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POSSIBLE MECHANISMS OF ELECTRODE REACTIONS OF ATOMIC HYDROGEN, FORMED IN PHOTOEMULSION EXPERIMENTS

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A comparison of data on the kinetics of electrode reactions of atomic hydrogen, formed by capture by H_3O^+ ions of electrons emitted into the solution, with data on the kinetics of the cathodic discharge of H_3O^+ ions was performed. The assumption of identity of the intermediate product in both these processes leads to serious internal contradictions. The photoelectrochemical data on the kinetics of the anodic and cathodic reactions of H prove incompatible with the kinetic principles observed for the portion of the polarization curve with slope 0.06 V. The influence of the nature of the metal on the characteristics of the reactions of "photoemission" hydrogen proves to be qualitatively opposite to that which should have been expected on the basis of the energy of adsorption of hydrogen. The isotope effects observed in photoelectrochemical and polarization measurements do not agree. The double layer effects indicate a substantial difference in the localization of the H_3O^+ ions arising in the ionization of "photoemission" hydrogen and of the proton donors participating in its reduction, which is also difficult to bring into accord with the assumption of the participation of tightly adsorbed hydrogen in the process.

After the processes of cathodic reduction ("electrochemical desorption") and anodic oxidation of hydrogen atoms generated in the layer near the electrode as a result of the reaction of H_3O^+ ions with photoemitted electrons were discovered [1-3] and studied in detail [4-6], the question arose of comparing these data with the results of an investigation of the kinetics of the discharging of hydrogen ions by the usual electrochemical methods. An analysis of the first quantitative results already indicated the presence of definite, although not indisputable discrepancies between the usual measurements and "photoemission" measurements. This led to cautious formulations of the possible nonequivalence of the energy state of adsorbed hydrogen, formed in the discharging of H_3O^+ ions, and the hydrogen obtained in the case of adsorption of an atom that had approached the electrode from the solution [7-9].

Recently certain aspects of these discrepancies have been extremely actively discussed; moreover, the data of photoemission measurements are considered as a decisive refutation of certain conclusions of kinetic electrochemical investigations [10]. On the other hand, a number of new results of photoemission experiments have appeared and have not yet been compared in detail with the data of the usual kinetics. In this article we make such a comparison.

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RATIO OF THE RATES OF IONIZATION AND REDUCTION OF H ATOMS AND THE PROBLEM OF BARRIERLESS DISCHARGE OF THE HYDROGEN ION

In [4] is was shown that on a mercury electrode at potentials appreciably more negative than the equilibrium hydrogen potential, the rates of ionization and "electrochemical desorption" of hydrogen atoms are comparable; at a somewhat more positive potential the rate of the anodic reaction is greater than that of the cathodic reaction. These results were then confirmed in [10, 11].

Thus, the existence of a region of potentials more negative than the equilibrium hydrogen potential, in which the main pathway of removal of atomic hydrogen is its ionization, follows from the photoemission experiments. On the basis of this and assuming that atomic H in photoemission experiments is identical with adsorbed H — an intermediate product of the reaction of liberation of hydrogen — Benderskii et al. [10] concluded that the liberation of hydrogen in this region of potentials occurs according to a mechanism of quasireversible discharging—slow electrochemical desorption. Since electrochemical desorption is assumed to be activationless, a Tafel slope of 59 mV corresponds to this mechanism [12]. On this basis the authors of [10] concluded that the previously detected portion of the polarization curves of liberation of hydrogen with slope ∿60 mV [9, 13, 14] corresponds not to barrierless discharging of hydrogen ions, but to a slow activationless electrochemical desorption..

Strictly speaking, the data of [4, 10, 11] still do not provide a basis for such decisive contrasting of these two alternative mechanisms, since the corresponding effects were observed at lower potentials and in solutions of different compositions in comparison with the experiments of 13]. However, recently [15] the same results were obtained in solutions close in composition to those used in [13] and in a region of potentials overlapping the potentials of the lower portion of the polarization curve of the liberation of hydrogen. Therefore the necessity arised for a detailed analysis of the problem.

A slope of the polarization curve $2.3RT/(1 + \alpha)F$ corresponds to the mechanism of delayed electrochemical desorption after quasireversible discharging. For the cathodic reaction of formation of H_2 ("electrochemical desorption"), in [11, 16] $\alpha = 0.21$ was found, i.e., a value differing appreciably from zero. From this follows a theoretical slope of 49 mV, i.e., a value that unquestionably does not agree with the experimental 58 ± 3 mV. Thus, within the framework of the explanation of the results of [13] proposed in [10], the data of the polarization and photoelectrochemical measurements prove incompatible.

Then it was shown in [4], and the data of subsequent measurements [10, 11, 15] confirmed this, that at an acid concentration of 0.1 M and above the cathodic reaction of formation of H_2 from H occurs primarily with the use of the H_3O^+ ion, and not H_2O molecules, as the proton donor. This means that the mechanism of delayed electrochemical desorption, which follows the quasiequilibrium discharging, should correspond to second-order with respect to the hydrogen ion at constant potential (or first order at constant overvoltage) [7, 9, 12]. This also means that the overvoltage should depend substantially on the ψ_1-potential. In the experiment it is observed that in solutions with acidity ∿0.1-1 M, on the portion of the polarization curve with b = 58 mV the overvoltage does not depend on the composition of the solution [9, 13], i.e., at a constant potential first order with respect to the hydrogen ion is observed; the ψ_1 effect is also absent. Thus, with respect to the dependence on the composition of the solution as well, the conclusions that follow from the photoemission experiments prove incompatible with the data of the polarization measurements.

Benderskii et al. [10] have suggested that under the conditions of the experiments of [13] "the independence of the current of discharging from the composition of the solution may be the result of compensation for changes in the rate of individual steps of the process as a whole." Such an explanation, however, cannot be correct, since the independence of the overvoltage from the acidity is observed against a background of a large and constant excess of iodide, i.e., under conditions of a constant structure of the double layer. Moreover, an independence of the overvoltage from the concentration and nature of the specifically adsorbed anion and the presence of the tetrabutylammonium cation was observed — all this can scarcely be explained by random compensations.

INFLUENCE OF THE NATURE OF THE METAL

As is well known, a higher overvoltage of hydrogen corresponds to a lower energy of adsorption of H. Consequently, for a metal with a large overvoltage the activation energy of

the removal of hydrogen, both by ionization and by desorption, should be lower and the transition from the usual to an activationless process should be facilitated. This conclusion, however, does not agree with the results of photoelectrochemical experiments. Thus, on bismuth, for which the overvoltage is 0.3 V lower than for mercury [14], a transition from $\alpha_d + \beta_i = 0.4$ to $\alpha_d + \beta_i = 0$ was observed, i.e., a transition to activationless ionization* at a potential of −0.6 V. The region with $\alpha_d + \beta_i = 0$ was investigated to a potential of −0.4 V [5]. And yet, for a mercury electrode in the same potential region, $\alpha_d + \beta_i = 0.5$, i.e., transition to activationless ionization is not detected [4].

At practically the same potential, −0.6 V, transition to a zero sum of the transport coefficients is detected for an antimony electrode [6], which possesses a somewhat lower overvoltage of hydrogen and bismuth. The detection of the same transition at a potential of ∿−0.4 V for a gold electrode [17], for which the activation energy of H is even greater (the overvoltage is ∿0.7 V lower than on mercury [14]), is even more unexpected.

On the other hand, on lead — a metal with the same or even a somewhat higher overvoltage of hydrogen — all the way to a potential of −0.6 V (the static potential) no drop in the photocurrent associated with the oxidation of H atoms could be detected [18]. Thus, ionization of hydrogen on lead proved to be substantially more inhibited than might have been expected on the basis of the activation energy of atomic hydrogen.

The data cited above show the absence of a regular relationship between the ease of ionization of H (or the transition of this process to an activationless region) and the energy of the bond of hydrogen to the metal; moreover, the latter quantity varied within an extremely wide range (up to 0.8 eV).

We should note still another circumstance. In [17] for a gold electrode several transitions between various summary values of $\alpha_d + \beta_i$ were detected. In this case the distance along the potential scale between $\alpha_d = 0$ and $\alpha_d = 1$ is ∿0.1-0.15 V; the interval between $\beta_i = 0$ and $\beta_i = 1$ is ∿0.1 V. These intervals correspond to twice the energy of reorganization, from which it follows that the activation energy of the usual discharging on gold should not exceed ∿5 kJ/mole. Such a low value does not agree with the rather large overvoltage of the discharging of hydrogen ions on gold. Another result also does not agree with the polarization measurements — according to [17], $\beta_i = 0$ (i.e., $\alpha_d = 1$) in the region of potentials in which polarization measurements give a value $\alpha_p \simeq 1/2$ [14].

THE ISOTOPE EFFECT

In [10, 11] an isotopic kinetic effect $S_{H/D}$ was detected for the cathodic (S_d) and anodic (S_i) reactions of atomic hydrogen. For acidic solutions these data can be brought into agreement with the data of the coefficient of separation of the isotopes in the cathodic liberation of hydrogen. A different situation arises for alkaline solutions. There is no isotope effect for the reaction of desorption with the participation of H_2O, according to the data of [11], i.e., $S_d = 1$. If we use an equation defining the summary coefficient of separation of isotopes S as a function of the coefficients of separation of the steps of desorption (S_d) and discharging (S_{dis}) [19]:

$$S = \frac{2S_dS_{dis}}{S_d + S_{dis}}, \qquad (1)$$

then when $S_d = 1$ we obtain $S \leqslant 2$.

The literature data on the coefficient of separation of H/D on mercury in alkaline solutions are not very reliable; values of S = 4-6 have been found [20]. Under pure conditions, excluding side effects, a coefficient of separation of H/T equal to 4.2 has been determined [21, 22]. Considering the ratio $S_{H/T} = S_{H/D}^{1.4}$, justified with good accuracy, we obtain from this $S_{H/D} = 2.8$. Thus, the data on the isotopic effect obtained in the photoemission experiment do not agree with the data on the isotope effect in the case of liberation of hydrogen from alkaline solutions.†

*α_d denotes the transport coefficient of the reaction of electrochemical desorption, β_i that of ionization. The potentials are cited relative to the saturated calomel electrode.

†In [16] the authors estimate the isotopic effect $S_d \leqslant 1.3$ according to the data of [11], considering possible experimental errors. If we take the value of the upper limit $S_d = 1.3$ and assume a value equal to 3 for S_{dis} (the maximum value of S_i is observed in [10]), then calculation according to formula (1) gives S = 1.8, i.e., an unrealistically low value.

SOME DOUBLE LAYER EFFECTS IN PHOTOELECTRONIC EXPERIMENTS

In [4] it was found that the potential φ^*, corresponding to equality of the current of ionization and electrochemical desorption, is shifted in the negative direction when surface-active anions are added, especially iodide. This effect was studied in more detail in [15] at a 0.5 M concentration of KBr and KI and acidities of the solution from 0.001 to 0.1 M. The shift of the potential φ^* is due to two effects — the change in the rate of ionization and the change in the rate of electrochemical desorption with changing ψ' potential. The value of the ψ' potential for reactions of ionization (ψ_i') corresponds to the potential at the position of the H_3O^+ ion, arising as a result of ionization of H, while the ψ' potential, affecting the reaction of electrochemical desorption (ψ_d'), pertains to the position of the center of gravity of the charge of the proton donor. In general, these two quantities are not equal to each other.

It can be assumed [15] that in the case of a predominant reaction with participation of H_2O the shift of φ^* in the case of adsorption of an anion should be negative, while in the case of the reaction with H_3O^+ a negative shift of φ^* is possible only in the case when $|\psi_d'| \ll |\psi_i'|$. Experimentally it was found that $\Delta\varphi^* < 0$; moreover, it is approximately equal to the shift of the ψ' potential for the discharging of H_3O^+ ions (ψ_{dis}'). It is important that practically the same $\Delta\varphi^*$ is observed in the pH regions corresponding both to predominance of the reaction with H_2O and to predominance of the reaction with H_3O^+. From all these facts it follows unambiguously that the ψ' potentials for ionization and "desorption" differ substantially: ψ_i' is close to ψ_{dis}' and even somewhat more negative than it (considering the coefficient $\beta_i/(\alpha_d + \beta_i) < 1$), i.e., close to the potential of the inner Helmholtz plane; ψ_d' is much lower and close to ψ^0, even perhaps somewhat less than it (an estimate based on the equality $\psi_d' = \psi^0$ and the data of [23] leads to an overestimated participation of the H_3O^+ ion in the reaction of "electrochemical desorption" in the most acidic of the iodide solutions studied, in comparison with the experiment [15]).

A substantially different localization of the H_3O^+ formed in ionization (the inner Helmholtz plane) and participating in the cathodic reaction (outer plane or even beyond it) is scarcely compatible with the concept of reactions of adsorbed hydrogen, since in this case we should have expected an analogous arrangement of the participants both in the anodic and in the cathodic reactions.

CONCLUDING REMARKS

In all the cases described above, contradictions arise when it is assumed that both in photoelectrochemical and in polarization measurements we are dealing with the same particle and that this particle is adsorbed hydrogen. It should be noted that all the arguments in favor of this hypothesis are based either on very far reaching extrapolations or contain supplementary assumptions in implicit form. Therefore it seems advisable to us to consider an alternative hypothesis — atomic hydrogen enters into electrochemical reactions before it is adsorbed.

The participation of dissolved, rather than adsorbed H immediately removes all the contradictions described above — the incompatibility of the data of photoemission experiments with the data on barrierless discharge, anomalies with the isotope effect, the clear disruption of the dependence of the rate of the electrode reactions on the energy of the bond of hydrogen to the metal.

The hypothesis on the reactions of dissolved hydrogen naturally explain the peculiarities of the double layer effect. When the reacting atom is situated outside the first monolayer of the water molecules, as is shown, for example, in Fig. 1a, in the process of ionization a proton might be added to a water molecule both of the first and of the second monolayers; however, the formation of an H_3O^+ ion in the first monolayer, i.e., in a site with a more negative electrical potential, is more profitable (Fig. 1b). For the same reasons, in the reaction of "electrochemical desorption" it is more profitable to use water molecules of the second monolayer — then the negatively charged OH^- ion is at a less negative potential (Fig. 1c). Thus, the inequality of the ψ' potentials for reactions of ionization and "electrochemical desorption" follows from this picture; moreover, for the former ψ' is closer to ψ^i, and for the latter to ψ^0.

The elementary event of reactions in which dissolved, i.e., weakly bound H participates should differ substantially from that for the usual reactions of covalently bonded H. Since the H atom is almost free, its energy is described by a rather gently sloping potential curve,

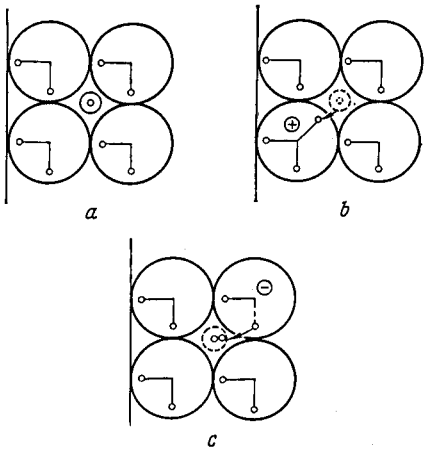

Fig. 1

and its behavior is classical, at least within a definite range of coordinates. In this case the movement of hydrogen along the coordinate, namely, its approach to the acceptor or donor, will contribute to the energy of reorganization and, consequently, to the activation energy of the process. The final state — tightly bound H — is described by a steep potential curve and is a quantum state. Transition from the gently sloping potential curve to a steep curve corresponds (in the presence of a substantial contribution of reorganization of the medium as well) to a value of the transport coefficient less that half [24]. Possibly the low experimental values of α_d and β_i are associated with this. The smaller isotopic effect of reactions of "desorption" in comparison with ionization can be explained within the framework of these concepts by less repulsion of H from H in comparison with H and O. This permits the partners of the first reaction to approach one another better, which ensures ease of subsequent tunneling of protons. Since the hydrogen atom is not very rigidly localized in the initial stage, its tunneling should occur more easily than for tightly adsorbed hydrogen [9], and this leads to the observed decrease in the isotope effect in comparison with the reaction of cathodic liberation of hydrogen.

We by no means regard the considerations cited above as unambiguous evidence that nonadsorbed hydrogen atoms participate in the process in photoemission experiments. Our aim was to show that the entire aggregate of experimental data can be described without contradiction within the framework of this hypothesis, and, consequently, this hypothesis merits further theoretical and experimental development. In any case, working out this or a similar variant seems necessary, since the scheme with the participation of adsorbed hydrogen used up to this time, identical with that obtained in the case of discharging, leads to serious internal contradictions.

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