

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE LABORATORY FOR NUCLEAR SCIENCE, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Effect of Complex Formation in the Polarographic Reduction of Arsenic(III) in Hydrochloric Acid¹

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From a knowledge of the species in solution and the effects of changes in the concentrations of chloride and hydrogen ions on the half-wave potential, electron-transfer to $\text{As}(\text{OH})\text{Cl}_2$ has been shown to be the slow step in the reduction of arsenic(III) to (0) in acidic chloride media. Evidence is cited for bridging by chloride.

Introduction

There have been few attempts to investigate quantitatively the effect of complex formation on electron-transfer-controlled reductions by polarography. Tanaka and Tamamushi³ extended the Nernst diffusion-layer theory of Eyring, Marker and Kwoh⁴ to this case and attempted to apply it to the reduction of nickel in thiocyanate media. However, other complicating factors, as evidenced by curious humps and dips, sometimes appeared in the waves. In addition, no equilibrium constants were available for the complexation reactions involved, so that these authors were limited to qualitative observations. Another investigation with essentially the same approach was the chromium(VI) study of Baumann and Shain.⁵ Matsuda and Ayabe⁶ applied the theoretical approach of MacGillavry and Rideal⁷ to this case and used the results to interpret the data of Morinaga⁸ for the reduction of nickel in ammoniacal media.

The purpose of the present study was to demonstrate the applicability of the theory of Koutecký⁹ to this case and to test it on a particular chemical system. The reduction of arsenic(III) to arsenic metal in acid chloride media was chosen for two reasons. First, the polarographic characteristics of this system¹⁰ were known to be favorable, the most complete study being that of Meites.^{10d} Two waves are observed due to the successive reductions to arsenic metal and arsine. Meites reported that in the absence of surface-active agents the first wave was well formed and shifted to less cathodic potentials with increasing concentration of hydrochloric acid. Secondly, quantitative information about the species present had just been reported.¹¹ Arcand showed that, in the range of chloride and hydrogen ion concentrations of interest, the species $\text{As}(\text{OH})\text{Cl}_2$, $\text{As}(\text{OH})_2\text{Cl}$, $\text{As}(\text{OH})_3$ and $\text{As}(\text{OH})_2$ are present in appreciable amounts.

Koutecký's theory of electron-transfer controlled processes at the dropping mercury electrode (d.m.e.) is directly applicable to cases in which there is a single simple reducible species. However, it can be extended readily to cases involving complex equilibria such as arsenic(III).

The diffusion of each arsenic species to the electrode surface is governed by an equation of the form of

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} + \frac{2x}{3t} \frac{\partial C}{\partial x} \quad (1)$$

in which C is the concentration of the species and D its diffusion coefficient; x is the distance from the electrode and t is time. However, only one diffusion equation need be considered if the complexed species are in rapid equilibrium.⁶ This combined equation is identical in form to equation 1 except that ΣC , the formal arsenic concentration, and D_m , a weighted-mean diffusion coefficient, are substituted for C and D , respectively. The problem is then the same as the one solved by Koutecký except for the boundary condition describing reaction at the electrode surface. Koutecký's condition is,

$$t > 0, x = 0; \quad D(\partial C/\partial x) = kC \quad (2)$$

In the present case, while $D(\partial C/\partial x)$ can be replaced by $D_m(\partial \Sigma C/\partial x)$, the term kC must be replaced by $\Sigma k_i C_i$. It can be shown that the concentration of the i th species can be represented by $g_i \Sigma C$, where g_i is a function of the concentration of complexing ligands but is independent of ΣC , so that instead of the condition of equation 2 one obtains

$$t > 0, x = 0, \quad D_m(\partial \Sigma C/\partial x) = \Sigma C \Sigma k_i g_i \quad (3)$$

Thus, after the substitutions have been made the solution in this case should be exactly the same as that in Koutecký's case except that for C , k and D are substituted ΣC , $\Sigma k_i g_i$ and D_m , respectively.

When many species are capable of reaction at the electrode, the equations resulting from this analysis are very difficult with which to work because of the large number of adjustable parameters. However, when only one species reacts appreciably, considerable simplification is possible. The factor $\Sigma k_i g_i$ reduces simply to kg .

From Koutecký's results, it is possible to show that, in the present situation, the half-wave potential can be represented by the equation

$$E_{0.5} = \frac{RT}{\alpha n_a F} \ln \frac{gk^0 \sqrt{t_d}}{0.87 \sqrt{D_m}} \quad (4)$$

where t_d is the drop-time of the d.m.e. From this

(1) This work was supported in part by the Atomic Energy Commission under Contract AT(30-1)-905.

(2) National Science Foundation Fellow, 1955-1957.

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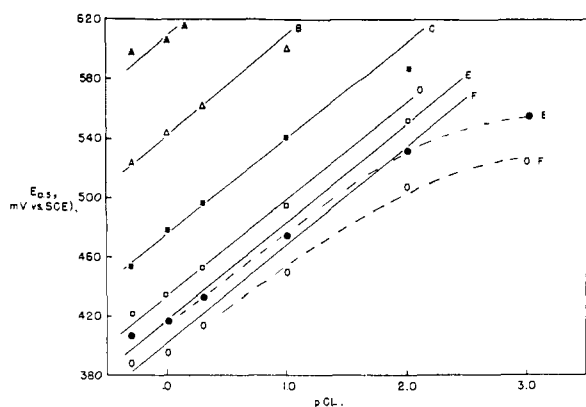


Fig. 1.—Effect of chloride on the reduction of arsenic(III) at the d.m.e. Solid lines are theoretical; points and broken lines, experimental: Curve A, 10^{-2} *N* hydrogen ion; Curve B, 10^{-1} *N* hydrogen ion; Curve C, 10^{-1} *N* hydrogen ion; Curve D, 0.5 *N* hydrogen ion; Curve E, 1.0 *N* hydrogen ion; Curve F, 2.0 *N* hydrogen ion.

equation, it should be possible to evaluate quantitatively shifts of $E_{0.5}$ with the concentrations of complexing ligands.

Results

A number of criteria were applied to make certain that the reduction of arsenic(III) was indeed electron-transfer controlled and was not complicated by chemical kinetic effects. It was first shown that plots of $\log(i_1 - i)/i$ or the equivalent *versus* potential were linear and had slopes markedly less than RT/nF , a value of 1.7 ± 0.2 having been observed for *n*. Furthermore, the current was independent of the height of mercury *H* at the foot of the wave (but proportional to $H^{1/2}$ on the plateau where diffusion was rate determining). For a diffusion-limited electron-transfer-controlled wave, $E_{0.5}$ should be proportional to $(RT/\alpha n_a F) \ln(1/t_d^{1/2})$, and this, too, was shown to be true. Finally, if no polynuclear species are involved in the electrode reaction, the $E_{0.5}$ should be independent of arsenic concentration. The experimental results indicated that there was a slight dependence in the range 0.01 to 1 *mM*, approximately a 10 mv. shift to less cathodic potentials having been observed in going from the lowest to the highest concentration of arsenic in 1 *M* hydrochloric acid. This shift, which probably reflects the partial coverage of the electrode surface by elemental arsenic,^{10d} was not considered to be large enough to affect significantly the results of this study.

The effects of the concentrations of chloride and hydrogen ions on the reduction of arsenic(III) are presented in Fig. 1 and 2. The $E_{0.5}$ values were determined by plotting $\log(i_1 - i)/i$ *versus* potential and taking the intercept with the abscissa of the resulting straight line. The value of αn_a was obtained from the slopes of the same plots. In some cases, the encroachment of the second wave made the valid estimation of the height of the diffusion plateau difficult. For these cases, a function of the derivative of the current-potential curve was plotted instead. This function allowed determination of the same quantities without the necessity of obtaining a valid estimate of i_1 . This

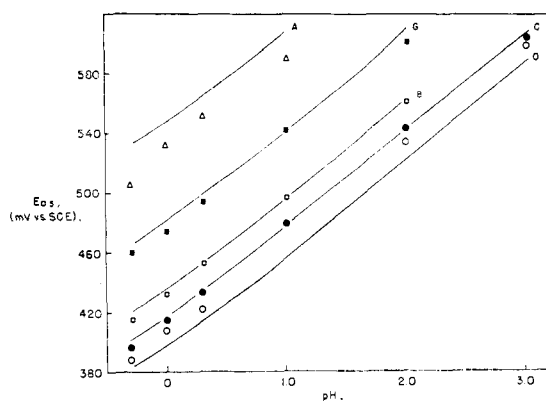


Fig. 2.—Effect of hydrogen ion on the reduction of arsenic(III) at the d.m.e. Solid lines are theoretical; points, experimental: Curve A, 10^{-2} *M* chloride; Curve G, 10^{-1} *M* chloride; Curve B, 0.5 *M* chloride; Curve C, 1.0 *M* chloride; Curve D, 2.0 *M* chloride.

procedure and its theoretical basis are discussed in the Appendix.

Great difficulty was encountered in obtaining reproducible values of $E_{0.5}$ at low concentrations of acid and chloride despite a number of precautions such as rinsing all apparatus with nitric acid to remove traces of surface-active material and boiling stock solutions to remove the last traces of oxygen. In this low-concentration region, the data indicate a transition between two reduction mechanisms. Evidently the relative efficiencies of these mechanisms are quite sensitive to some uncontrolled factor. At these low concentrations, the validity of the theoretical treatment becomes questionable also because the concentrations of chloride and hydrogen ion are not sufficiently greater than the arsenic concentration to assume that they remain constant at the electrode surface at all potentials.

The equations represented above indicate that the values of drop-time and diffusion coefficient should affect the position of $E_{0.5}$. Evidently the diffusion coefficients of the various species involved were approximately the same because D_m was not observed to change appreciably in the region studied except at very low hydrogen and chloride concentrations.

The complexity constants for the arsenic species present in the media under investigation have been determined recently by Arcand.¹¹ By calculating the values of *g* to be expected for the various species at the various concentrations of chloride and hydrogen ion and plotting $RT/\alpha n_a F$ times the natural logarithm of this function *versus* the logarithms of these concentrations, several families of curves were obtained similar to those in Fig. 1 and 2. If the equations of the theoretical section are applicable, one of these sets of curves should be superimposable on the experimentally observed values of $E_{0.5}$ *versus* log concentration by simple displacement along the potential axis.

Because k^0 could not be calculated or estimated independently, the theoretical values of $E_{0.5}$ were of the form

$$E_{0.5} = \frac{RT}{\alpha n_a F} \ln g + \text{constant} \quad (5)$$

The additive constant was calculated by assuming

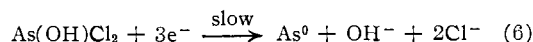
the experimental $E_{0.5}$ to be equal to the theoretical $E_{0.5}$ for the particular case of $(H^+) = 0.5 M$ and $(Cl^-) = 0.5 M$. All other theoretical values of $E_{0.5}$ were then calculated from the value of the constant thus obtained.

Discussion

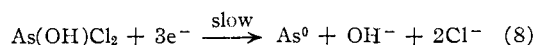
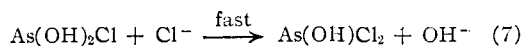
Comparison of theoretical with experimental values of $E_{0.5}$ gave a reasonable fit only with the hypothesis of $As(OH)Cl_2$ as the formula of the activated complex as shown in Fig. 1 and 2. The agreement seems reasonably good in view of the large number of unavoidable assumptions involved. These include the neglect of activity coefficients, inaccuracies in the polarographic equations, experimental variabilities, possible oversimplification of the electrode process, and inaccuracies in the values of the equilibrium constants.

At low hydrogen ion and chloride concentrations there are wide deviations from theory. These are attributable to two causes. First, as already mentioned, the assumptions regarding the constancy of hydrogen ion and chloride concentrations are no longer valid at the electrode surface. Secondly, as witnessed by the fact that little change from these cases is noted in the complete absence of chloride ion, a second mechanism, which does not involve chloride ions, evidently becomes feasible at these more cathodic potentials. Because of the difficulties associated with the close proximity of the second wave and the poor reproducibility of results, no attempt was made to interpret quantitatively the results in this region.

The problem next arises of suggesting a mechanism consistent with the observed results in the region of interest. First, it should be noted that the treatment of the experimental data allows only the determination of the formula of the activated complex. Because we have assumed $As(OH)Cl_2$ and $As(OH)_2Cl$ to be in rapid equilibrium, there is no distinction between a mechanism of the type



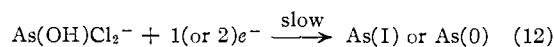
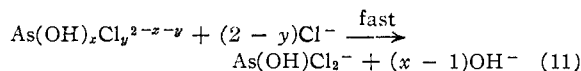
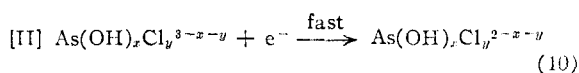
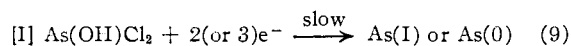
and one of the type



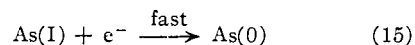
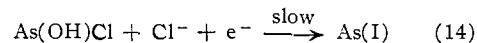
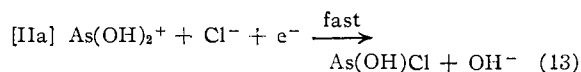
Indeed, both would operate simultaneously.

Since the observed αn_a is 1.7 ± 0.2 , it is apparent that at least two, and possibly three, electrons must be added in reactions occurring through the rate-determining step. However, not more than one electron can be added in a Nernst-controlled reaction prior to the rate-determining step because the apparent αn_a should be equal to the number of electrons involved in reversible steps preceding the slow step plus the αn_a for the slow step.

In view of these considerations, there are two different types of possible mechanisms



The latter is the more inviting because it suggests the possibility of an ion-bridge mechanism of the type shown for some oxidation-reduction reactions in solution by Libby¹² and Taube.¹³ Such a mechanism might proceed in the fashion



The transfer of each electron would be accompanied by acceptance of a chloride and ejection of a hydroxide ion. Presumably the chloride would come from the tightly bound double layer and act as a bridge between the arsenic ion and the electrode. As noted by Meites,^{10d} the wave is very sensitive to traces of surface-active species in solution and can be obliterated completely by small amounts of gelatin. If a mechanism of type IIa were operative, this behavior would be readily explicable; *i.e.*, gelatin displaces chloride in the double layer and thus removes the possibility of a direct bridge to the electrode.

Conclusions

For reasonably uncomplicated cases, in which some knowledge of the nature of the actual species present in solution is available, quantitative investigation of the change of $E_{0.5}$ with the concentration of complexing ligands can lead to the composition of the activated complex and give some indication of the number of electrons involved in reactions through the rate-determining step. However, except in fortuitous cases, independent information is necessary for the determination of the mechanism of an electrode reaction.

Experimental Details

Polarograms were run at $30.0 \pm 0.1^\circ$ using standard techniques with a recording polarograph, built in these Laboratories, which resembles commercially available ones.

Standard solutions of 3 M sodium chloride, sodium perchlorate and perchloric acid were prepared from reagent-grade materials. Appropriate amounts of these were mixed on the day of use to form solutions having an ionic strength of two and a range of concentrations of chloride and acid. Because surface-active agents are known to affect the arsenic wave adversely, no maximum suppressor was used. Instead of conventional agar salt bridges, the end of the salt bridge of a Hume-Harris type reference cell¹⁴ was plugged with a small (0.5 cm.) length of unfused Vycor rod¹⁵ which previously had been leached with hydrochloric acid to remove iron.

A saturated sodium chloride calomel cell was prepared and found to have a potential within 1 mv. of the saturated calomel electrode. To prevent contamination of the solution with chloride, a double salt-bridge was used, the bridge

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in contact with the cell containing saturated sodium perchlorate and the other saturated sodium chloride.

Meites^{10a} indicated that at high concentrations of arsenic the height of the limiting-current plateau became independent of arsenic concentration. He suggested that at these concentrations the electrode surface became completely coated with a non-conducting layer of elemental arsenic and that the current then became limited by the electrode area rather than by diffusion. These observations were qualitatively confirmed in the present study. To avoid anomalous results due to this behavior, all experiments were performed with 0.1 *mM* solutions. Calculations indicated that at this concentration the electrode should not have a coating on more than 5% of its area at any time during drop life. Experimentally, the current was found to be proportional to arsenic(III) concentration in this concentration region.

Appendix (by W. H. R.)

Relations of Derivative Polarography.—By rearranging

$$E = E_{0.5} + \frac{RT}{\alpha n_a F} \ln (i_1 - i)/i \quad (16)$$

it can be shown that for an electron-transfer-controlled wave the current at any point can be written as

$$i = \frac{i_1}{1 + \sigma} \quad (17)$$

where

$$\sigma = \exp \left(\frac{\alpha n_a F}{RT} (E - E_{0.5}) \right)$$

Differentiation yields

$$\frac{di}{dE} = \left(\frac{\alpha n_a F}{RT} \right) \frac{i_1 \sigma}{(1 + \sigma)^2} \quad (18)$$

Substituting the equality $i_d/(1 + \sigma)^2 = i^2/i_d$ into the above equation gives

$$\frac{di}{dE} = \frac{\alpha n_a F}{RT} \frac{i^2 \sigma}{i_1} \quad (19)$$

Rearranging and taking logarithms of both sides

shows that

$$E = E_{0.5} + \frac{RT}{\alpha n_a F} \ln \left(\frac{1}{i^2} \frac{di}{dE} \right) + \frac{RT}{\alpha n_a F} \ln \frac{RT i_1}{\alpha n_a F} \quad (20)$$

Since the first and third terms on the right-hand side are independent of potential, plotting $\ln (di/dE)/i^2$ versus E should give the slope $RT/\alpha n_a F$. However, in contrast to the usual procedure of plotting $\ln (i_1 - i)/i$, it is possible to obtain this slope without the necessity of obtaining an accurate measure of i_1 . Since the current-potential relation has the same form in the Nernst-controlled (reversible) case, similar equations hold. The only difference is that for αn_a should be substituted n .

Equivalent relations can be derived for the case in which not the plateau current but the residual current level is uncertain. This can be done by assuming that $(i_1 - i)$ rather than i is the easily measurable quantity.

It should be pointed out that this method is much more tedious than the conventional procedure of plotting $\ln (i_1 - i)/i$ and is subject to much greater inherent inaccuracy because of the error in estimating the finite difference $\Delta i/\Delta E$ which is substituted for the derivative di/dE in practical applications. In addition, the method cannot be used when the interfering wave contributes significantly to the measured i . However, for cases such as the one discussed in the text, it is useful. It may find further application in the analysis of Tafel-type plots where curvature is found due to concentration polarization but limiting-current plateaus often are not reached because of experimental limitations.

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Hot-Atom Chemistry of Bromine Atoms in Crystalline Potassium Bromate¹

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The reactions of recoil bromine atoms in potassium bromate have been further investigated. The retention (yield of bromate) has been determined as a function of the bombardment time, flux of neutrons, conditions of dissolution and the particular isotope investigated. The yield of bromate from the isomeric transition process in Br^{80m}-labelled potassium bromate also has been measured as a function of the ambient temperature. The results of these experiments are compared with previous work and significant differences are found.

Introduction

A number of investigators²⁻⁸ have studied the reactions of recoil bromine atoms in crystalline bro-

mates, and the factors which influence the yields of the several oxidation states.^{4,6-8} Despite these studies, one cannot yet be sure as to the nature of the primary fragments formed by recoil in the crystal, or the reactions of these fragments on dissolution in aqueous media, although a promising beginning has been made on this problem.⁸ The experiments reported in this paper were undertaken (a) to extend our knowledge of this system both on lines suggested by previous work and in other directions, (b) to clear up some discrepancies in the published literature and (c) to examine in detail a particular aspect in which the recoil reaction in po-

(1) Research carried out under the auspices of the U. S. Atomic Energy Commission.

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