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The Mechanism of the Reduction of Molybdenum(VI) by Tin(II) in Hydrochloric Acid Solutions[1]

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Product analyses show that in concentrated hydrochloric acid, Sn(II) and Mo(VI) react to give equimolar concentrations of Mo(V) and Mo(III) as initial products. This result strongly suggests that the reaction proceeds by the steps Mo(VI) + Sn(II) $\longrightarrow$ Sn(IV) + Mo(IV) (1), and 2Mo(IV) $\longrightarrow$ Mo(V) + Mo(III) (2).

Introduction

Kinetic[2] and polarographic[3] studies on systems involving various oxidation states of molybdenum have indicated the possible existence of Mo(IV) as an active intermediate in oxidation-reduction reactions. The present study represents the results of a search for definite evidence that Mo(VI) is reduced to Mo(IV) in a single divalent step by Sn(II) in acid solution. The results presented here strongly suggest a mechanism for the Sn(II)-Mo(VI) reaction which requires production of Mo(IV) as the initial step. The study also revealed the existence of a slow reduction of Mo(V) to Mo(III) by Sn(II).[4]

Experimental

Reagent grade sodium molybdate dihydrate (Merck and Co.) and stannous chloride dihydrate were dissolved in reagent grade hydrochloric acid of the desired concentrations. All Sn(II) solutions were stored under nitrogen. Fresh Sn(II) solutions were prepared for each series of runs and standardized both before and after use to make sure no air oxidation occurred.

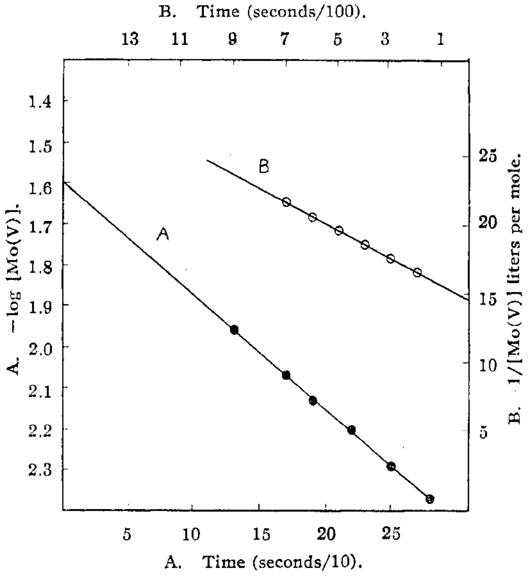
A Beckman Model DU spectrophotometer with 10.0-mm. absorption cells was used for all product analyses. [Mo(V)] concentrations were calculated from readings of absorbance of solutions at 720 mμ. Mo(III) concentrations were calculated from the absorbance at 525 mμ. No absorbance due to Mo(III) is observed at 720 mμ while a very small correction for Mo(V) must be applied at 525 mμ. Following the reaction of Sn(II) with Mo(VI) the absorbance due to Mo(V) decreased with time in the presence of excess Sn(II) because of the reaction

$$\mathrm{Sn(II)} + \mathrm{Mo(V)} \longrightarrow \mathrm{Mo(III)} + \mathrm{Sn(IV)} \quad (3)$$

The relative concentrations of Mo(V) and Mo(III) obtained initially were found by extrapolation of a plot of the integrated form of the rate equation[5]

$$d[\mathrm{Mo(V)}]/dt = k[\mathrm{Sn(II)}][\mathrm{Mo(V)}] \qquad (I)$$

to zero time. The method is illustrated in Fig. 1 for the case where [Sn(II)] is high and virtually constant and for the case where [Sn(II)] = [Mo(V)].



A. Run 3: excess Sn(II); [Mo(VI)$_0$ = 0.050 *M*; [Mo(V)]$_0$ = 0.025 *M*.

B. Run 2: 3[Sn(II)] = 2[Mo(VI)]; [Mo(VI)]$_0$ = 0.1156; [Mo(V)]$_0$ = 0.0693.

Fig. 1.—Graphical extrapolation of [Mo(V)] data to zero time using the integrated form of the rate law $d[\mathrm{Mo(V)}]/dt = k[\mathrm{Sn(II)}][\mathrm{Mo(V)}]$.

Potentiometric titrations were performed using platinum and calomel electrodes and a Beckman Model G pH meter. Of primary interest were positions of breaks in the curves relative to titer rather than exact measurement of

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[1] This paper presents a part of the work submitted by A. A. Bergh to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) G. P. Haight, Jr., and W. F. Sager, *J. Am. Chem. Soc.*, **74**, 6056 (1952).

(3) G. P. Haight, Jr., *Anal. Chem.*, **23**, 1505 (1951).

(4) A. A. Bergh and G. P. Haight, Jr., to be submitted for publication.

(5) A. A. Bergh, Thesis, University of Pennsylvania, 1959, to be published. This is a simplified form of the rate law which holds true when [Mo(V)] = [Sn(II)]. In excess [Sn(II)] the reaction is first order in [Mo(V)] but tends toward zero order in Sn(II) at high [Sn(II)]. Equation I is valid for the purpose used here.

TABLE I

Run	[Sn(II)] mole/l.	[Mo(VI)] mole/l.	[Mo(V)][a] calcd. mole/l.	[Mo(V)] found mole/l.	(HCl) mole/l.	Type[b]
1.	0.0813	0.1152	...	0.0910[c]	9.0	A
2.	.1734	.1156	0.0578	.0693	9.0	A
3.	.500	.0500	.0250	.0250	9.0	B
4.	.340	.0750	.0375	.0375	9.0	B
5.	.1905	.1081	.0540	.0627	8.0	A
6.	.1700	.1135	.0568	.0638	8.0	B
7.	.1370	.0286	.0143	.0145	12.0	A
8.	.1370	.0286	.0143	.0243[d]	12.0	A
9.	.38	.040	.020	.020	12.0	A
10.	.48	.1000	.0500	.0503	12.0	B

[a] Calculated as if one-half of the Mo(VI) becomes Mo(V) and one-half Mo(III) initially. [b] A = Sn(II) added to Mo(VI); B = Mo(VI) added to Sn(II). [c] This figure did not change with time since all Sn(II) was consumed. Excess Mo(VI) reacts with Mo(III) to give Mo(V). [d] Sn(II) added very slowly. In all other cases mixing was as rapid as possible.

potentials. In cases where slow reduction of Mo(V) with Sn(II) was relevant both slow and fast titrations were performed and the results compared.

Results

Product Analyses in 9–12 *M* Hydrochloric Acid.—If Sn(II) is added to a 20-fold excess of Mo(VI) ([Sn(II)] = 0.020 *M*), the reaction

$$2\mathrm{Mo(VI)} + \mathrm{Sn(II)} \longrightarrow 2\mathrm{Mo(V)} + \mathrm{Sn(IV)} \quad (4)$$

is observed to be rapid and quantitative. Measurements of the absorbance due to product Mo(V) at 720 mμ provided a quick method for standardization of Sn(II) solutions. Although the reaction is very fast, there is visual evidence that more than one step is involved. The initial color appears to be intermediate to that of Mo(V) (green) and Mo(III) (red) and changes rapidly to the pure green of Mo(V).

If 0.020 *M* Mo(VI) is added to equivalent or excess amounts of Sn(II), optical density measurements at 720 and 528 mμ show that equal amounts of Mo(V) and Mo(III) are formed initially. Results of measurements summarized in Table I show the effects of changing order of mixing, rate of mixing, and variation of hydrochloric acid concentration in the range 9 to 12 *M*. It is evident that, if mixing is rapid, and if no Mo(VI) is available to react with Mo(III), equal concentrations of Mo(V) and Mo(III) are produced initially in solutions 9.0 to 12.0 *M* in hydrochloric acid. The same result is obtained if Sn(II) in excess is added rapidly to Mo(VI), but not if the addition is carried out slowly.

Potentiometric Titrations. A. $SnCl_2$ Solutions Titrated with Mo(VI).—Titration curves obtained with solutions containing less than 5 *M* hydrochloric acid show a single break corresponding to reduction of Mo(VI) to Mo(V) as in reaction 4. (At low acidities the product Mo(V) probably is dimerized.)

As the acidity is increased, a second break appears in the titration curves at titers between those required for mole ratios of Mo(VI) to Sn(II) of 2:1 and 1:1. This second break approaches the position corresponding to a 1:1 mole ratio at 9 *M* hydrochloric acid. In concentrated (12 *M*) acid the break may occur at Mo(VI)/Sn(II) mole ratios slightly less than 1:1 due to the slight amount of reaction 3 which occurs during a rapid titration. If the titration is stopped at a 2:3 mole ratio and the mixture allowed to stand for an hour, the first break is observed at that point. Figure 2 illustrates the various potentiometric titration curves observed. Equilibrium was not reached instantaneously at the second break in

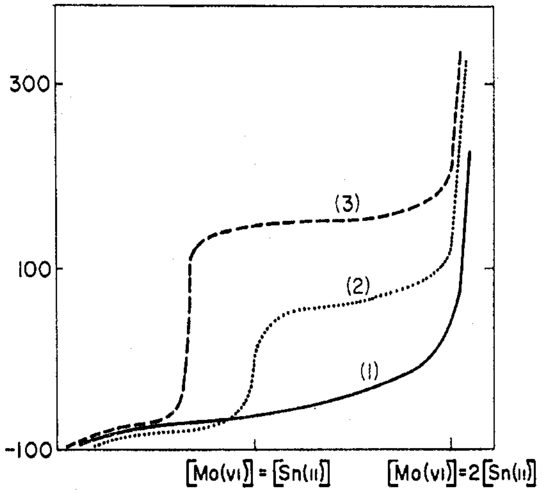

Fig. 2.—Potentiometric titrations of Sn(II) by Mo(VI) in various concentrations of hydrochloric acid using a platinum-saturated calomel electrode system: curve 1, 3 *M* HCl; curve 2, 9 *M* HCl; curve 3, 12 *M* HCl. In curve 3 [Mo(VI)] = 2/3[Sn(II)] mixed rapidly and allowed to stand for 30 min. before continuing titration.

concentrated acid, indicating that the reaction of Mo(VI) with Mo(III) is slower than the reaction of Mo(VI) with Sn(II).

B. Mo(VI) Solutions Titrated with Sn(II).—For all concentrations of hydrochloric acid, titration curves showed only a single break corresponding to reduction of Mo(VI) to Mo(V) by reaction 4. In 9 to 12 *M* hydrochloric acid the final potential following the break in the titration curve suggested that a second break would be observed for reaction 3 in which Mo(III) is produced. However, since 20 min. were required for reaching oxidation–reduction equilibrium at the indicator electrode for each addition of Sn(II) after the first break, reaction 3 was not investigated further by this method.

C. Reactions of Mo(III).—Qualitative observations on reactions of Mo(III) with potential oxidizing agents present in solutions involved in this study show that Mo(III) does not react with Sn(IV) in concentrated hydrochloric acid and only slowly in dilute acid; Mo(VI) reacts with red Mo(III) to produce Mo(V) at observable rates with half-times of the order of only a few seconds. In dilute acid the reaction of Mo(III) with Mo(VI) is virtually instantaneous.

Mechanism of the Reduction of Mo(VI) with Sn(II).—The above results can be explained in terms of the sequence of reactions

$$\mathrm{Mo(VI)} + \mathrm{Sn(II)} \longrightarrow \mathrm{Mo(IV)} + \mathrm{Sn(IV)} \quad (1)$$

$$2\mathrm{Mo(IV)} \longrightarrow \mathrm{Mo(V)} + \mathrm{Mo(III)} \quad (2)$$

$$\mathrm{Mo(V)} + \mathrm{Sn(II)} \longrightarrow \mathrm{Mo(III)} + \mathrm{Sn(IV)} \quad (3)$$

$$\mathrm{Mo(III)} + \mathrm{Mo(VI)} \longrightarrow \mathrm{Mo(V)} + \mathrm{Mo(IV)} \quad (5)$$

In concentrated hydrochloric acid the initial production of equimolar Mo(V) and Mo(III) provides very strong evidence for a mechanism involving only reactions 1 and 2. Reaction 3 occurs only as a slow following reaction if Sn(II) is in excess. Reaction 5 is too slow to be competitive with reaction 1 except where Sn(II) is added slowly to Mo(VI) as in run 8.

The mechanism of reaction in dilute hydrochloric acid cannot be described with such certainty. Previous results[2,3] indicate that even in dilute hydrochloric acid Mo(VI) is reduced in one two-electron step to Mo(IV). Thus steps 1 and 2 could be important in dilute acid as well. Mo(V) could become the ultimate product if reaction 5 or another reaction such as

$$\mathrm{Mo(VI)} + \mathrm{Mo(IV)} \longrightarrow (\mathrm{Mo(V)})_2 \quad (6)$$

became fast compared with step 1. Qualitatively it has been observed that Mo(III) is more rapidly oxidized by Mo(VI) and other oxidants in dilute acid than in concentrated acid and that reaction 1 becomes measurably slow in the absence of chloride. Nothing can be said about relative rates of Mo(IV) reactions in concentrated and dilute acid.

In summary, reactions 1 and 2 are definitely established as steps in the mechanism of reduction of Mo(VI) with Sn(II) in concentrated hydrochloric acid. Other studies[3,4] suggest these reactions as also occurring in dilute hydrochloric acid, but further study of the interactions of the various oxidation states of molybdenum is required to elucidate the mechanism in dilute acid. Mo(IV) now can be regarded as an established reactive intermediate.

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