

<Note>

## Molybdenum Catalyzed Reduction of Hydroxylamine at Dropping Mercury Electrode

SIR: Haight Jr. and Carl von Frankenberg<sup>(1)</sup> studied the Molybdenum catalyzed chemical reduction of hydroxylamine with stannous ion. Comments were made that they failed to find a catalytic polarographic reduction for hydroxylamine similar to those observed for perchlorate<sup>(2,3)</sup> and nitrate<sup>(3,4)</sup>.

Afterwards, the study of molybdenum catalyzed polarographic reduction was extended to oxalate<sup>(5)</sup> and chlorate<sup>(6)</sup>. Moreover, Davis et al<sup>(7)</sup> reported that among Ti(III), Mo(III), Cr(II) etc., only Ti(III) was oxidized by hydroxylamine rapidly and Blazek<sup>(8)</sup> observed the catalytic wave in the Ti(III)-hydroxylamine system.

In the present note the evidence of the presence of catalytic action of molybdenum on the polarographic reduction of hydroxylamine and some of the characteristics of the catalytic waves are reported.

### EXPERIMENTAL

Sodium molybdate, hydroxylamine hydrochloride and the other chemicals used were of reagent grade. Most of the polarograms were recorded with Electro-Chemograph using polarotron. The characteristics of the capillary used were; drop time, 3.55 sec.,  $m$ , 1.77 mg per sec. at an applied potential of  $-0.4$  V vs. S. C. E. in 0.01 M HCl 0.2 M in KCl and 0.2 M in hydroxylamine hydrochloride.

### RESULTS AND DISCUSSION

**Catalytic waves of Hydroxylamine**; In Fig. 1, the wave C' indicates normal three waves of molybdenum in weak acid medium<sup>(9,10,11)</sup>, whereas hydroxylamine gives no waves. Evidently the second wave (labelled B<sub>1</sub><sup>(9)</sup>) of the normal Mo(VI) polarogram is enhanced about fourteen times by the addition of hydroxylamine. Thus the effect of hydroxylamine on the B<sub>1</sub> is too great to be understood as the effect of variation of acid and/or chloride ion concentration

by addition of hydroxylamine hydrochloride. The characteristics of this catalytic wave is different from those of nitrate, perchlorate and chlorate as we shall see later.

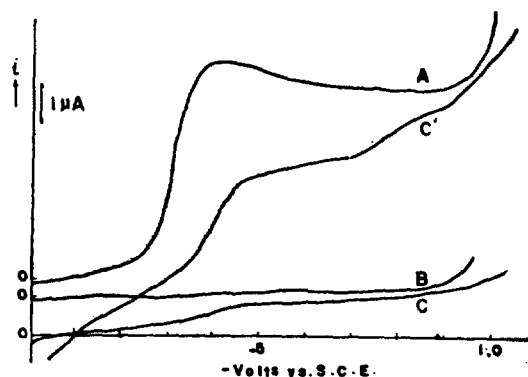
Effect of Hydrochloric acid concentration is shown in Fig. 2. When hydrochloric acid is not added to the solution, single limiting current curve that exhibits a rounded maximum(peak) appears. As the acid concentration is increased, the peak splits into two. Up to 0.01 M in HCl the relative second peak height increases and its peak potential shifts towards more positive, and resulting in a regular wave finally. Above 0.01 M HCl, the height of limiting current plateau decreases gradually. The second peak which appears at acid concentration between 0.001 and 0.06 corresponds to the third wave(labelled B<sub>2</sub><sup>(9)</sup>) of the normal Mo(VI) polarogram, by observing the effect of acid concentration, which is similar to those of normal wave behavior and its peak potential.

**Effect of Hydroxylamine Concentration**; Polarograms were run in 0.01 M hydrochloric acid and 0.2 M KCl being 0.1 M in Mo(VI) at hydroxylamine concentrations between 0.01 and 0.5 M, corresponding currents are listed in Table I. Plots of the dependence of catalytic currents on the square root of hydroxylamine concentration give a straight line. At other acid or Molybdenum concentrations where two peaks appear, both peak currents also show the same dependence. Thus the strong dependence of currents on hydroxylamine concentration indicates hydroxylamine acts as the oxidant.

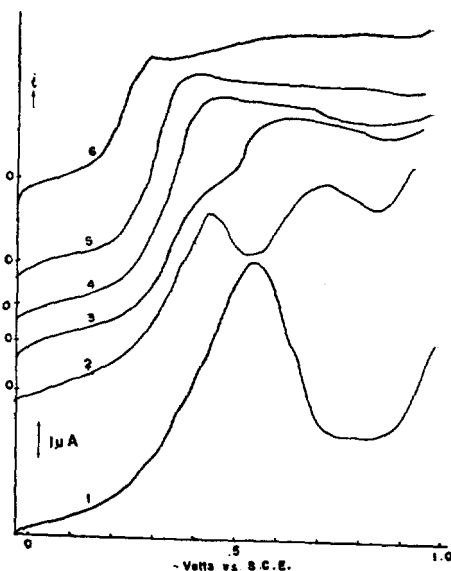
**Effect of Molybdenum(VI) Concentration and Height of Mercury Head**; As shown in Fig. 3, even in 0.01 M HCl, when the molybdenum concentration exceeds 0.1mM, the wave splits into two peaks. In low molybdenum concentration and high acid concentration (Fig. 2), the only one catalytic wave corresponding to normal B<sub>1</sub> wave, and the limiting

catalytic currents ( $i_c$ ) are constant over a range of potentials covering at least 0.4 V. This constancy shows almost conclusively that the catalysis must be due to Mo(III). As shown in Fig. 4, up to 0.1 mM in Mo(VI), relation of  $i_c$  vs. Mo(VI) concentration is linear and  $i_c/i_d$  values are equal to 14. From this relation, it is possible to estimate the rate constant of the catalyzed reduction of hydroxylamine<sup>(12,13)</sup> to be  $9.2 \times 10^2 \text{ l} \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$ . It is of interest to note that the sum of the two peak currents in concentration of molybdenum above 0.1 mM fits on the same line as shown in Fig. 4. This fact appears to imply that the two peaks are due to equal oxidation state. The appearance of the peak on the first catalytic hydroxylamine wave could be attributed to partition of Mo(IV) in the catalysis. In this connection the interpretation of the second peak is somewhat complicated. However, it can be understood that molybdenum catalyzes the polarographic reduction of hydroxylamine in weak acid, giving rise to two catalytic waves, corresponding to normal  $B_1$  and  $B_2$ , in contrast to nitrate and perchlorate give only one ( $B_1$ ) and chlorate two (on A and  $B_1$ ).

The test of the effect of mercury head has been made in several instances and found to be independent, indicating the catalytic nature of the system. The catalytic limiting currents remain nearly constant toward the variation of the chloride concentration between 0.1 and 0.4 M KCl.

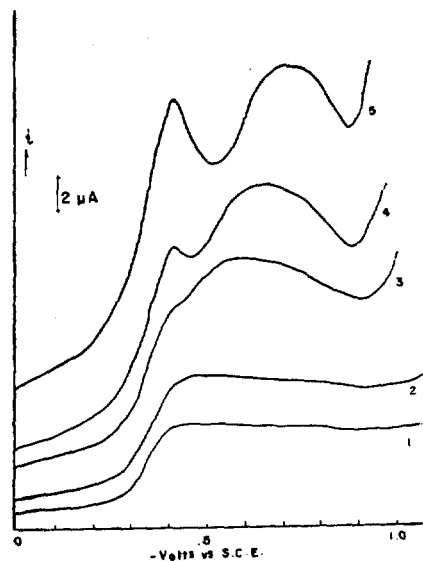


**Fig. 1.** Polarograms of hydroxylamine and molybdenum solutions. Supporting electrolyte: 0.01M in HCl and 0.2M in KCl.  
A, 0.1 M hydroxylamine and 0.1 mM molybdenum(VI);  
B, 0.1 M hydroxylamine;  
C, 0.100mM molybdenum  
C'; same as C but current sensitivity increased fivefolds.

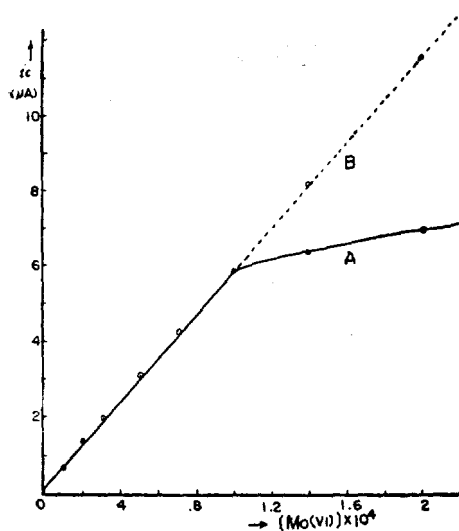


**Fig. 2.** Effect of hydrochloric acid concentration on catalytic hydroxylamine waves in the presence of 0.100mM molybdenum, 0.2 M KCl, and 0.2 M hydroxylamine. Molar concentration of hydrochloric acid;

(1)0, (2)0.002, (3)0.005, (4)0.01, (5)0.02, (6)0.06



**Fig. 3.** Catalytic hydroxylamine waves in 0.01 M HCl, 0.2 M KCl and 0.2 M hydroxylamine solution at varying molybdenum (VI) concentration. Millimolar concentration of Mo(VI):  
(1) 0.07, (2) 0.1, (3) 0.2, (4) 0.3, (5) 0.5



**Fig. 4.** Catalytic currents ( $i_c$ ) as a function of molybdenum concentration in 0.01 M HCl, 0.2M KCl and 0.2M hydroxylamine. Curve A; Values obtained from the plateau or first peak. Curve B; Sum of the first and second peak currents.

**Table I;** Effect of Hydroxylamine Concentration on the Catalytic Currents in 0.2M KCl, 0.01M HCl in the Presence of 0.1 mM Molybdenum (VI)

Concentration of $\text{NH}_2\text{OH}\cdot\text{HCl}(\text{M})$	$i_c^*$ ( $\mu\text{A}$ )	$E_{1/2}$ -volts vs. S. C. E.
0.5	10.40	.346
0.2	5.60	.353
0.1	3.80	.367
0.05	2.55	.370
0.02	1.54	.374
0.01	1.01	.374

\* Limiting catalytic currents are averaged and corrected for residual current obtained from separate blank curve.

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