Studies on the Brdicka Catalytic Wave of Hydrogen by the Potential-step Method, Part 1. Cystine and Cysteine

By

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In continuation of our studies of the Brdicka catalytic wave of hydrogen¹⁻⁷⁾, it became necessary to know more about the electrode reaction which produces the catalytic wave due to sulfhydryl groups in ammoniacal buffered solution of cobalt ion. Although there have often been discussions on the mechanism of the Brdicka catalytic wave of hydrogen⁸⁻¹⁰⁾, further research should be conducted to ascertain the intricate electrode reaction which leads to the characteristic form of the wave.

The authors have become convinced that the adsorption of reducible surface active substance on the dropping mercury electrode and the contending complex formation of a new ligand with ammonia for cobalt are the leading factors for the formation of the characteristic wave.

In the present investigation, the exact measurements of current-potential curves for the Brdicka catalytic wave of hydrogen are carried out by the potential-step method¹¹⁻¹³⁾.

Experimental

Materials. All the reagents used were of analytical grade. The test solutions used are tabulated in the following:

Test Solution No.	Constituent
1	0.1 <i>F</i> NH ₄ Cl-NH ₃
2	10 ⁻³ <i>F</i> CoCl ₂ + 0.1 <i>F</i> NH ₄ Cl-NH ₃
3	10 ⁻⁵ <i>M</i> Cystine + 0.1 <i>F</i> NH ₄ Cl-NH ₃
4	10 ⁻³ <i>F</i> CoCl ₂ + 0.1 <i>F</i> NH ₄ Cl-NH ₃ + 0.01% Gelatin
5	10 ⁻⁵ <i>M</i> Cystine + 10 ⁻³ <i>F</i> CoCl ₂ + 0.1 <i>F</i> NH ₄ Cl-NH ₃
6	10 ⁻⁵ <i>M</i> Cysteine + 10 ⁻³ <i>F</i> CoCl ₂ + 0.1 <i>F</i> NH ₄ Cl-NH ₃

Apparatus. A Shimadzu Recording Polarograph, Type RP-2, was used to obtain the ordinary polarographic data. A mercury pool electrode was used as anode. The capillary used had *m*-value of 2.063 mg. sec⁻¹ and a drop time of 3.74 sec in the solution of 0.1 *F* NH₄Cl-NH₃ at open circuit with mercury head of 63.6 cm.

An electronic potentiostat¹¹⁾ constructed by Oka was utilized. The potential-controlling switch of this instrument was replaced by an outside switch with a polarization unit. Reproducibility of the controlled potential was better than ± 3 mV. The rise time for the potential change was approximately 1×10^{-5} sec. Current-time curves were recorded with an Iwasaki Synchroscope Model SS-5302 with a SP-20 DF-A preamplifier.

A cell with a hanging mercury drop electrode similar to the one used by Gerischer¹³⁾ and by Delahay¹⁹⁾ was utilized. The hanging mercury electrode was prepared by attaching one drop of mercury taken from the capillary on a gold-plated platinum wire by means of a glass spoon. The potential of the hanging mercury electrode was measured against the mercury pool electrode.

Procedure. In the potential-step method, the potential of the working electrode was changed abruptly from a short-circuited equilibrium value to a fixed value and the electrolytic current-time curve was registered by the synchroscope. Collecting the data of those current-time curves, the current at any time elapsed since the beginning of the electrolysis can be plotted against the corresponding applied voltage. Thus the current-potential curves were obtained.

Results

Current-Time Curves. Current-time curves obtained with the various test solutions are shown in Figs. 1-A, B, C and D. The electrode potential was changed abruptly from an initial value of potential, at which no appreciable electrolytic current was observed on polarographic waves, to a fixed value of potential, as indicated on the curves.

Current-Potential Curves. Current-potential curves obtained by the potential-step method are shown in Figs. 2, 3, 4, 5 and 6. The ordinary polarograms of the test solutions are also shown in the figures.

Discussion

The problem on the mechanism of the electrode process associated with the catalytic wave has not been solved. Our knowledge concerning with this problem is as follows¹⁻¹⁰⁾: Cobaltous ions forms chelates with compounds containing sulfhydryl groups^{6,8,9)}. These chelates decrease the overvoltage of the hydrogen evolution in the buffered solution. Though the catalytic waves are observed at potentials at which cobalt ammine complex ions have been reduced, cobaltous chelates with sulfhydryl groups are not reduced to metallic state, or even when it is reduced to lower state of valency it still remains without liberation of its ligands. However, the exact mechanism of the electrode reaction itself is not yet known satisfactorily. In addition to the complex formation involved, the catalytic effect may be affected by the orientation (adsorption) of catalytically active complex, *i.e.* the cobalt chelates with sulfhydryl groups, at the surface of the electrode.

Although the electronic potentiostat with fast response has been developed recently, the potential-step method has not been applied to the elucidation of catalytic processes. This method can be applied to the study on chemical reactions which are too fast for kinetic study by ordinary polarography. In this method, the working electrode potential is abruptly changed from its equilibrium value to a definite potential in a very short time. In reality, concentration polarization cannot be completely avoided but can be minimized by fast observation of the electrode response, hence partial or total control of the electrode process by mass transfer will be avoided.

Potential-Time Curves.

The potential-time curves obtained with the various test solutions are shown in Fig. 1. Curve a in Fig. 1-A shows the current-time curve obtained with the solution containing only supporting electrolyte. Curve b shows the current-time curve for the reduction of cobaltous ions in the ammoniacal buffered solution and also indicates that the charging

current is quite negligible after 5×10^{-4} sec elapsed from the beginning of the electrolysis. The peak *p* in Fig. 1-B corresponds to the peak seen in Fig. 1-A-a and it is understood to be due to the charging current of the differential capacity of the double layer. In Figs. 1-B, -C and -D, it is seen that anomalous humps occur on current-time curves. These humps suggest the presence of surplus current which does not appear in usual current-time curve. This is explained by that the depolarizer (*i.e.*, cystine as in Fig. 1-B or cobalt chelate as in Fig. 1-C, -D) is concentrated initially at the electrode surface and that the surplus current is due to the reduction of the concentrated depolarizer, as described by Oka in the case of thallous ion in potassium chloride solution¹³⁾. After the accumulated depolarizer has been consumed the electrolytic current decreases to the ordinary electrolytic current.

Fig. 1. Current-Time Curves

Current-Potential Curves.

In Figs. 2, 3, 4, 5 and 6, the ordinary polarograms are compared to the current-potential curves obtained by the potential-step method. Figs. 2 and 3 show the curves of cobalt (II) in the ammoniacal buffered solutions without and with gelatin. As seen in

Fig. 2. Current-Potential Curves of Cobalt.

Fig. 3. Current-Potential Curves of Cobalt with Gelatin.

Fig. 2-A', the maximum wave of cobalt seen on the ordinary polarogram is suppressed remarkably in the case of potential-step method. In the latter case, since the solution and the mercury drop electrode are stationary, the stirring effect of the solution in the vicinity of electrode surface can hardly occur within very short time (10^{-3} sec) of observation. Therefore, the maximum of cobalt wave is assumed to be based on convection effect in accordance with Antweiler¹⁶⁾ and von Stackelberg¹⁷⁾. Fig. 6 shows current-potential curves with the ammoniacal buffered solution of cystine.

C) ordinary polarogram : test solution No. 5.

C') current-potential curves by potential-step method : test solution No. 5 :

a) 25 msec, b) 50 msec, c) 100 msec, d) 250 msec.

Fig. 4. Catalytic Wave of Cystine

D) ordinary polarogram : test solution No. 6.

D') current-potential curves by potential-step method : test solution No. 6

a) 25 msec, b) 50 msec, c) 100 msec, d) 250 msec.

Fig. 5. Catalytic Wave of Cysteine

Half-Wave Potential for Cobalt Wave and Peak Potential for Catalytic Wave.

In the comparison of the half-wave potentials of ordinary polarograms with those of current-potential curves obtained by the potential-step method, it was found that the difference of the latter from the former, ($\Delta E_{1/2}$), varies with the time of observation. This effect was pointed out by Oka¹⁾, who took this shift accounting for much shorter time (t) of observation of the electrolytic current than the drop time of dropping mercury electrode (τ). Equation of the relationship between the difference of the half-wave potentials ($\Delta E_{1/2}$) and the time of observation can be written in the following form¹³⁾:

$$\Delta E_{1/2} = \frac{RT}{\alpha n F} \ln \sqrt{\frac{t}{\tau}}$$

where R = gas constant

T = absolute temperature

α = transfer coefficient for the electrode process

n = number of electrons involved in the electrode process

F = Faraday constant

τ = drop time of dropping mercury electrode for the ordinary polarography

t = time of observation

According to the equation a plot of $\Delta E_{1/2}$ versus $\ln\sqrt{\frac{t}{\tau}}$ should yield a straight line whose slope is $\frac{RT}{\alpha nF}$. Plot a in Fig. 7 shows variation of $E_{1/2}$ for cobalt (II) wave with $\ln\sqrt{\frac{t}{\tau}}$. Thus the parameter α can be calculated for cobalt (II) wave by taking up the linear part of the plot. The curved part of the plot is remained unexplained. From the slope of the plot a, it is obtained that $\alpha=0.3$. Plots b and c in Fig. 7 show similar relationships on ΔE_p for catalytic peaks of cystine and cysteine. Namely, plotting ΔE_p , instead of $\Delta E_{1/2}$, versus $\ln\sqrt{\frac{t}{\tau}}$, one can find linear relationships at fairly small values of time. Slopes of these straight lines yield " α -" values of 0.9 for cystine and 0.3 for cysteine if the above

Fig. 6. Current-potential curves of cystine by potential-step method, test solution No. 3 : a) 5 msec, b) 10 msec, c) 25 msec.

Fig. 7. Relationships between ΔE and $\ln\sqrt{\frac{t}{\tau}}$, a) cobalt wave, b) catalytic wave of cystine, c) catalytic wave of cysteine.

A) Catalytic wave of cystine.

B) Cystine wave.

Fig. 8. Three-dimensional models.

equation is applied formally. This kind of α -value may, though quite formal ones at present, serve as an index value for the characterization of the catalytic wave of hydrogen evolution.

Three-dimensional Models.

From the above results based on current-time and current-potential curves, one can build up the three-dimensional models consisted of rectangular coordinates i , E and t , as shown in Fig. 8. It should be recognized that the current-potential curve which has been discussed in the ordinary polarography corresponds to the curve projected on a longitudinal section (i - E plane) at a few seconds on t -axis. From these models, morphological characteristics of the current-potential curves which have been questioned so far are expected to be clarified. The experimental survey and criticism of these models and their applications to the fields of medicine and biology are left for future.

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