Mechanism of the Molybdate Catalyzed Reductions of Perchlorate and Nitrate Ions at the Dropping Mercury Electrode

G. P. HAIGHT, Jr.

Department of Chemistry, Swarthmore College, Swarthmore, Pa., U.S.A., and Kemisk Laboratorium A, Danmarks Tekniske Højskole, Copenhagen, Denmark

Data on the catalytic waves found for molybdate in acid solutions containing nitrate and perchlorate have been reexamined and extended. Various theories of catalytic polarographic currents are applied. The conclusion from studies in homogeneous systems (that Mo(IV) is the catalyst) is introduced and the consequence tested. Given this assumption it is possible to determine the order of magnitude of rate constants for the bimolecular reactions of Mo(IV) with nitrate, perchlorate, and chloride, and for the disproportionation of Mo(IV).

The powerful catalytic effect of molybdate toward the reduction of perchlorate and nitrate has been observed to occur when reduction is effected by stannous ion [1], zinc [2], or at the dropping mercury electrode [3,4]. By showing that Mo(VI), Mo(V), and Mo(III) are not the catalyst, Haight and Sager concluded [1] that the unstable Mo(IV) state is the catalytically active form of molybdenum in these systems. It has been interesting for the author, in connection with studies of the reduction of nitrate in homogeneous systems [5], to reexamine the polarographic data [3,4] in the framework of the theories of polarographic catalytic currents developed by Koutecky [6], Delahay and Stiehl [7], and Orlemann and Kern [8] in order to test the assumption that Mo(IV) which disproportionates is the catalytic species.

EXPERIMENTAL

Much of the data used in drawing the conclusions of this paper have been drawn from Refs.[3,4]. Additional data reported here were obtained in conventional manner using Radiometer model PO-4 recording polarograph. Since the primary interest is in limiting currents, mercury pool anodes were employed. Polarographic cells were thermostated at 25°C.

THEORETICAL

Considering a sequence of reactions giving a catalytic polarographic wave:

$$A + ne \longrightarrow B \quad \text{(Diffusion controlled)} \tag{1}$$

$$B + Z \xrightarrow{k_2} A \tag{2}$$
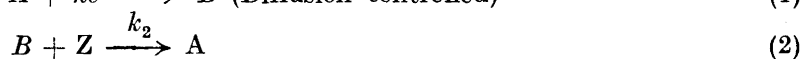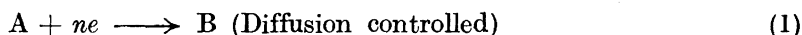
Delahay and Stiehl [7] derived an equation for the catalytic current

$$i_c = 0.753 \times 10^6 nm^{2/3}t^{2/3}D_A^{1/2}C_A C_Z^{1/2}k_2^{1/2} \tag{I}$$

where i_c is the catalytic current in microamperes; n is the number of electrons in the electrochemical reduction (1); m is the number of milligrams of mercury per second flowing from the capillary; t is the time, in seconds, of formation of each drop of mercury; D_A is the diffusion coefficient of substance A in cm²/sec.; C_A is the concentration in moles per liter of substance A in the bulk of the solution; C_Z is the concentration in moles per liter of substance Z, and k_2 is the rate constant in liters per mole per second for reaction (2). Koutecky, considering spherical, rather than linear diffusion, for the same chemical situation, derived the equation

$$i/i_d = 0.812 \ (C_Z k_2 t)^{1/2} \tag{II}$$

where i is the total current observed and i_d is the current if no catalysis takes place. If one considers the situation when $i_c \gg i_d$, division of eqn. (I) by the Ilkovic equation [7] for i_d gives
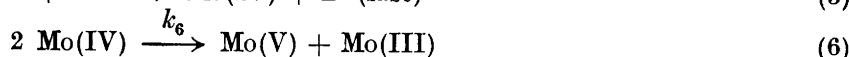
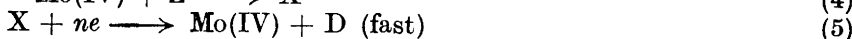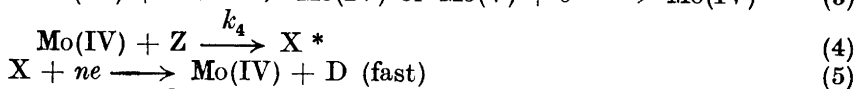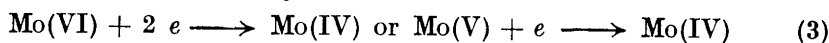$$i_c/i_d = 1.2(C_Z k_2 t)^{1/2} \tag{III}$$

Thus k_2 is 2.25 times as great if eqn. (II) is employed as it is if eqn. (I) is used. Delahay and Stiehl require $C_Z k_2 > 100$ reciprocal seconds for their equation to be valid. Koutecky requires $C_Z k_2 t > 100$, which is considerably less restrictive since t is generally between 2 and 6 sec. It should be noted that k_2 in Koutecky's derivation is replaced by $(k_t + k_b)$ where k_t is k_2 and k_b is the rate constant for the reverse reaction;

$$A \longrightarrow B + Z \tag{-2}$$

PROPOSED MECHANISM FOR CATALYTIC CURRENTS

The evidence for Mo(IV) as the catalytic species of molybdenum should be presented since most of the analysis and discussion hinges on this assumption. As stated, it has been shown [1] that the other common valence states are not catalytically active. Further, the author has observed [13] that 10^{-4} M Mo(VI) in 0.5 M hydrochloric acid gives a single polarographic wave with the characteristics of a reversible two-electron reduction. This wave is enhanced by the presence of either perchlorate or nitrate indicating that the product, which is assumed to be Mo(IV), is the catalyst. Further evidence is found in the nature of the catalytic waves themselves. Mo(III) is inert toward catalysis. Thus the catalytic waves should cease at potentials where Mo(III) is produced. (Such a discontinuity is observed in the tungstate catalyzed reduction of perchlorate [14]). In this case no such discontinuity occurs, indicating that the Mo(V)→ Mo(III) wave, which is enhanced by the catalysis in question, consists of electroreduction of Mo(V) to Mo(IV) followed by rapid disproportiona-

tion of Mo(IV). Mo(III) is not produced by electro-reduction, thus the steady state concentration of Mo(IV) is unaffected by increasing the potential of the electrode beyond that needed to give a limiting current. The principle evidence for Mo(IV) as the catalytic species continues to be the evidence against the other valence states, however. The following reactions are proposed as contributing to the observed catalytic effects.

$$\text{Mo(VI)} + 2\ e \longrightarrow \text{Mo(IV) or Mo(V)} + e \longrightarrow \text{Mo(IV)} \qquad (3)$$

$$\text{Mo(IV)} + \text{Z} \xrightarrow{k_4} \text{X} * \qquad (4)$$

$$\text{X} + ne \longrightarrow \text{Mo(IV)} + \text{D (fast)} \qquad (5)$$

$$2\ \text{Mo(IV)} \xrightarrow{k_6} \text{Mo(V)} + \text{Mo(III)} \qquad (6)$$

Z will be either nitrate or perchlorate ion. X is an electroreducible species which may be Mo(VI), Mo(V), or a complex of Mo(IV) with Z which allows the electroreduction of nitrate or perchlorate. The kinetics of homogeneous reductions has suggested complexes [1,9], but no choice can be made on the nature of X nor the value of n. D would be chloride ion if perchlorate is electrolytically reduced and one of many reduction products if nitrate is so reduced. It is seen that n may be any integer from 1 to 8. It will most likely be 2, if Mo(IV) is oxidized to Mo(VI); 8, if perchlorate is reduced to chloride, or 4, if nitrate is reduced to N_2O, the product with this catalyst and Sn(II) as reducing agent in solutions containing sulfate [5]. Eqns. 3, 4, and 5 are seen to give the same pattern as eqns. 1 and 2. Thus the catalytic current should be proportional to the concentration of Mo(VI) in the bulk of the solution and proportional to the half power of the concentration of perchlorate or nitrate. If disproportionation becomes important at high Mo(VI) concentrations the catalytic current should become dependent upon the square root of the bulk concentration of Mo(VI), as follows.

Consider a steady state for Mo(IV) at the surface of the mercury drop. Mo(IV) will be formed at the same rate at which Mo(VI) diffuses from the bulk of the solution into the reaction layer at the surface of the drop. Mo(IV) will leave the reaction layer by diffusion and by disproportionation into Mo(V) and Mo(III).

$$dN/dt = k_D A[\text{Mo(VI)}] - k_D A[\text{Mo(IV)}] - k_6[\text{Mo(IV)}]^2 V = 0 \qquad (IV)$$

where N is the number of atoms of Mo(IV) in the reaction layer at the drop surface, k_D is a diffusion rate constant, A is the area of the mercury drop, V is the volume of the reaction layer, [Mo(VI)] is the concentration in moles per liter of molybdate in the bulk of the solution, and [Mo(IV)] is the concentration in moles per liter in the reaction layer at the surface of the mercury drop. From the Ilkovic equation [10] it can be calculated that

$$k_D = 1.27(D/t)^{1/2} \qquad (V)$$

where D is the diffusion coefficient in cm^2/sec (assumed to be the same for Mo(VI) and Mo(IV) and t is the time required for the formation of each mer-

* k_4 and k_2 correspond to one another.

cury drop. Letting $V = A\mu$, where μ is the thickness of the reaction layer, and solving for Mo(IV) we find

$$[\text{Mo(IV)}] = \frac{-k_D}{4\,\mu k_6} + \left(\frac{k_D^2}{4\,\mu^2 k_6^2} + \frac{k_D}{\mu k_6}\,[\text{Mo(VI)}] \right)^{1/2} \qquad (\text{VI})$$

Thus, at high concentration of Mo(VI), the second term under the square root sign in eqn. (VI) becomes dominant. A plot of catalytic current *vs.* [Mo(VI)]$^{1/2}$ should give a straight line, the slope and intercept of which will yield values of the product μk_6. The validity of this reasoning was checked by applying it to the disproportionation of U(V) studied by Orlemann and Kern [8]. The equations which they used were directly derivable and the values of constants found to be identical. We shall assume that reaction (4) leading to catalytic current does not remove Mo(IV) from the reaction layer, and that disproportionation removes only one Mo(IV) atom, the one which becomes Mo(III). If Mo(VI) or Mo(V) are formed by either or both of these reactions it is assumed that they will be electrolytically reconverted to Mo(IV) at rates which are very high compared with the purely chemical processes.

Effect of chloride ion on catalytic waves

Inhibition of catalytic waves by foreign anions such as chloride ion can best be ascribed to competitive reaction for sites on the catalytically active Mo(IV):

$$\text{Mo(IV)} + \text{Z} \xrightarrow{k_4} \text{C} \qquad (4)$$
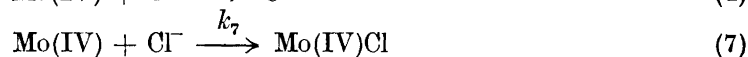
$$\text{Mo(IV)} + \text{Cl}^- \xrightarrow{k_7} \text{Mo(IV)Cl} \qquad (7)$$

Let α be the fraction of Mo(IV) reacting with Z to give catalytic current. If $(i_c)_0$ is the catalytic current for ClO$_4^-$ in the absence of chloride

$$\alpha = \frac{k_4[\text{Mo(IV)}][\text{ClO}_4]}{k_4[\text{Mo(IV)}][\text{ClO}_4] + k_7[\text{Mo(IV)}][\text{Cl}^-]} = \frac{i_c}{(i_c)_0} \qquad (\text{VII})$$

Table 1. Effect of changing perchlorate and nitrate concentrations on catalytic current *.
    8.95 × 10^{-5} M Mo(VI), $m = 1.01$ mg/sec, $t = 6.0$ seconds, $T = 25°C$.

$i_c\ \mu A$	[ClO$_4^-$] m/l	i_c/[ClO$_4^-$]$^{1/2}$
1.35	0.05	6.0
1.78	0.10	5.7
4.05	0.50	5.7
5.65	1.00	5.7
8.30	2.00	5.9
	[NO$_3^-$]	i_c/[NO$_3^-$]$^{1/2}$
20.6	1.00	20.6
6.9	0.10	21.8

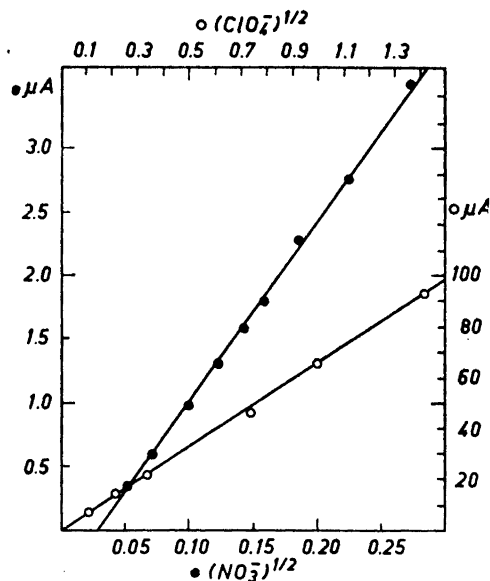* Ion strength could not be maintained constant.

Fig. 1. Dependence of catalytic currents on the square root of the concentrations of nitrate (closed circles) and of perchlorate (open circles).

Eqn. (VII) rearranges to

$$\frac{(i_c)_0}{i_c} = 1 + \frac{k_7[Cl^-]}{k_4[ClO_4]} \tag{VIII}$$

Thus, if k_4 has been determined, k_7 is readily calculable from observed catalytic currents in the presence of chloride.

Table 2. Rate constants from kinetic currents.

Reaction	Medium	k_4 l m^{-1}sec^{-1}	Data source
Mo(IV) + NO$_3^-$	0.1 M HNO$_3$	2700/n^2	New
	1.0 M HNO$_3$		
Mo(IV) + NO$_3^-$	0.05 M HNO$_3$	2370/n^2	Ref.[4]
	0.10 M H$_2$SO$_4$		
	0.20 M Na$_2$SO$_4$		
Mo(IV) + ClO$_4^-$	1.0 M HClO$_4$	250/n^2	Ref.[3]
	1.0 M HClO$_4$	180/n^2	Ref.[3]
	0.75 M H$_2$SO$_4$		

$D = 6.88 \times 10^{-6}$ cm^2/sec for Mo(VI) in 0.2 M NaHSO$_4$ used for nitrate calculations.
$D = 5.76 \times 10^{-6}$ cm^2/sec for Mo(VI) in 1 M H$_2$SO$_4$ used for perchlorate calculations.
$m^{2/3}t^{1/6}$ had to be estimated for nitrate calculations.
3.45 cm^2 was used. Only $m^{2/3}t^{1/6}$ values are available.
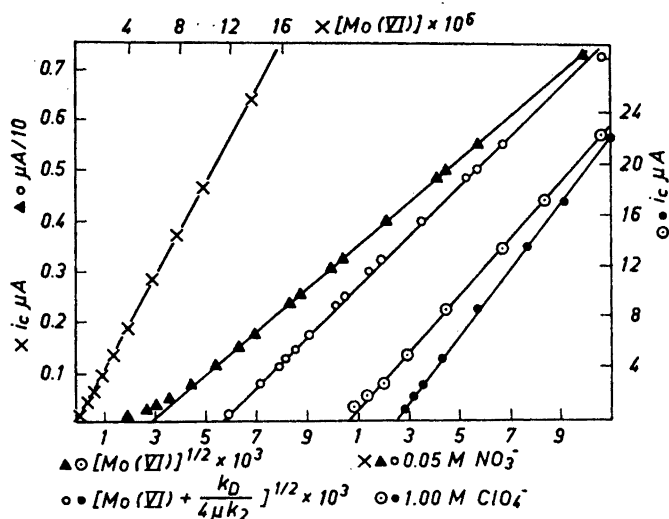k_4 values determined from eqn. (1), then multiplied by 2.25.

Fig. 2. Dependence of i_c on molybdate concentration. At low concentration (crosses) i_c is directly proportional to [Mo(VI)]. The test of eqn. (VI) at higher concentrations of Mo is shown in the other plots. The points represented by open and closed circles are estimated from the adjacent lines.

EXPERIMENTAL TESTS OF THEORETICAL PREDICTIONS

The term $m^{2/3}t^{2/3}$ in eqn. (I) requires that catalytic currents be independent of the head of mercury in the reservoir of the dropping electrode. This test has been made in several instances in the case of the perchlorate catalysis and found to be true. One rough measurement in 1 M nitric acid showed that the catalytic current was independent of head of mercury. However, this test was not applied under the conditions used to obtain the data on the nitrate reduction upon which calculations in this study are based[4].

Previously unreported data on the dependence of i_c on perchlorate concentration is given in Table 1.

Figs. 1 and 2 show clearly the dependence of catalytic currents on the square root of nitrate and perchlorate ion concentrations, and on the first power of the molybdate concentration when it is lower than 10^{-5} M. The plot of i_c *vs.* $[NO_3^-]^{1/2}$ reflects the fact that the nitrate concentrations were below those required to maintain $k_2 C_z t > 100$ at the lower values.

For $[Mo(VI)] > 10^{-5}$ M a dependence of i_c on $[Mo(VI)]^{1/2}$ as predicted by eqn. (V) is found. However, slope and intercept give disparate values of $k_D/k_6\mu$ because the two terms under the square root sign in eqn. (V) are of comparable magnitude. It is possible to estimate μk_6 from the slope of the plot which is insensitive to the changes to be made and then to plot i_c *vs.* $\dfrac{k_6}{4k_6\mu} + [Mo(VI)]$.

Such a procedure brings slope and intercept into fair agreement. The analysis has ignored the possibility of polymerization of Mo(VI) and the possibility
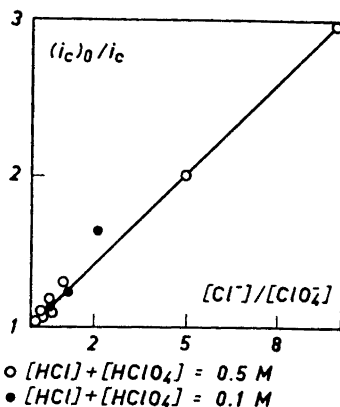
$Fig.$ $3.$ Chloride inhibition of catalysis. A test of eqn. (VIII).

of reoxidation of Mo(III). High acidity and low concentrations of molybdate justify ignoring polymerization and the absence of catalysis when Mo is introduced in the trivalent state justifies the latter assumption. However, freshly formed Mo(III) may be much more reactive than that previously prepared and subsequently added to solutions to be polarographed.

Fig. 3 shows a plot of $(i_c)_o/i$ $vs.$ $[Cl^-]/[ClO_4^-]$ using the intercept at $[Cl^-]$ $= 0$ as the origin. New data (summarized in Table 3) has been obtained for ion strength 0.5 and combined with that reported for ion strength 0.1 in Ref.[3]. The previous observation that i_c was proportional to perchlorate concentration is seen to be a fortuitous result in which the combined effects of perchlorate dilution and chloride inhibition participate.

Evaluation of rate constants. k_4 may be determined from eqn. (I) using data obtained under conditions where i_c is proportional to [Mo(VI)]. Values of the diffusion coefficient, D, for molybdate used in the calculation were derived from non-catalytic currents obtained in similar media. Sources are indicated in Table 1. Only $m^{2/3}t^{1/6}$ was recorded for Robinson and Johnson's data [4] on the nitrate waves and not individual values of m and t. For purposes of estimating k_1 and k_2 from these data, the values 3.5 for $m^{2/3}t^{2/3}$ and 3 sec. for the drop time have been selected arbitrarily in order to obtain the order of magnitude of the constants.

Table 3. Disproportionation constants for Mo(IV).

Medium	μ/n (cm) $=$ $[D/k_1 C_Z]^{1/2}$ $\times 10^4$	nk_e (l m^{-1}sec^{-1}) $\times 10^{-4}$
0.05 M HNO$_3$	2.58	5.78 (intercept)
0.20 M NaHSO$_4$		6.5 (slope)
1.0 M HClO$_4$	1.52	0.91 (intercept)
		0.70 (slope)
1.0 M HClO$_4$	1.80	2.4 (intercept)
0.75 M H$_2$SO$_4$		2.61 (slope)

In the case of perchlorate an estimate of the equilibrium constant $K = [Mo(IV)ClO_4]/[Mo(IV)][ClO_4^-]$ is available from the kinetic data of Haight and Sager[1]. In 2.5 M sulfuric acid $K = 8.15$ l mole^{-1} if the rate constants for disproportionation of different Mo(IV) species are assumed to be the same. Thus if $k_4 = k_f + k_b$, k_f is about 89 % of k_4 and k_b about 11 %. For strict comparison a polarographic study must be undertaken in the same medium used for the homogeneous kinetics[1]. It is likely that K is larger in the polarographic case here reported since sulfate may be expected to decrease complex formation with perchlorate.

The values of k_4 reported in Table 1 are the results of such calculation multiplied by 2.25 to give the result consistent with Koutecky's treatment of spherical diffusion. Values of k_4 for reactions involving nitrate and perchlorate ions in various media are summarized in Table 1. Given values of k_4, k_7 can be readily calculated from eqns. (VII) and (VIII). Individual results for k_7 are included in Table 3. The slope of the line in Fig. 3 gives $k_7 = 50/n^2$ l/m/sec.

Values for the disproportionation rate constant, k_6 depend on the assignment of a value for the thickness of the reaction layer, μ. Comparing Koutecky's theoretical result[6] with that of Brdicka and Wiesner[11] based on the concept of the reaction layer, μ is found to be equal to $D^{1/2}/k_1^{1/2}C_Z^{1/2}$(Ref.[12]). Orlemann and Kern[8] evaluated μ for the case of a simple disproportionation reaction giving catalytic current and obtained the value $\mu = 0.3D^{1/2}t^{1/2}$. Normally these values will differ by about a factor of 10. Since the main effect being studied is the catalytic current due to reaction with Z, the reaction layer will be assigned the former value, which is the smaller, on the assumption that only disproportionation within this smaller region affects the catalytic current. Values of k_6 and of μ based on these assumptions are recorded in Table 2.

Table 4. Effect of chloride ion on catalytic currents for perchlorate. $[Mo(VI)] = 10^{-6}$ M, $m = 4.24$ mg/sec, $t = 2.0$ sec. $(i_c)_0$ is calculated on the basis of the square root law for perchlorate concentration.

i_c	$(i_c)_0$	a	$[ClO_4^-]$	$[Cl^-]$	$k_7\ n^2$
4.88	4.88	1	0.5	0.0	—
4.58	4.66	0.982	0.455	0.045	44
4.08	4.46	0.916	0.417	0.083	105
4.20	4.46	0.943	0.417	0.083	74
3.70	4.09	0.904	0.35	0.15	62
3.56	4.09	0.871	0.35	0.15	85
2.68	3.46	0.775	0.25	0.25	72
1.00	2.00	0.500	0.083	0.417	50
0.50	1.48	0.338	0.0455	0.455	49
2.01	2.01	1	0.10	0.0	—
1.46	1.65	0.885	0.067	0.033	66
1.14	1.42	0.803	0.05	0.05	61
0.71	1.16	0.612	0.033	0.067	77

Average $k_7 = 67/n^2$

The accuracy is extremely limited by the inherent difficulty in making precise polarographic measurements. K values depend on small differences in these measurements. Note — a difference of 3 % in i_c in the 3rd and 4th lines makes a 30 % difference in k_7. See Fig. 3.

DISCUSSION

The figures show that the proposed mechanism is clearly consistent with available data. The straight line plots confirm the form of the equations consistent with the theory. It is unfortunate that lack of knowledge of n values and the inaccessibility of details of capillary characteristics leaves doubt as to values for the rate constants. However, the results give added weight to a general pattern for the manner in which molybdenum functions as a catalyst in the reduction of oxy-ions. In papers to follow dealing with the homogeneous catalysis of the reduction of hydroxylamine and nitrate, it will be observed that disproportionation becomes an effective part of kinetics at concentrations of molybdenum (added as V or VI) in the neighborhood of 10^{-5} M consistent with the polarographic finding. Direct information about the disproportionation from polarographic data in the absence of catalysis may be difficult to obtain in view of the low concentrations at which it becomes important. Polymerization of Mo(VI) leads to changing character of polarographic waves with changing molybdate concentration and such effects will be difficult to sort out from others such as those due to disproportionation.

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