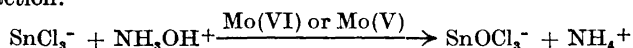


The Molybdenum Catalyzed Reduction of Hydroxylamine with Stannous Chloride

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Hexavalent molybdenum in the presence of stannous chloride has previously been shown to be a powerful catalyst for the reduction of oxyanions such as perchlorate and nitrate. This paper reports conditions for catalytic reduction of hydroxylamine and the kinetics of the reaction:



Reactions initiated by Mo(V) showed a much shorter induction period than in the case of perchlorate reductions. Reactions initiated by Mo(VI) gave an initial surge as with perchlorate. The two cases gave the same final steady state kinetics with Mo(V) as the dominant form of molybdenum remaining except in cases where reactions initiated by Mo(VI) were completed without reaching steady state conditions. The kinetics apart from induction periods and initial surges gave the rate law:

$$d[\text{Sn(II)}]/dt = k'[\text{Sn(II)}]^{1/2}[\text{NH}_2\text{OH}^+]^{1/2}[\text{Mo(V)}]^{1/2}[\text{H}^+]^2/(1 + k''[\text{NH}_2\text{OH}^+])$$

Since k' is a maximum where SnCl_3^- is at maximum concentration relative to other SnCl_n^{2-n} species, SnCl_3^- is judged to be the most reactive form of Sn(II) present. A mechanism is deduced based on the assumption that Mo(IV) is the catalyst and compared with a mechanism previously deduced for the reduction of perchlorate.

Interest in the previously observed ability of molybdate to catalyze the reduction of oxyanions¹⁻⁴ such as perchlorate and nitrate has been heightened by the discovery that molybdate is a necessary participant in the enzymatically catalyzed conversion of nitrate to ammonia in biochemical systems.⁵ We have accordingly undertaken a study of the catalytic removal of oxygen

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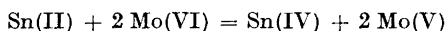
from nitrate and its oxygen containing reduction products, nitrite and hydroxylamine. The reduction of hydroxylamine reported here has been studied in dilute hydrochloric acid. The rate of the catalytic reduction has been found to be significant only over a very narrow range of hydrochloric acid concentration (in the vicinity of 3.0 M) suggesting that conditions for conversion of nitrate as well as hydroxylamine to ammonia must be very carefully specified.

EXPERIMENTAL

Reagent grade chemicals were used without further purification. Solutions were prepared as follows:

$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in standard hydrochloric acid and diluted to give 3.0 M H^+ assuming no hydrolysis. Hydroxylamine hydrochloride was dissolved in standard hydrochloric acid and the solution diluted to give 3.0 M chloride ion. Sodium molybdate dihydrate was dissolved in 3.0 M hydrochloric acid. These solutions with total ion concentrations of 3.0 M were used for the more significant experiments. Some results with other concentrations of H^+ and Cl^- are reported in the tables.

Reactions initiated by Mo(VI) were started by adding sodium molybdate solution to a predetermined mixture of the Sn(II) and hydroxylamine solutions. Reactions initiated by Mo(V) were started by adding the hydroxylamine last, enabling the Sn(II) to reduce Mo(VI) to Mo(V). All reactions were carried out under nitrogen to prevent air oxidation of stannous chloride. The concentration of Sn(II) remaining at various times was determined by titration with iodine. A few runs were made in which the reaction was quenched in solutions of 0.1 M Mo(VI) in concentrated hydrochloric acid. The green Mo(V) species produced by the reaction



was measured spectrophotometrically at $720 \text{ m}\mu$ with a Beckmann model DU spectrophotometer. Both analytical methods gave the same kinetics. Hydroxylamine does not react with iodine in the time required for a titration at the acidities used in this study, and reacts too slowly with Mo(VI) in concentrated hydrochloric acid to interfere with the spectrophotometric measurement. Tests of each procedure showed no interference from hydroxylamine. Although iodine is used to titrate hydroxylamine to nitrous oxide in neutral solutions⁸, one drop of 0.01 molar iodine gave a permanent starch test in 0.5 M hydroxylamine in solutions 1.0 to 3.0 M in hydrochloric acid.

RESULTS

Runs containing an excess of Sn(II) all proceeded until the Sn(II) concentration had decreased an amount equal to the initial concentration of hydroxylamine indicating that each substance changes two equivalents in oxidation number. For convenience we shall write the equation for the reaction:



No evidence of formation of intermediates such as hydrazine was found.

Reliable kinetics were obtained only with runs initiated by Mo(V) although some runs initiated by Mo(VI) gave the same kinetics following an initial surge. A suggestion of an induction period covering 1–5 min was observed in several reactions initiated by Mo(V), following which the kinetics to be described were valid for up to 95 % completion of the reaction. Similar runs initiated by Mo(VI) are illustrated in Table 1.

Determination of the empirical rate law. In runs containing a high excess of hydroxylamine, plots of $[\text{Sn(II)}]^{1/2}$ vs. time gave straight lines as illustrated in

Table 1. Comparison of runs started with Mo(V) and Mo(VI).

Run 13 [NH ₂ OH] = 0.659 M Added [Mo(VI)] = 1.6 × 10 ⁻⁵		Run 22 [NH ₂ OH] = 0.665 M Added [Mo(V)] = 1.7 × 10 ⁻⁵	
Time min.	[Sn(II)], M	Time min.	[Sn(II)], M
0	0.0338	0	0.0327
1	0.0253	1.2	0.0320
3.17	0.0210	5	0.0287
6	0.0145	10	0.0249
9	0.0133	20.25	0.0174
14	0.0107	40	0.00700
17	0.0090	50	0.00425
25	0.0061	60	0.00255

Note. Kinetics for run 13 are the same as run 22 after the first 6.0 minutes.

Fig. 1. These plots have slopes proportional to [Mo(V)]^{1/2} as shown by runs 20, 21, and 22 in Table 2. These results suggest the reaction is 1/2 order in respect to Sn(II) and in respect to Mo(V).

In runs containing equimolar Sn(II) and hydroxylamine plots of 1/[Sn(II)] vs. time give straight lines as illustrated in Fig. 2. (The correction term in Fig. 2 is required by the final rate law.) These results suggest the rate law:

$$d[\text{Sn(II)}]/dt = k[\text{Sn(II)}]^{1/2}[\text{NH}_3\text{OH}^+]^{1/2}[\text{Mo(V)}]^{1/2} \quad (1)$$

The results of runs 5 and 24 (Table 2) with the same chloride concentration and fairly similar hydroxylamine concentrations suggest that k is proportional to the square of the hydrogen ion concentration. If this is true a comparison of runs 20, 21, and 22 with run 38 requires that

$$k = k'[\text{H}^+]^2/(1 + k''[\text{NH}_3\text{OH}^+]). \quad (2)$$

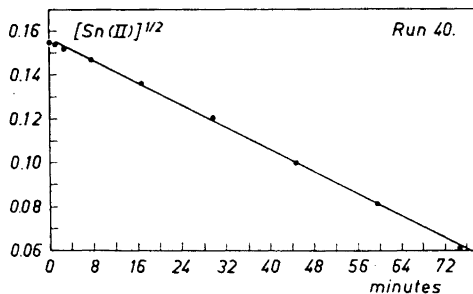


Fig. 1. Plot showing the reaction to be half order in Sn(II) in the presence of excess hydroxylamine. Details of run 40 are shown in Table 2.

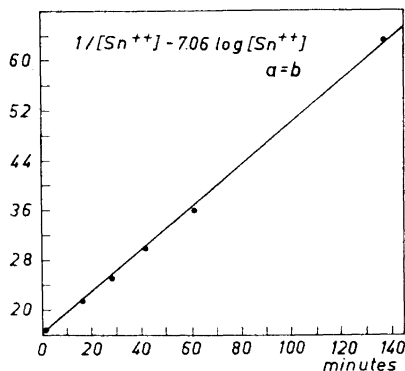


Fig. 2. Plot showing the reaction to be second order in Sn(II) when concentrations of Sn(II) and hydroxylamine are equal.

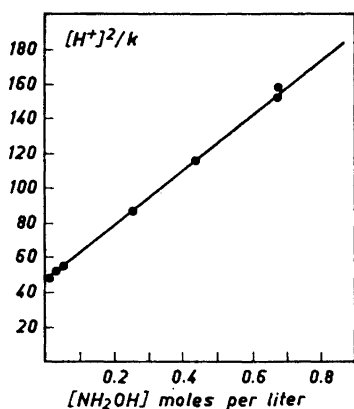


Fig. 3. Plot showing calculation of k' and k'' from the dependence of k on concentrations of hydrogen ion and hydroxylamine for runs containing 2.9 M chloride ion. Intercept = $48 = 1/k'$; $k' = 2.08 \times 10^{-2}$; slope = $148 = k''/k'$; $k'' = 3.07$.

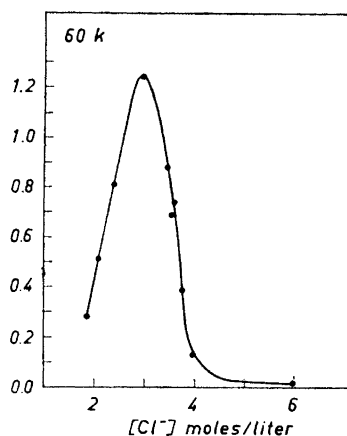


Fig. 4. Variation of k' with changing chloride ion concentration, k'' assumed to be constant.

All runs performed at $[\text{Cl}^-] = 2.90 \text{ M}$ (allowing for 3.0 combined chloride ions per tin atom) were used to test eqn. (2). Fig. 3 shows a plot of $[\text{H}^+]^2/k$ vs. $[\text{NH}_3\text{OH}^+]$. From the slope and intercept of the straight line obtained k' and k'' were evaluated. In all other cases k' was evaluated assuming $k'' = 3.07$. If $[\text{NH}_3\text{OH}^+]_0 < 0.03$, the term containing k'' can be ignored. The final empirical rate law thus obtained is

$$d[\text{Sn(II)}]/dt = \frac{k'[\text{Sn(II)}]^{1/2}[\text{NH}_3\text{OH}^+]^{1/2}[\text{Mo(V)}]^{1/2}[\text{H}^+]^2}{1 + k''[\text{NH}_3\text{OH}^+]} \quad (3)$$

The values of the constants for $[\text{Cl}^-] = 2.90 \text{ M}$ are $k' = 0.020$ and $k'' = 3.07$ if concentrations are in moles per liter and time is in seconds. The rate law is valid for concentrations of Sn(II) from 0.1 to 0.002 M, of hydroxylamine from 0.67 to 0.020 M, of Mo(V) from 5×10^{-3} to 10^{-5} M , and of hydrogen ion

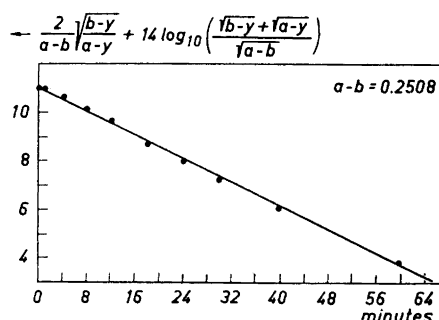


Fig. 5. Plot showing validity of eqn. 3 at chloride ion concentration of 2.3. Run 37 in Table 2.

Table 2. Data on runs giving characteristic Mo(V) kinetics in moles/liter
 $k'' = 3.07$, time in seconds

Run	Sn(II)	NH ₃ OH ⁺	H ⁺	Cl ^{-a}	Mo(V)	Plot vs. <i>t</i>	Slope	<i>k'</i>	
38	0.1000	0.0999	2.81	2.81	1.62×10^{-3}	1a	5.77×10^{-3}	0.0182	
9	0.0309	0.421	2.60	2.93	1.32×10^{-3}	2	2.73×10^{-5}	0.0198	
12	0.0300	0.296	2.70	2.97	1.58×10^{-4}	2	2.00×10^{-5}	0.0165	
20	0.0370	0.665	2.28	2.90	7.50×10^{-5}	2	7.70×10^{-5}	0.0198	
21	0.0280	0.665	2.28	2.90	6.24×10^{-4}	2	2.37×10^{-4}	0.0198	
22	0.0330	0.665	2.28	2.90	1.74×10^{-5}	2	3.83×10^{-5}	0.0215	
34	0.0311	0.311	2.61	2.89	7.50×10^{-5}	2	4.50×10^{-5}	0.0167	
36	0.0211	0.0311	2.97	2.96	2.03×10^{-3}	3a	4.38×10^{-5}	0.0222	
40	0.0246	0.248	1.91 ^c	2.91	6.00×10^{-5}	2	2.08×10^{-5}	0.0208	
51 ^b	0.1157	0.1157	2.88	2.88	4.63×10^{-4}	1a	3.68×10^{-3}	0.0204	25°C
52 ^b	0.1000	0.1000	2.90	2.90	4.00×10^{-4}	1	6.25×10^{-3}	0.0377	35°C
53 ^b	0.1000	0.0400	2.90	2.90	4.00×10^{-4}	3a	6.67×10^{-4}	0.0076	13°C
39	0.248	0.248	1.11	1.11	1.62×10^{-3}	1a	2.33×10^{-4}	0.00471	
42	0.0247	0.249	1.78	2.00	6.00×10^{-5}	2	8.12×10^{-5}	0.00853	
19	0.545	0.545	2.31	2.31	1.30×10^{-4}	1a	6.40×10^{-4}	0.0104	
37	0.304	0.620	2.94	2.32	2.45×10^{-3}	3b	7.47×10^{-2}	0.0116	
41	0.247	0.498	2.96	2.46	2.70×10^{-3}	3b	1.20×10^{-1}	0.0148	
17	0.382	0.382	2.51	2.51	1.30×10^{-4}	1a	8.67×10^{-4}	0.0116	
18	0.348	0.348	2.56	2.56	1.31×10^{-4}	1a	8.90×10^{-4}	0.0118	
10	0.329	0.329	2.57	2.57	1.60×10^{-3}	1a	3.47×10^{-4}	0.0122	
35	0.308	0.311	2.64	2.67	7.50×10^{-3}	1a	7.45×10^{-4}	0.0124	
5	0.030	0.400	2.84	3.21	5.2×10^{-5}	2	5.83×10^{-5}	0.0175	
24	0.0283	0.313	1.11*	3.27	7.5×10^{-5}	2	7.00×10^{-6}	0.0147	
11	0.0310	0.296	3.15	3.45	1.6×10^{-5}	2	1.60×10^{-5}	0.00115	
43	0.025	0.249	3.75	4.00	1.2×10^{-4}	2	1.21×10^{-4}	0.0022	
44	0.025	0.249	5.75	6.00	1.2×10^{-4}	2	6.00×10^{-7}	3×10^{-6}	

^a. Assuming 3 combined Cl⁻ per Sn(II).

^b. Runs at varying temperature, analyzed by spectrophotometric method. ^c. LiCl present

Plots vs. time: 1. $1/[\text{Sn(II)}]_0$ 2. $[\text{Sn(II)}]^{1/2}$ 3a. $\frac{[\text{Sn(II)}]^{1/2}}{\text{NH}_3\text{OH}^+}^{1/2}$

1a. $1/[\text{Sn(II)}] + 7.06 \log_{10}[\text{Sn(II)}]$.

3b. $2/(a-b)\sqrt{(b-y)/(a-y)} + 14 \log_{10}(\sqrt{(b-y)} + \sqrt{(a-y)})/\sqrt{(a-b)}$.

All reactions at 25°C unless otherwise indicated.

from 1.0 to 3.0 M. The form of the rate law holds for [Sn(II)] up to 0.5 M with changing *k'* values caused by changes in the concentration of free chloride ion.

*Effect of other ions present in the solution on the rate constant *k'*.* The products, Sn(IV) and NH₄⁺ had no effect on the reaction kinetics. Increasing chloride ion concentrations accelerated the reaction if [Cl⁻] < 3.0 M, and inhibited the reaction for [Cl⁻] > 3.0 M, as shown by the graph in Fig. 4. The effect could not be studied at constant ion normality since no anion could be found which was inert toward the system.

Effect of temperature. The results of runs carried out at three different temperatures are summarized in Table 2, runs 51–53. These runs were of the type where the term involving *k''* was unimportant. Therefore the temperature dependence of *k'* only has been determined. The results are described by the equation:

$$k' = 1.6 \times 10^7 e^{-13600/RT} \quad (4)$$

The activation energy of 13.6 kcal. may be compared with an activation energy of 23.0 kcal. found for the direct oxidation of Mo(V) by hydroxylamine in 3.0 M hydrochloric acid.⁹

Tests of the rate law.

Let y = the number of transformations in moles per liter
 a = initial concentration of hydroxylamine
 b = initial concentration of Sn(II).
 t = time in seconds following the start of reaction.
 $A = k''/(k'[\text{Mo(V)}]^{1/2}[\text{H}^+]^2)$
 $B = A/k''$

From eqn. (3)

$$dt/dy = A/(a-y)^{1/2}(b-y)^{1/2} + B/(a-y)^{3/2}(b-y)^{1/2} \quad (5)$$

Integrating (5)

$$t = Af_1 + Bf_2 \quad (6)$$

where

$$f_1 = 2 \ln(\sqrt{a} + \sqrt{b})/(\sqrt{a-y} + \sqrt{b-y})$$

and

$$f_2 = (2/(a-b))(\sqrt{b/a} - \sqrt{(b-y)/(a-y)})$$

When $a = b$

$$f_1 = \ln(a/(a-y))$$

$$f_2 = 1/(a-y) - 1/a$$

The quantities f_1 and f_2 may be evaluated for each experimental point from the measured quantity $(b-y)$, the time t calculated and compared with observed times. Initial discrepancies between calculated and observed times were in general due to the occurrence of either initial surges of reaction or short induction periods. Such discrepancies could be removed by taking one of the early points as representing $t = 0$. Later deviations occurred most frequently when a and b were of comparable magnitude. In such cases small errors due to the difficulty in handling stannous chloride solutions would be magnified. Calculated and observed times for several representative runs of different types are shown in Tables 3 and 4. In all cases where hydroxylamine was in large excess, the correlation is extremely good.

DISCUSSION

Derivation of a reaction mechanism. A plausible mechanism for reaction (I) must not only allow derivation of the empirical rate law (3), but must also explain the observed initial surges and induction periods and be consistent with the known chemistry of Sn(II) and Sn(IV), of hydroxylamine and ammonia, and of the various oxidation states of molybdenum.

The knowledge of species of the various reagents in 3.0 M hydrochloric acid is limited, and this will to some extent limit the discussion.

Table 3. Comparison of calculated and observed times for runs with excess hydroxylamine. Symbols are those used in eqn. 4. All concentrations are in moles per liter.

Run 20. $A = 3\ 420$ $B = 1\ 110$ $a = 0.665$ $b = 0.0370$ $\sqrt{a} + \sqrt{b} = 1.012/(a-b) = 3.18$
 $\sqrt{b/a} = 0.236.$

$t_{\text{obs.}}$ sec.	$b-y$	$\sqrt{a-y} + \sqrt{b-y}$	f_1	$\sqrt{(a-y)/(b-y)}$	f_2	$t = Af_1 + Bf_2$ sec.
60	0.0350	1.003	0.0125	0.230	0.0191	64
240	0.0295	0.983	0.0360	0.212	0.0765	208
480	0.0247	0.960	0.1010	0.195	0.131	490
780	0.0180	0.939	0.145	0.167	0.219	739
1 080	0.0117	0.908	0.212	0.135	0.321	1 081
1 440	0.0065	0.879	0.276	0.101	0.429	1 421

Run 21^a. $A = 1\ 190$ $B = 385$ $a = 0.665$ $b = 0.0247$ $\sqrt{a} + \sqrt{b} = 0.9722/(a-b) = 3.12$
 $\sqrt{b/a} = 0.193.$

180	0.0147	0.928	0.092	0.146	0.146	169
300	0.0080	0.895	0.166	0.111	0.256	297
390	0.0046	0.872	0.216	0.0843	0.339	387
480	0.0022	0.850	0.266	0.0592	0.417	478
600	0.0008	0.831	0.313	0.0358	0.490	562

Run 36^b $A = 390$ $B = 127$ $a = 0.0286$ $b = 0.0198$ $\sqrt{a} + \sqrt{b} = 0.310$
 $2/(a-b) = 227$ $\sqrt{b/a} = 0.832.$

480	0.0177	0.296	0.092	0.817	3.40	470
780	0.0162	0.286	0.160	0.806	5.9	812
1 200	0.0144	0.273	0.260	0.787	10.2	1 400
2 280	0.0121	0.244	0.478	0.744	20.1	2 740
3 480	0.0078	0.217	0.709	0.687	32.9	4 430

^a. Second or third point used for t_0 to eliminate induction period.

^b. Run most subject to large deviations late in run due to small initial errors.

Mo(VI) is either H_2MoO_4 or HMoO_3Cl . It is probably completely depolymerized.

Mo(V) is a dimer of unknown structure¹⁰.

Mo(IV) is unstable.

Mo(III) has an unknown structure derived from the hydrolysis of MoCl_6^{3-} .

NH_2OH is basic enough to be completely protonated to NH_3OH^+ .

Sn(II) is a mixture of SnCl_n^{2-n} . Average $n = 3.0$ ^{7,8}.

Sn(IV) is some species resulting from hydrolysis of SnCl_6^{2-} . For convenience, we assume SnOCl_3 as a product of oxidation of SnCl_3 .

The following reactions have been observed among the various species above.

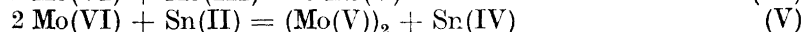
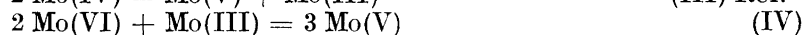
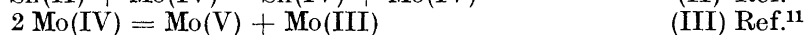


Table 4. Comparison of calculated and observed times for runs with $a = b$.Run 38 $A = 488$ $B = 159$ $a = 0.100 = b$

t_{obs} sec.	$a-y$	$\ln(a/(a-y))$	Af_1	$1/(a-y)$	Bf_2	t_{calc} seconds	Δt_{obs}	Δt_{calc}
180	0.0954	0.046	22.5	10.5	80	103	180	103
375	0.0875	0.133	65	11.4	226	291	195	189
900	0.0735	0.308	150	13.6	575	725	525	434
1 620	0.0604	0.506	270	16.5	1 045	1 315	720	590
2 400	0.0479	0.735	358	20.9	1 730	2 088	820	773
3 600	0.0385	0.950	465	26.0	2 540	3 000	1 200	912
8 160	0.0195	1.630	795	51.4	6 570	7 365	4 560	4 365
14 340	0.0111	2.210	1 075	90.0	12 720	13 800	6 200	6 435

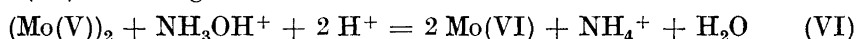
There is definitely an induction period of slow reaction initially. All but the last point give a better fit with the individual k' recorded for this run in Table 2, increasing t_{calc} by about 10 %.

Run 51 $A = 860$ $B = 280$ $a = b = 0.1157$.

708	0.0901	0.248	214	11.1	680	894	708	894
2 658	0.0557	0.650	560	16.67	2 240	2 780	1 950	1 886
3 798	0.0484	0.780	672	12.0	3 360	4 032	1 140	1 252
4 728	0.0436	0.975	840	15.0	4 200	5 040	930	1 008
6 120	0.0366	1.150	990	18.6	5 200	6 190	1 392	1 150

This run started with Mo(V), indicating a gross error in measurement of the first point. The last four points fit the rate law.

Reaction (V) is the overall process observed in 3.0 M HCl, but reactions (II), (III), and (IV) are thought to be intermediates.¹¹



The rate of (VI) is independent of $[\text{Mo(VI)}]$ and of $[\text{NH}_4^+]$.⁹ In addition, Mo(VI) reacts extremely slowly with hydroxylamine forming yellow complexes of unknown composition. Hydroxylamine shifts the absorption band for Mo(V) in the same manner as additional hydrochloric acid, suggesting intermediate complex formation between NH_2OH and $(\text{Mo(V)})_2$.⁹

Mo(IV) catalyzes the reduction of perchlorate.²

Assumptions.

Mo(IV) is the catalytically active state of molybdenum.

The slow step involves breaking of the N—O bond since hydroxylamine is kinetically inert towards most reducing agents.

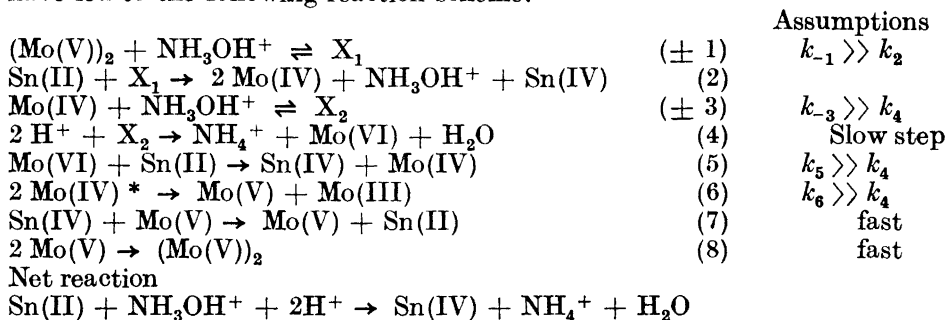
Half powers in the rate law may be derived from (a) the existence of an equilibrium



or (b) the possibility that Mo(IV) disappears mainly through disproportionation. Of these the second possibility is most difficult to find fault with. It is hard to visualize how equilibrium (VII) can be the source of Mo(IV) in view of

the tendency of the reaction under discussion and other reactions to exhibit induction periods when initiated by Mo(V). In addition Mo(VI) plays no part in the kinetics of reaction (VI). We therefore conclude that (VII) plays no part in the steady state kinetics, though it may serve as an initial source of Mo(IV) during the so-called induction period.

Assuming that Mo(IV) disproportionates, the half powers in each reactant suggest a concerted process leading to the formation of Mo(IV). It is assumed that hydroxylamine oxidizes Mo(IV) to Mo(VI), which is rapidly reduced back to Mo(IV) by Sn(II). The oxidation of Mo(IV) by hydroxylamine is very slow compared with the disproportionation of Mo(IV). These assumptions have led to the following reaction scheme.



Only valence states are indicated where formulas are not known or where mixtures exist as with SnCl_2^{2-} complexes. Hydrogen ion is introduced in reaction (4) and in the net reaction only to preserve the notation and balance atoms. The participation of hydrogen and chloride ions may not be rigorously included until the structures of the various species involved are better known.

Derivation of the empirical rate law from the reaction scheme.

K 's are equilibrium constants.

k 's are rate constants.

$$\text{Rate} = K_3 k_4 [\text{NH}_3\text{OH}^+][\text{Mo(IV)}][\text{H}^+]^2$$

If a steady state exists for all forms of Mo(IV), and reaction (5) does not effectively decrease the concentration of Mo(IV),

$$d([\text{Mo(IV)}^*]/dt = 0 = K_1 k_2 [\text{Sn(II)}][\text{NH}_3\text{OH}^+][(\text{Mo(V)})_2] - k_6 [\text{Mo(IV)}^*]^2$$

$$[\text{Mo(IV)}^*] = (K_1 k_2)^{1/2} [\text{Sn(II)}]^{1/2} [\text{NH}_3\text{OH}^+]^{1/2} [(\text{Mo(V)})_2]^{1/2}$$

$$[\text{Mo(IV)}^*] = [\text{Mo(IV)}] + [\text{X}]$$

$$[\text{Mo(IV)}] = [\text{Mo(IV)}^*]/(1 + K_3([\text{NH}_3\text{OH}^+]^{1/2}))$$

$$\text{Rate} = \frac{k'[\text{NH}_3\text{OH}^+]^{3/2}[\text{Sn(II)}]^{1/2}[(\text{Mo(V)})_2][\text{H}^+]^2}{1 + k''[\text{NH}_3\text{OH}^+]^{1/2}}$$

as given by eqn. (3).

Discussion of the reaction scheme. Evidence for reaction (± 1) has been observed⁹. Reaction 2 is postulated to fit the kinetics. If reaction (± 1) were to give Mo(VI) followed by reduction of the latter by Sn(II), the term $[\text{Sn(II)}]^{1/2}$

* Indicates all species containing Mo(IV)

drops out of the rate expression. Equilibrium (± 3) is postulated in order to obtain the denominator term in the final rate expression. Reaction (5) is known to be very fast compared with the net catalytic reaction. Reaction (6) is postulated on the assumption that all Mo(IV) disproportionation reactions have comparable rate constants. Oxidation of Mo(III) might be accomplished by hydroxylamine or by hydrogen ion. However, reaction (7) is most consistent with the stoichiometric studies involving Mo(VI) and Sn(II) described in the Ph.D. thesis of A. Bergh¹¹, as is the assumption that it is fast. Reaction 8 is known to be very fast¹⁰.

Virtual equilibrium is assumed in reactions (± 1) and (± 3) because of the general lability of H—O bonds and Mo—O bonds as compared with the N—O bond in hydroxylamine. The dimer of Mo(V) is also rather inert toward reduction.

In reactions initiated by Mo(VI) reaction (5) serves as a source of Mo(IV) leading to the initial surge observed. In the steady state reaction (5) merely restores Mo(IV) consumed by reaction (4). Apparently some time is needed to build [Mo(IV)] up to its steady state level when (Mo(V))₂ is the initiator.

The concentration of hydrogen ion has been introduced into the reaction scheme in a purely arbitrary manner. It may be involved in any or all of the steps to give the net effect observed. The effect of chloride ion on the rate is extremely interesting. The peak in value of k' occurs at the same hydrochloric acid concentration as the minimum solubility⁸ of (CH₃)₄NSnCl₃. This means that the concentration of SnCl₃⁻ is at a maximum at exactly the same concentration that the rate is a maximum, suggesting that SnCl₃⁻ is by far the most reactive of the SnCl_n²⁻ⁿ species present as found by Duke and Peterson¹². It is interesting also that an assumption that k'' is constant in varying concentrations of chloride does not lead to departures from linearity for plots of the integrated form of equation 3 vs. time (Fig. 5). This adds weight to the suggestion that the whole of the chloride effect is due to varying relative concentration of SnCl₃⁻ vs. other Sn(II) species. In any case it appears that the effect of changing chloride ion concentration on the disproportionation of Mo(IV) is negligible.

*Comparison of the kinetics and mechanism with that observed for the reduction of perchlorate.*² Both the kinetics and proposed mechanisms are understandably similar in the two cases. Two differences stand out and require explanation, however. The first is the decrease in the length of the induction period when (Mo(V))₂ initiates the reaction, and the second is the decrease in order of Sn(II) by one in the case of hydroxylamine reduction. The decrease in induction period is probably related to the greater reactivity of hydroxylamine over perchlorate both as an oxidant and as a ligand in the formation of complex ions. Actually, if disproportionation rate constants are about the same for all species, K_3 is less than half for hydroxylamine than it is for perchlorate suggesting that the qualitative argument above is not entirely valid. The oxidation of Mo(V) by hydroxylamine is faster than that by perchlorate. The change in order for Sn(II) comes about through the failure of Sn(II) to participate in the rate determining step in the present case. If the hydroxylammonium ion is coordinated to Mo(IV) through its oxygen atom, it is effectively protected from attack by Sn(II). No such protection exists for Cl—O bonds in perchlorate

coordinated to Mo(IV). Thus $\text{H}_3\text{N}-\text{O}-\text{Mo}$ (IV) must undergo internal oxygen transfer to reduce the hydroxylamine, while $\text{O}_3\text{Cl}-\text{O}-\text{Mo}$ (IV) has three oxygen atoms attached to chlorine which are vulnerable to attack by Sn(II). Further evidence that species X_2 does not undergo reduction by external reducing agents is the failure by the authors to find a catalytic polarographic reduction for hydroxylamine similar to those observed for perchlorate and nitrate.

The kinetics of a very complicated reaction and a possible mechanism for the reaction have been described. This reaction is of interest as a possible step in the conversion of nitrate to ammonia and for the way it fits an emerging pattern for reactions involving oxygen-transfer catalyzed by molybdenum. The tendency for molybdenum to undergo one step divalent changes is seen once again as in the reduction of perchlorate. The acceleration of reactions of Sn(II) by chloride ion¹²⁻¹⁴ has again been vividly demonstrated. The rather specific conditions of 3.0 M chloride found for maximum catalytic effect suggest that this medium might be suitable for reduction of nitrate to ammonia. Such has been found to be the case and this reaction is discussed in a following paper.

The reaction studied is quantitative as is the uncatalyzed reduction of hydroxylamine by stannous chloride at elevated temperatures^{15,16}. However, application to analysis for hydroxylamine would have to be in the absence of reducible oxy-anions such as nitrate and perchlorate which are also catalytically reduced by Sn(II) in the presence of molybdate.

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