

DIRECT MEASUREMENT OF THE RATE CONSTANTS AND REACTION
MECHANISMS OF THE ELECTROCHEMICAL DESORPTION OF HYDROGEN
ON MERCURY

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A method of investigating fast electronic and bulk reactions of intermediate particles based on the emission of electrons into a solution when a metal-electrolyte boundary of separation is subjected to pulsed irradiation has been developed [1-4]. The formation of intermediate particles in solutions takes place as the result of the capture of electrons by added acceptors. The diffusion coefficients of $H^\cdot$, $D^\cdot$, $OH^\cdot$, and $OD^\cdot$ in aqueous solutions have been measured by this method [4]. In the present work, the method has been used to measure the absolute values of the rate constants of the electrochemical desorption of hydrogen on mercury. Since the rate of these reactions is several orders of magnitude higher than the discharge of hydrogen ions on mercury, such information cannot be obtained by traditional electrochemical methods.

Hydrogen atoms are formed in solution through the capture of solvated electrons e_{aq}^- by hydrogen ions, diffuse to the electrode, are adsorbed on it and, in the cathode range of potentials ($\varphi \leq -0.8$ V),* take part in electrochemical desorption reactions [5]:



For the surface concentration of H_{ads} (N_s) the following equation is valid:

$$dN_s/dt = D_H \left(\frac{\partial n}{\partial x} \right)_{x=0} - (W_0 + W_1 N) N_s, \quad (3)$$

where D_H is the diffusion coefficient of H atoms, $D_H (\partial n / \partial x)_{x=0}$ is the flow of hydrogen atoms to the electrode, and N is the bulk concentration of H_3O^+ . The change in the charge Q emitted into the solution due to the return to the electrode of e_{aq}^- not captured by H_3O^+ ions, to reactions (1) and (2) at $Wt \geq 1$ found from the solution of Eq. (3), and to the diffusion equations for e_{aq}^- and $H^\cdot$ has the form [4]

$$Q(t)/Q_\infty \approx 1 - 1/2 e^{-Wt} - \frac{1}{2\sqrt{\pi k_e N \delta t}} \left(1 + \frac{1}{2Wt} \right), \quad (4)$$

where $W = W_0 + W_1 N$, $\delta = D_H/D_e$, D_e being the diffusion coefficient of e_{aq}^- , and k_e is the rate constant of the capture of e_{aq}^- ions by H_3O^+ . As can be seen from (4), the value of W can be found from the deviation of the curve $Q(1/\sqrt{t})$ from its asymptote. At concentrations of H_3O^+ greater than $2 \cdot 10^{-3}$ M, the rates of reactions (1) and (2) are considerably smaller than that of the capture of e_{aq}^- by H_3O^+ ions and of the diffusion of $H^\cdot$ for the electrode, so that the shape of the kinetic curve $Q(t)$ is determined by the values of W . (The accuracy of measuring W_0 and W_1 is 20-30%.)

The method of measurement has been described previously [3, 4]. The results given relate to 1 M KCl solutions with additions of HCl.

*All the potentials are given relative to the saturated calomel electrode.

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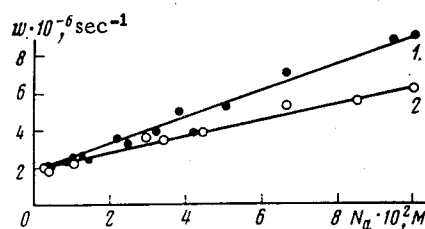


Fig. 1. Dependence of the rate of electrochemical desorption on the concentration of hydrogen ions. 1 M KCl. 1) H_3O^+ in H_2O ; 2) D_3O^+ in D_2O .

In agreement with (1)-(3), the dependence of W on N is linear (Fig. 1). The values of W_0 found in the range of potentials from -0.9 to 1.3 V rise from $1 \cdot 10^6$ to $9 \cdot 10^6$ sec^{-1} and the values of W_1 from $3 \cdot 10$ $M^{-1} \cdot \text{sec}^{-1}$ to $8 \cdot 10^8$ $M^{-1} \cdot \text{sec}^{-1}$ (Fig. 2a). In the range of temperatures from 3 to 60°C , W_1 rises by a factor of four to five, which corresponds to an activation energy of reaction (1) of $4-5$ kcal/mole, while in the same temperature interval the change in W_1 does not exceed the accuracy of the measurements (Fig. 2b).*

When H_2O is replaced by D_2O (and H_3O^+ by D_3O^+), W_0 does not change, but W_1 decreases by a factor of $1.5-2$ (Fig. 1). The change in the isotope effect in the interval from -1.0 to -1.2 V, where W_1 rises by a factor of four to five, does not exceed the accuracy of the measurements.

In the range of potentials studied, where the rate of electrochemical desorption on mercury is far higher than the rate of ionization of atomic hydrogen, its surface concentration on the discharge of H_3O^+ ions is

$$N_s = k_{H_3O^+} / W a_{H_3O^+}, \quad (5)$$

where $k_{H_3O^+}$ is the discharge rate constant and $a_{H_3O^+}$ is the activity of the H_3O^+ ions in solution. Table 1 gives the values of $N_s(\varphi)$ for $a_{H_3O^+} = 1$ M. The values of $k_{H_3O^+}$ were taken from the literature [7]. In view of the weak dependence $W(\varphi)$, N_s rises exponentially with $-\varphi$, as assumed by Krishtalik [8]. It can be seen from a comparison of the values of $k_{H_3O^+}$ and W (the former corresponds formally to the constant $k_{H_3O^+}^2 / D_{H_3O^+}$) that the rate constant of electrochemical desorption is greater than that of discharge over the whole working range of cathodic potentials (0 to -2 V). This confirms Frumkin's hypothesis [9] that the degree of occupancy of the surface of the mercury by atomic hydrogen is extremely small, and the limiting stage of the electrochemical evolution of hydrogen on mercury is the discharge of H_3O^+ ions.

The results obtained show that reaction (2) is activationless, in agreement with a previous hypothesis [8, 10], and that at the same time it is characterized by a small isotope effect and by an appreciable dependence of the rate constant on the potential of the electrode. This forces one to consider that, in the range of potentials studied, reaction (2) is connected with the tunnel passage of e_{Me}^- to an H_3O^+ ion located close to the surface. The alternative possibility of the transfer of a proton to an adsorbed hydrogen atom, as has been suggested in a number of publications (see, for example, the review [11]), would be accompanied by a large isotope effect, changing with φ , which does not agree with the experimental facts. The transfer probability w is connected with the measured value of W by the relation

$$W = f(b) v w(b), \quad (6)$$

where b is the distance at which $w(b)$ is a maximum, $f(b) \sim 1$ is the probability of finding the reagents at this distance, and v is the reaction volume ($1-5 \cdot 10^{-24}$ cm^3). To the experimental values of W_0 and W_1 correspond values of w of the order of 10^6-10^7 sec^{-1} and $10^{10}-10^{11}$ sec^{-1} , respectively. Figure 3 shows schematically the arrangement of the characteris-

*The value of k_e rises with the temperature in accordance with radiation-chemical results (activation energy 3.2 kcal/mole [6]). The value of δ remains constant with the same accuracy as that of W_1 , i.e., the temperature dependence of the diffusion coefficients of H^+ and e_{aq}^- (and also of H_3O^+) coincide in the given temperature range.

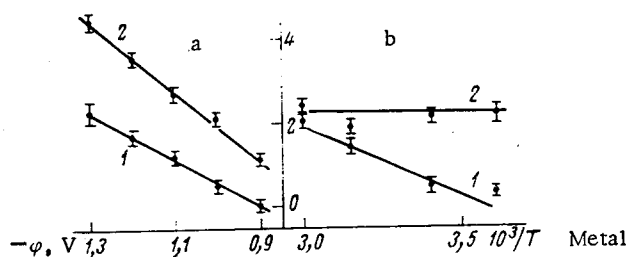


Fig. 2

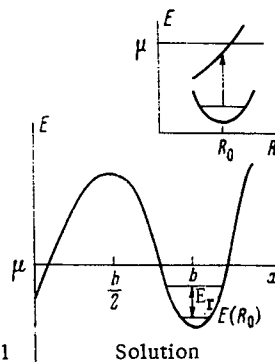


Fig. 3

Fig. 2. Dependence of the rate constants of electrode reactions (1) and (2) on the electrode potential (a) and on the temperature (b). 1) W_0 ; 2) W_1 . For a: $T = 294^\circ K$; b: $\varphi = 1.0 V$; 1) $\ln W_0 \cdot 10^{-6}$ (sec^{-1}); 2) $\ln W_1 \cdot 10^{-7}$ ($M \cdot \text{sec}^{-1}$).

Fig. 3. Scheme of the distribution of the characteristic energy levels of the Me, $H_{ads}^{\cdot}$, H_3O^+ system. The x axis is the electron coordinate, and μ is the chemical potential of the electron in the field of H_3O^+ .

TABLE 1. Surface Concentration of Hydrogen Atoms on a Mercury Electrode in the Discharge of H_3O^+

$-\varphi, V$	0.9	1.0	1.1	1.2	1.3	1.5*
N_s, cm^{-2}	$1.2 \cdot 10^5$	$4.3 \cdot 10^5$	$1.8 \cdot 10^6$	$6.0 \cdot 10^6$	$2.3 \cdot 10^7$	$2.7 \cdot 10^8$

*Extrapolated value of W .

tic energy levels of the system. The potential of an electron in the field of H_2O^+ can be approximated, for example, by the parabolic barrier:

$$U(x) = V - \frac{k}{2} \left(x - \frac{b}{2} \right)^2. \quad (7)$$

The potential U includes the applied potential difference, $e\varphi$,* and the energy of the zero vibrations ($1/2 \hbar \omega$) of H^+ (or D^+) in H_3O^+ (D_3O^+):

$$V = V_0 - \frac{\hbar \omega}{2} + e\varphi. \quad (8)$$

The probability of the tunnelling of an electron at this potential depends on its energy, since

$$\Gamma(E) = \Gamma_0 e^{-(V-E)/\gamma}, \quad \gamma = \frac{\hbar}{2\pi} \sqrt{\frac{k}{m}}, \quad (9)$$

where Γ_0 is the frequency of tunnelling ($\sim 10^{15} \text{ sec}^{-1}$).

Since $H_3O^{\cdot}$ is unstable, particularly close to $H_{ads}^{\cdot}$, the passage of an electron takes place into a repulsive energy level along the R coordinate, R being the distance between H and H_2O in $H_3O^{\cdot}$. The H_3O^+ and $H_3O^{\cdot}$ levels as functions of R are shown schematically at the top of Fig. 3, R_0 being the equilibrium distance $H^+ - H_2O$.

The passage of the electron takes place vertically, and therefore (E) must be multiplied by the Franck-Condon factor Φ_E :

$$\Phi_E = \frac{1}{\Delta F \sqrt{\pi}} e^{-(E - E(R_0)/\Delta F)^2}, \quad (10)$$

*A possible relationship $V(\varphi)$ is referred to by Brodskii and Urbakh [12]. Relation (8) is valid at $b/2 \geq d$, where d is the thickness of the Helmholtz layer.

where F is the slope of the repulsive level, and $\Delta^2 = 2\hbar/M\omega$ is the square of the amplitude of the zero vibrations of $H^+(D^+)$ in $H_3O^+(D_3O^+)$. The complete probability of tunnelling is given by the integral with respect to the Fermi electron distribution in the metal $f_\Phi(E, T)$:

$$w = \int_{-\infty}^{\infty} \Phi_E \Gamma(E) f_\Phi(E, T) dE. \quad (11)$$

The integral (11) is calculated by methods of steepest descent, and if the reorganization energy $E_r = F^2 \Delta^2 / 2\gamma$ is such that $|E(R_0) + E_r| > |\mu|$, then

$$w = \Gamma_0 \exp \left\{ -\frac{1}{\gamma} (V_0 + E(R_0) + e\varphi - \frac{\hbar\omega}{2} - \frac{E_r}{2}) \right\}. \quad (12)$$

When $|E(R_0) + E_r| < |\mu|$, the relationship $f_\Phi(T)$ becomes important and the relationship $w(T)$ becomes an activation relationship with the activation energy

$$E_{act} = |E(R_0) + E_r - \mu|. \quad (13)$$

It is reasonable to assume that the first case applies to reaction (2) and the second to (1). According to (6) and (12), the relationship $W(\varphi)$ has the form

$$W \sim e^{-e\varphi/\gamma}, \quad (14)$$

which agrees with experiment. According to Fig. 2, $\gamma = 0.18$ and 0.12 eV for W_0 and W_1 , respectively.* Then the factor $e^{E_r/2\gamma}$ is unimportant if a reasonable value (~ 1 eV/Å) is adopted for F and, consequently, the isotope effect is determined by the factor $e^{\hbar\omega/2\gamma}$ and at the values of γ found the isotope effect in reaction (2) must be greater than in (1), which agrees qualitatively with experiment. For a quantitative description, accurate values of F and $\hbar\omega$ are required. The influence of other, vibrational, degrees of freedom is taken into account by the usual method [14, 15] and leads to some qualitatively insignificant re-standardization of the constants F and E_r .

Thus, the results of this work show that one of the simplest electrode reactions — the electrochemical desorption of hydrogen on mercury — is activationless and its rate is determined by the tunnel passage of an electron, the probability of which depends fundamentally on the potential of the electrode.

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*Taking into account the influence of the adsorption ψ' potential in 1 M KCl [13] on the concentration of H_3O^+ in the Helmholtz plane and the replacement of ψ by $-\psi'$, $\gamma = 0.14$ for reaction (2). The authors thank L. I. Krishtalik, who pointed out the possibility of this correction.