QUASI-BARRIERLESS HYDROGEN ION DISCHARGE

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The suggestion was put forward in [1] that hydrogen ion discharge is associated with some displacement of the O atom, which takes place after the proton transfer. For this reason, barrierless hydrogen ion discharge strictly speaking is quasi-barrierless. Let us examine some arguments in support of this suggestion.

The number of collisions of H_3O^+ with adsorbed H (per second and cm^2 of surface) is given by

$$v = kcN\pi r^2, \tag{1}$$

where k is the diffusion rate constant, which according to [2] is estimated as being 10^3 to 10^4 cm/sec; c is the H_3O^+ concentration (ions/cm^3); N is the concentration of H_{ads} (atoms/cm^2), and r is the collision radius ($r = r_H + r_{H_3O^+}$). The average lifetime of the H_{ads} between collisions with H_3O^+ is given by

$$\tau_i = N/v = 1/kc\pi r^2. \tag{2}$$

For one-molar solution, $\tau_{coll} \geqslant 10^{-10}$ sec. The lifetime of H_{ads} up to its disappearance via the ionization reaction is

$$\tau_i = \tau_{vib}/\varkappa, \tag{3}$$

where τ_{vib} is the vibration period for the M–H bond (for the Hg cathode, the corresponding frequency is about 800 cm^{-1}, i.e., $\tau_{vib} \sim 4 \times 10^{-14}$ sec), and $\varkappa$ is the transmission factor governing the tunneling probability ($\varkappa \sim 10^{-3}$) [3]. Hence $\tau_i \sim 4 \times 10^{-11}$ sec, i.e., less than the collision time τ_{coll}. Thus, the tunneling probability still is not sufficiently low to guarantee that the H_{ads} are stable over the length of time required for the approach of H_3O^+. Therefore some additional stabilizing mechanism is required for the intermediate state. This may be the development of the additional barrier associated with the coordinate change of the heavy O atom, as suggested in [1].

On the other hand, Rotenberg and Pleskov [4] found that the rate of ordinary hydrogen ionization at mercury is changing more rapidly with temperature than the rate of activationless electrochemical desorption. The activation energy of ionization at $\eta = 0.25$ V in 1 M HCl is 4 kcal when the activation energy of desorption is counted as zero.* Upon extrapolation, the Tafel line for ordinary discharge in 1 M HCl intersects the straight line for barrierless discharge at $\eta \simeq 0.22$ V. At this potential the activation energy of ionization will decrease only to about 3.7 kcal, i.e., it will be markedly different from zero. Thus, it is found that in the region of barrierless discharge, ionization is quasi-activationless not activationless, and discharge, accordingly, is quasi-barrierless. We note that a barrier of 3.7 kcal will increase the lifetime of adsorbed hydrogen by a factor of $10^{2.7}$, i.e., prolongs it entirely sufficiently for an approach of the H_3O^+ ion and for the reaction with it, even when the lower limit of the diffusion rate is accepted ($k = 10^3$ cm/sec; $\tau_{coll} = 10^{-9}$ sec; and $\tau_i = 2 \times 10^{-8}$ sec).

LITERATURE CITED

1. L. I. Krishtalik, R. G. Érenburg, and V. M. Tsionskii, Élektrokhimiya, 13, 385 (1977).
2. H. Reiss, J. Chem. Phys., 18, 996 (1950).
3. L. I. Krishtalik, Élektrokhimiya, 10, 1862 (1974).
4. Z. A. Rotenberg and Yu. V. Pleskov, Élektrokhimiya, 13, 749 (1977).

*If desorption is quasi-activationless, i.e., its activation energy $E_d^{\neq}$ is not zero but does not depend on potential, then the activation energy of ionization $E_i^{\neq} = E_d^{\neq} + 4$ kcal.

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