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**Abstract**

**Full Text**

## **Reports of the Academy of Sciences of the USSR**

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### **PHYSICAL CHEMISTRY**

**S. G. MAIRANOVSKII**

## **ON IRREVERSIBLE CATALYTIC WAVES OF HYDROGEN IN POLAROGRAPHY**

*(Presented by Academician A. N. Frumkin, February 27, 1958)*

Earlier <sup>(1,9)</sup> it was shown that the catalytic evolution of hydrogen at a mercury cathode is not associated with a decrease in the activation energy of the discharge of hydrogen ions, and that it is determined only by the electrochemical and chemical properties of the catalyst substance. It was also shown that the electrochemical stage of the catalytic process may in some cases be reversible, and equations were derived for reversible catalytic hydrogen waves in buffered and unbuffered solutions. The present work is devoted to the study of irreversible catalytic hydrogen waves.

As the object of investigation, catalytic waves caused by quinine were chosen; quinine has a number of advantages over other catalysts. Quinine possesses two active groups, differing in their catalytic properties, and therefore gives two catalytic waves observed at different potentials: the first wave appears in an acidic medium, the second in neutral and weakly alkaline solutions. Both quinine waves, unlike waves caused by many other catalysts, can under appropriate conditions be obtained well before the background discharge, which considerably facilitates the study of their form. In addition, for quinine the influence of the concentrations of the proton donor and of the catalyst on the height of the catalytic wave has been studied in considerable detail <sup>(2)</sup>.

The work was carried out on a visual polarograph at  $25 \pm 1^\circ$ . The dropping electrode with a blade for forced detachment of drops <sup>(3)</sup> had the following characteristics:  $m = 3.82$  mg/sec,  $t = 0.26$  sec. The working procedure was the same as in studies <sup>(1,9)</sup>.

Analysis of the form of the waves observed in buffer solutions showed that their lower part, as in ordinary irreversible polarographic waves, in the region where concentration polarization is still absent, is described by the equation

Fig. 1

Figure 1: Fig. 1

$$E = \text{const} - \frac{RT}{\alpha n F} \ln i \quad (1)$$

(see curves 2-5 in Fig. 1), where  $E$  is the potential,  $i$  is the current strength,  $n$  is the number of electrons participating in the electrochemical stage (for catalytic hydrogen currents  $n = 1$ ), and  $\alpha$  is the transfer coefficient, which for both quinine waves, irrespective of the pH of the medium, proved to be equal to 0.6.

The upper part of the waves, however, has no limiting-current plateau; instead, on the polarograms there is observed a characteristic rounded maximum, which is a specific feature of irreversible catalytic hydrogen waves. It may be assumed that, as the cathodic potential increases, a change occurs in the mechanism of the electrode process, leading to a decrease in the current<sup>(4)</sup> and distortion of the upper part of the wave. On the basis of this assumption, by the methods described<sup>(8)</sup>, values were found for the limiting currents ( $i_{\text{lim}}$ ) of the catalytic waves that would be observed in the absence of a decrease in current. The values of  $i_{\text{lim}}$  found in this way proved to be

proportional to the concentration of quinine (at not very high values of it). The values of  $i_{\text{pr}}$  were used to construct plots  $E(\lg i/(i_{\text{pr}} - i))$ , which showed that irreversible catalytic hydrogen waves, up to the potentials corresponding to the onset of the decrease in current, are described by the equation

$$E = E_{1/2} - \frac{RT}{\alpha F} \ln \frac{i}{i_{\text{pr}} - i}. \quad (2)$$

Experiment shows that all logarithmic plots obtained with a given catalyst at a definite pH fall on one straight line (see Fig. 1), i.e., for a given wave at one and the same pH of the solution, the value  $E_{1/2}$ , within the experimental error (2-3 mV), does not depend on the catalyst concentration.

**Fig. 1.** First catalytic wave of quinine in a buffer solution of pH 3.0.  
2-5: curves  $\lg i(E)$  for quinine concentrations, respectively: 2.8; 5.5; 7.8, and  $10 \cdot 10^{-6} M$ .  
1 –dependence

$$\lg \frac{i}{i_{\text{pr}} - i}(E)$$

for the same solutions.

**Fig. 2.** Dependence of the logarithm of the decrease in currents on the potential.

Fig. 2

Figure 2: Fig. 2

Figure 3 and Figure 4

Figure 3: Figure 3 and Figure 4

- 1 –for the first catalytic wave at pH 3.0 (for four quinine concentrations).
- 2 –for the second wave at pH 8.3 (for two quinine concentrations).

To determine the form of the curve along which the decrease in current takes place, distorting the upper part of the irreversible catalytic waves, the observed currents  $i_{\text{obs}}$  were compared with the values  $i_{\text{theor}}$  that would occur in the absence of the decrease, i.e., with the values found from (2). It turned out that the curves expressing the magnitudes of the current decrease  $\Delta i$  (see Fig. 2) do not depend on the catalyst concentration and can be described by the empirical equation

$$\gamma \lg \Delta i = \gamma \lg(i_{\text{theor}} - i_{\text{obs}}) = E'_0 - E, \quad (3)$$

where  $E'_0$  is a constant characteristic of the given pH and equal to the potential at which  $\Delta i$  reaches unity;  $\gamma$  is a proportionality factor. Fig. 2 gives the curves  $\lg \Delta i(E)$ : 1 –for the first wave at 4 concentrations of quinine (the same as for the curves in Fig. 1) in a citrate-phosphate buffer with pH 3.0, and 2 –for the second catalytic wave in a lithium-borate buffer with pH 8.3 at two quinine concentrations. The values of  $E'_0$  for these curves lie near  $-1.42$  and  $-2.00$  V, respectively; the value of  $\gamma$  in both cases lies within 60-80 mV. It must be noted that at potentials at which a noticeable discharge of the background occurs, the decrease in current diminishes and ceases to obey equation (3). This explains the bend in the right-hand part of the curves in Fig. 2.

Fig. 3 gives curves for catalytic waves observed in a borate-lithium buffer at two quinine concentrations (curves 1 and 2). Their upper part, drawn as a dash-dot line, is constructed according to the equation

(3). Curve 3 in the upper part of the figure represents the decrease in current  $\Delta i(E)$ , curve 4—the background discharge with allowance for the lowering of the charging current caused by adsorption of quinine (linear extrapolation from less negative potentials). The currents in Fig. 3 have been corrected for the residual current. Comparison of curves 1, 2, and 3 shows that the shape of the irreversible catalytic wave (up to potentials preceding appreciable background discharge currents) is due to the occurrence of two processes expressed by equations (2) and (3). The nature of the phenomena leading to the decrease in current is not yet clear; its study is continuing.

**Fig. 3.** Catalytic waves of hydrogen (1 and 2) at pH 8.3 and quinine con-

centrations of  $4.7$  and  $8.6 \cdot 10^{-7}$  M; 3—current-decay curve; 4—residual-current curve

**Fig. 4.** Plots of  $\lg \frac{i}{i_{pr} - i}(E)$  for catalytic hydrogen waves in a solution with pH 8.5. 1, 2—in the presence of BTEA (0.1 M); 3—without BTEA. Quinine concentrations: 1— $5.6$ ; 2— $1.35 \cdot 10^{-5}$  M; 3— $\sim 4$  and  $\sim 8 \cdot 10^{-7}$  M.

Catalytic waves caused by quinine, under identical conditions, exceed by several orders of magnitude the reversible catalytic waves observed in the presence of pyridine. Bearing in mind the considerably greater surface activity of quinine at the mercury–solution interface than that of pyridine, this phenomenon can be explained by a large (in comparison with pyridine) increase in the concentration of quinine in the near-electrode layer relative to its value in the bulk of the solution. Indeed, introduction into the solution of tetraethylammonium benzenesulfonate (BTEA), which has very high surface activity, substantially lowers the irreversible catalytic waves. Thus, when the solution is brought to 0.1 M in BTEA, the second catalytic wave of quinine in borate–lithium buffer (pH 8.5) decreases by more than 30 times, whereas the reversible wave caused by pyridine is reduced under these conditions by only 20% (<sup>9</sup>).

Most significant, however, is that the addition of BTEA, as was found for the second quinine wave, shifts the wave toward positive potentials, increases its steepness, and eliminates the decrease in current in the upper part of the wave. The plot  $E(\lg i/(i_{pr} - i))$  of the catalytic wave in a buffer solution with 0.1 M BTEA is a straight line with a reciprocal slope of about 60 mV (Fig. 4, 1), i.e., it is extremely similar to the plot of the reversible pyridine wave observed in the same solution.

It should be noted that at low concentrations of quinine in the BTEA solution (Fig. 4, 2), just as for waves caused by pyridine, the lower part is described by an equation that takes into account the influence of dimerization (<sup>1,9</sup>).

$$E = \varepsilon_0 - \frac{RT}{F} \ln \frac{i^{2/3}}{i_{pr} - i}. \quad (4)$$

These facts show that the addition of BTEA to the solution imparts to the second

to the second catalytic wave of quinine has a clearly reversible character. Attempts to obtain the first wave of quinine in the presence of BTEA were not successful: the catalytic wave is masked by the background current.

The irreversibility of the catalytic hydrogen wave, at least in the case of the wave caused by quinine, is apparently associated with adsorption of the oxidized form of the catalyst  $BH^+$  on the electrode surface, leading to inhibition of the direct electrode process. R. Brdička (<sup>5</sup>) assumes that stronger adsorption of the oxidized form of a reversibly reducible substance leads to the appearance,

following the usual reversible reduction wave, of a small adsorption step. At a very low concentration of the substance, when the electrode surface is not yet filled with the adsorbed depolarizer, only one ( "subsequent" ) adsorption wave is observed. As the concentration of the depolarizer increases, the adsorption wave reaches a limiting value corresponding to saturation of the electrode surface by the adsorbed substance, and before the adsorption wave there appears the usual reversible reduction wave corresponding to the reversible reduction of the nonadsorbed depolarizer <sup>(5)</sup>.

The irreversible catalytic hydrogen wave may be regarded as Brdička's "subsequent" adsorption wave, the height of which is greatly increased by the catalytic effect. Since the concentration of the catalyst is usually much lower than that required to fill the electrode surface, only one "adsorption" irreversible catalytic wave is observed, corresponding to the catalytic action of adsorbed quinine (more precisely, of the product of its reduction, since the catalytic waves of quinine are preceded by the reduction wave of the quinoline nucleus of quinine <sup>(6)</sup>). When BCTEA is added to the solution, the catalyst is displaced from the electrode surface, and the desorbed  $BH^+$  particles give a reversible catalytic wave similar to the wave caused by pyridine. In Fig. 4, for comparison, curves are given for reversible—in the presence of BCTEA (1 and 2)—and for irreversible (3) catalytic waves caused by quinine.

The half-wave potential of the reversible quinine wave in a buffer solution with BCTEA shifts rather markedly toward positive values as the quinine concentration increases. This is explained, in part, by an increase in the rate of dimerization of the reduced form <sup>(7)</sup>.

The author takes this opportunity to express his gratitude to Academician A. N. Frumkin for repeated discussions of the question and valuable comments.

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\* In my article “On the Nature of Catalytic Hydrogen Currents in Polarography,” published in DAN, vol. 114, No. 6, 1957, the following corrections should be made:

On p. 1272, in equation (2), on the left-hand side before  $i$  there should be a minus sign:

$$-i = \chi ([B]_0 - [B]_s) - sF\mu_1 (k_1 [DH^+]_s [B]_s - k_2 [BH^+]_s [D]_s) : \quad (2)$$

On p. 1273, line 15 from the bottom, instead of “...becomes 19 mV more negative ...” one should read “...becomes 19 mV more positive...” \*

*Note: Figure translations are in progress. See original paper for figures.*

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