is observed only when nearly all the molybdenum is in the (V) state. Faster reaction is observed in the presence of Mo(VI) as was the case with hydroxylamine and perchlorate reduction.

(c) The slow rate is comparable with rates of reactions catalyzed by Mo(V) at elevated temperatures.

(d) The reaction is zero order in Sn(II).

(e) The reaction is half order in molybdenum as were all other reactions employing molybdenum concentrations $> 10^{-5}$ M.

If the same reaction scheme is employed as for the kinetics in hydrochloric acid with the substitution of $Sn^{++}$ for $SnCl_3^-$ with only the relative rates of the individual steps changed, we may derive the rate law as follows. If the forward reaction (6) is the rate determining step and reaction (7) is fast compared to $(-6)$ we obtain the rate law with $k'''' = k_6(k_5/k_2)^{1/2}$. This seems unlikely in view of the fact that $Sn^{++}$ is much less reactive than $SnCl_3^-$. Alternatively, the fact that Sn(II) is so unreactive in sulfuric acid suggests that nitrate is reduced by:

$$Mo(IV) + NO_3^- = Mo(VI) + NO_2^- \qquad (9)$$
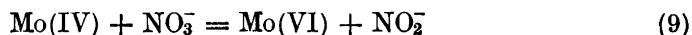
Reaction (9) is slow compared with reaction (1) so that the steady state in Mo(IV) is still given by eqn. (9). The function of Sn(II) is merely to restore Mo(IV) lost by reaction (9). That it does this efficiently via reaction (1) is indicated by the faster pace of reaction when Mo(VI) is added initially. If reaction (9) is the rate determining step we have $k'''' = k_9(k_5/k_2)^{1/2}$.

There is little point in further speculation on the reaction in sulfuric acid until further work is done. The fact that processes are very slow makes it feasible to study individual steps in the reaction in this case. Test tube experiments have shown that reaction (1) is slow enough to study kinetically in sulfuric acid. Study of the direct oxidation of $(Mo(V))_2$ and of Mo(III) by nitrate in sulfuric acid could throw more light on the nature of the catalytic process.

The anomaly that perchlorate is easier to reduce in sulfuric acid and nitrate is easier to reduce in hydrochloric acid using Sn(II) and molybdate catalyst is interesting. Catalytic polarographic waves are ten fold larger for nitrate than for perchlorate even in sulfuric acid [5]. This must mean that more Mo(IV) is available during the perchlorate reduction with Sn(II) than during the nitrate reduction. This is consistent with the observation that a steady state is reached in perchlorate reductions with less than half of the molybdenum in the (V) state [7]. The reduction products of perchlorate such as chlorate, chlorite, and hypochlorite are able to reoxidize Mo(V) to Mo(VI) which is easily converted to Mo(IV). Since nitrite is reduced to nitrous oxide instantly by Sn(II) the only source of Mo(IV) available for nitrate reduction is reaction (5). Apparently the reduction of nitrate in sulfuric acid corresponds to the very slow reaction taking place before a steady state is achieved in perchlorate reductions started by adding Mo(V).

It is probably true that reduction of perchlorate employing only Mo(IV) made available by reaction (5) is slower than reduction of nitrate in both hydrochloric and sulfuric acids, as evidenced by induction periods for reactions started with Mo(V). The ability of perchlorate to furnish oxidants for Mo(V) more than compensates in sulfuric acid, but not in hydrochloric acid.

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