HOKKAIDO UNIVERSITY

Instructions for use

EXPERIMENTAL STUDY OF THE MECHANISM OF AN ELEMENTARY ACT OF THE PROTON DONORS DISCHARGE

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One of the first models of an elementary act of the electrode reaction, of the proton transfer reaction in particular, which has played an extremely important role in the development of electrochemical and, generally speaking, also of chemical, kinetics is the Horiuti-Polanyi theory[1]. This theory, which is in many respects of importance also at the present time, has made it possible to explain some basic laws of electrochemical kinetics, such as the dependence of the reaction rate on potential and on the adsorption energy of the intermediate reaction product. As applied to the proton transfer reaction, this model describes the activation process as a gradual stretching of the bond between proton and its donor (*e.g.* the O–H bond) up to the distance when the formation of a bond with acceptor becomes possible (the M–H bond for a cathodic reaction). In other words, it is only the energy barrier in the path of proton which is considered. In the original version of the theory the proton transfer over the barrier was considered. In later, refined versions proton tunneling in the upper part of the barrier was thought possible (for review see *e.g.* ref. (2)). But the possibility of proton tunneling from a lower unexcited level was not envisaged.

Further development of the theory of an elementary act of proton transfer was suggested in 1967 by Dogonadze, Kuznetsov and Levich[3][**]. This theory has two distinctive features. Firstly, along with the proton motion, it takes into account the motion of dipole molecules of the solvent. This factor is of prime importance for any electrochemical reactions, and in a more general case, for any reactions involving charge transfer in polar

medium. In polar solvent a charged particle interacts strongly with dipoles of the medium. The charge transfer in space is associated with a significant change in the dipoles orientation, *i.e.* with reorganization of the medium. The interaction energy of the charge with polar medium being large (of the order of some tens of kcal/moles), it is clear that the reorientation of dipoles requires a considerable activation energy. Therefore, it is necessary to take into account the energy barrier associated with the motion of solvent molecules. Its existence is a common feature of any charge transfer processes. This fact is responsible for the analogy in the kinetic laws of a great variety of reactions, both those accompanied by breaking of chemical bonds (*e.g.* proton transfer) and those involving no atom displacements in reacting particles (electron transfer reactions).

The second distinctive feature of the theory is consistent quantum-mechanical treatment of all kinds of molecular motions attending the reaction. This treatment showed that the behavior of this or another kind of motion (degrees of freedom) depends essentially on its characteristics.

If the characteristic vibration frequency along the coordinate corresponding to a given degree of freedom is small, so that the vibration quantum $\hbar\omega \ll kT$, this degree of freedom behaves in a classical manner, *i.e.* the transition along this coordinate from initial to final state occurs over the barrier. As we know from the data on the absorption of radio waves, the characteristic vibration frequencies of solvent dipoles are not large, so that the corresponding quanta are less than kT tens and hundreds times. Therefore, the solvent is a classical subsystem, and transition from initial to final dipoles configuration occurs over the energy barrier. If the vibration frequency along some breaking chemical bond also proves to be small, this bond behaves in a classical manner, *i.e.* during activation it stretches and then changes into another bond. In other words, the transformation of such bonds occurs in accordance with the original HORIUTI-POLANYI model. But if the vibration frequency is large, then for this degree of freedom it is necessary to take into account the competition of two types of transfer: over- and under the barrier. At $\hbar\omega \gg kT$ the behavior of the respective degree of freedom becomes essentially a quantum one, and the transfer under the barrier is much more probable than the transfer over the barrier. This is the case when we have to do with the breaking of hydrogen covalent bonds (for the O–H bond $\hbar\omega \geqslant 15\,kT$). Already in the unexcited state, at the zero vibration level, proton is delocalised to such an extent that the probability of its presence in the classically forbidden region is so great that the most advantageous manner of its transfer to

the final state is the transfer under the barrier from the ground initial to the ground final state. It should be emphasized that this picture is by no means an *a priori* assumption of the theory. The theroy considers the competition of all possible manners of proton transfer, both over and under the barrier from any initial to any final level. But a direct comparison of the probability of each of the process versions shows that the main contribution is made by the tunnel transfer from the zero initial to the zero final level[*].

The two models discussed above—the gradual stretching of the O–H bond and the quantum proton transfer from initial to final state—afford practically the same explanation to the majority of known experimental facts. This is no wonder because for a semiquantitative treatment of most of the relationships it is sufficient to satisfy a few simple phenomenological relations associated with the existence of the energy barrier without regard to its reasons. Therefore, in order to choose between the two models it was necessary to find also the dependences for which they would give qualitatively different predictions.

It seemed to us that these models should give different results for the pre-exponential factor values, to be more precise, the deviations of its value from the predictions of the absolute reaction rates theory. These deviations, described by the transmission coefficient value $\kappa < 1$, are associated with the probability of proton transfer under the barrier (we shall use also a less rigorous, but a very widely used term-proton tunneling).

The correction for tunneling in the bond stretching model was estimated in a number of works. The common and most important feature of all the works of this type is that in the above model tunneling is determined by the same barrier as the activation energy value, *viz.* the barrier along the proton coordinate. But in the model of DOGONADZE *et al.* the activation energy is determined by the barries along the coordinate describing the character of solvent dipoles orientation, and the probability of the transfer under the barrier by the energy profile along proton coordinate. Thus in the former model the activation energy and the preexponential factor are related in a definite manner, whereas in the latter they can in principle vary independent of each other.

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[*] A certain participation of excited levels takes place also in the case of barrier- and activationless processes (it is either initial or final excited levels which participate, respectively), their contribution becoming more appreciable with sufficient distance from the transition point from the ordinary process ($\alpha \simeq 1/2$) to the reaction with $\alpha = 1$ or 0.

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Earlier we proved the existence of barrierless electrode processes, in particular, of the barrierless hydrogen ion discharge, for which the activation energy is equal to the heat of the elementary act and the transfer coefficient $\alpha = 1$ (for the main characteristics of the barrierless processes, see the reviews[7]). In the bond stretching model the barrierless process represents the absence of a barrier in the path of proton and hence the absence of the tunneling effect. Consequently, in this model for a barrierless process κ should be equal to unity, whereas for an ordinary discharge $\kappa < 1$. In the quantum-mechanical model it is the energy profile along the solvent coordinate which is barrierless, while the barrier along the proton coordinate is practically the same, as for an ordinary discharge. Thus, this theory leads to the conclusion that the values $\kappa < 1$ are practically the same for barrierless and ordinary discharges*).

It is known that the theoreitcal calculation of the preexponential factor by means of the absolute reaction rates theory presents certain difficulties as regards the estimation of the entropy of activated state[8]. These difficulties are especially great in the case of electrochemical reactions owing to the fact that it is impossible to measure the "ideal" energy and entropy of activation (at constant absolute potential drop) and only the so-called "real" quantities can be experimentally determined at constant overvoltage[9]. However, for the barrierless discharge all these difficulties disappear, for in this case the activated state coincides with the final state. Thus, it is possible to calculate quite rigorously the theoretical value of the real preexponential factor for the barrierless discharge[10]. The theoretical value $\log K = 5.7$ (the preexponential factor K is expressed in a/cm^2) is much larger than the experimental value $\log K = 3.0$[10]. This discrepancy points to an essentially nonadiabatic nature of the process ($\kappa = 10^{-2.7}$), *i.e.* to a rather low probability of the proton transfer under the barrier. As has been shown above, the value of $\kappa \ll 1$ for the barrierless discharge can hardly be explained by assuming the stretching of the O–H bond to determine the ancivation process, but it is readily explained in terms of the quantum-mechanical theory**).

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*) In the theory of DOGONADZE *et al.* κ for the barrierless discharge can be a little higher than for an ordinary one owing to the participation in the barrierless discharge of the excited state of the O–H bond, which was mentioned earlier.

**) In the theoretical calculation given above no account is taken of the correction for the entropy of activated state, associated with the motion along the reaction coordinate. If the reaction coordinate is the proton coordinate (the O–H bond stretching model), then due to its high frequency, the contribution to the entropy is negligible and hence for this model $\kappa = ^{-2.7}$. But if the reaction coordinate describes the motion of dipoles of the medium, the correction in question decreases the theoretical value of K no more than by an order, *i.e.* in this model $\kappa < ^{-1.7}$. Thus, taking account of this correction does not introduce any qualitative changes.

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The same conclusion can be drawn from the comparison of the preex-ponential factors for barrierless and ordinary discharges. The experimental value of the real preexponential for an ordinary discharge is $\log K = 3.9$ (0.1 N HCl in the presence of salt excess[11]). For comparison of th tunneling probabilties it is necessary to compare the ideal preexponential factors rather than the real ones, *i.e.* a correction should be made for the change in the entropy of the electrode processes and account should be taken of the con-centration dependence of the preexponential factor. This calculation was carried out[12]. It showed that the tunneling probablilities for barrierless and ordinary discharges are close by magnitude (the difference between them being within the experimental error). This result also agrees with the quantum-mechanical theory but it is difficult to explain it on the basis of the bond stretching model.

Let us consider the influence of the metal nature on the tunneling probablility for proton[13]. In terms of the bond stretching model (see Fig. 1), the greater is the energy of the M–H bond ($E_{\text{M-H}}$), the less is the barrier height for tunneling and the narrower it is (for a more rigid bond the potential curve rises more steeply*)). Thus from Fig. 1 we can conclude that at large $E_{\text{M-H}}$ proton tunneling becomes easier. In the model of DOGONADZE *et al.* the probability of the transfer under the barrier increases
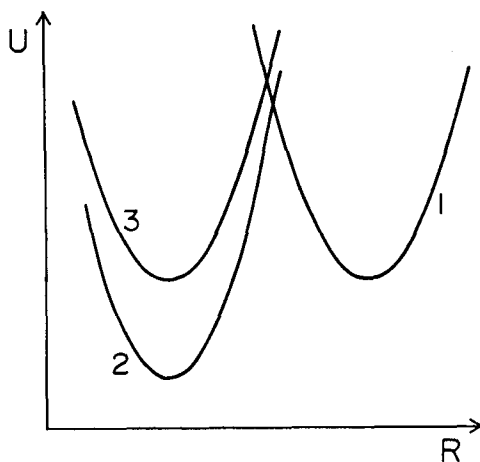

Fig. 1. Scheme of potential energy: 1) Term describing the OH bond, 2, 3) Terms describing the MH bond: $E_{\text{MH}_2} > E_{\text{MH}_3}$

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*) As was shown[14], for some hydrides the frequency of the stretching vibrations of the M–H bond (proportional to the root of the quasi-elastic force constant) rises in proportion to $E_{\text{M-H}}$.
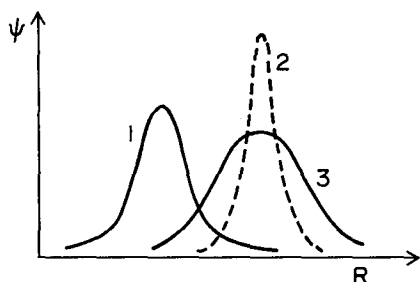
Fig. 2. Wave functions of proton in OH (1) and MH (2 and 3). $E_{MH_2} > E_{MH_3}$
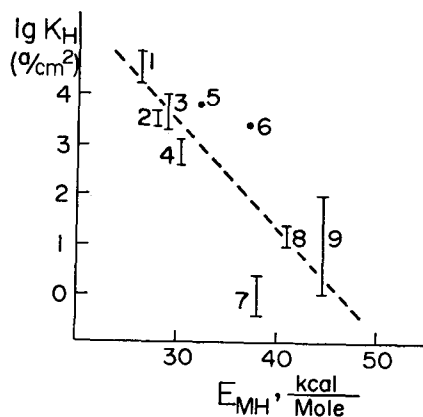

Fig. 3. Dependence of the preexponential factor of the hydrogen evolution reaction in acid solutions on the energy of the MH bond: 1) Tl amalgam 40.6 at. %[26]; 2) Pb[27]; 3) Hg[9~11]; 4) In amalgam 60.3 at. %[28]; 5) Ga 16.4 at. % In[11]; 7) Ag(0.1N HCl)[29]; 8) Ag(0.1N H$_2$SO$_4$)[29]; 9) In[30].

with increasing overlapping of proton wave functions in the initial and final states. The more rigid is the bond, the more localized is the proton and the less is the overlapping of the wave functions (see Fig. 2). Therefore, in this model the tunneling probability would be expected to decrease with increasing E_{M-H}. As is clear from Fig. 3, experiment agrees with this conclusion.

The probability of proton tunneling affects significantly another measurable quantity—the separation factor of isotopes S. Experimentally this quantity is determined by the kinetic isotope effects for two irreversible steps : discharge (S_d) and electrochemical desorption (S_{ed})[15,16].

$$S = 2 \frac{S_d S_{ed}}{S_d + S_{ed}} \qquad (1)$$

The electrochemical desorption at mercury and similar cathodes is highly exothermic process, so that its activation energy should turn to zero[7,17]. Though no direct measurements of the fast step of electrochemical desorption of hydrogen have been carried out so far, the data obtained by ROTENBERG and PLESKOV[18] by the photoemission method show that for mercury-like cathodes the transfer coefficient for the electrochemical desorption step is zero. This is a very serious argument in favor of the process being activationless.

If the activation process consists in stretching of the bond, then the activationless electrochemical desorption should occur at the same rate for all hydrogen isotopes, since there is no barrier for proton tunneling and

the effect of the difference in zero energies dissappears due to the activation energy being zero. In other words, in this model $S_{ed}=1$. But hence it follows that $S=2S_a/(S_a+1)<2$. This conclusion is completely at variance with experimental data. As will be shown later, much greater affects can be observed at mercury and similar metals ($S_{H/T}$ from ~3 to ~17). On the other hand, in the new quantum-mechanical theory this difficulty is absent because the activationless process is associated only with the absence of the barrier along the solvent dipoles coordinate, whereas along the proton coordinate the barrier remains[13].

In the bond stretching model the nature of cathode metal affects the valus of S mainly due to its influence on the isotope effect in the discharge step. It affects the value of S_{ed} much less (and in the case of activationless desorption not at all). If we consider the overlapping of the proton wave functions in the initial and final states, we can see that the change in the energy of the M–H bond affects in the same way the tunneling probability, both during discharge and electrochemical desorption, *i.e.* it affects both S_a and S_{ed}[*]. The influence of the metal nature on the tunneling probability was considered earlier in terms of the two models discussed. In accordance with the quantum-mechanical model and the experimental data on the preexponential factors of the reaction, we found[13] that the increase in the energy of the M–H bond, inhibiting the proton transfer, enhances the kinetic isotope effect (Fig. 4)[**].

Figure 4 shows a significant decrease of the separation factor of isotopes with increasing surface charge, *i.e.* with potential increase. In the bond stretching model this character of the dependence is explained by decrease of the activation barrier with rising potential and, accordingly, with greater ease of proton tunneling[2]. The new theory leads to the conclusion that there is no direct connection between the activation energy (barrier along the solvent dipoles coordinate) and the tunneling probability for proton.

*) As shown[13], the effects associated with the change of zero energies are much less than those due to the change in the tunneling probability.

**) In Fig. 4 different metals are compared at the same surface charge, *i.e.* practically in the presence of the same electric field acting on the discharging ion. The necessity of comparison under such conditions follows from the data[19], where it was shown that the separation factors of isotopes at a mercury cathode in different solutions coincide if they are compared at the same potential drop in the dense part of the double layer.

The comparison for different metals at the smae activation energy of hydrogen evolution leads to a nonmonotonic dependence of S on E_{M-H}. This fact points to the absence of a direct connection between the activation barrier height and the tunneling probability[13].
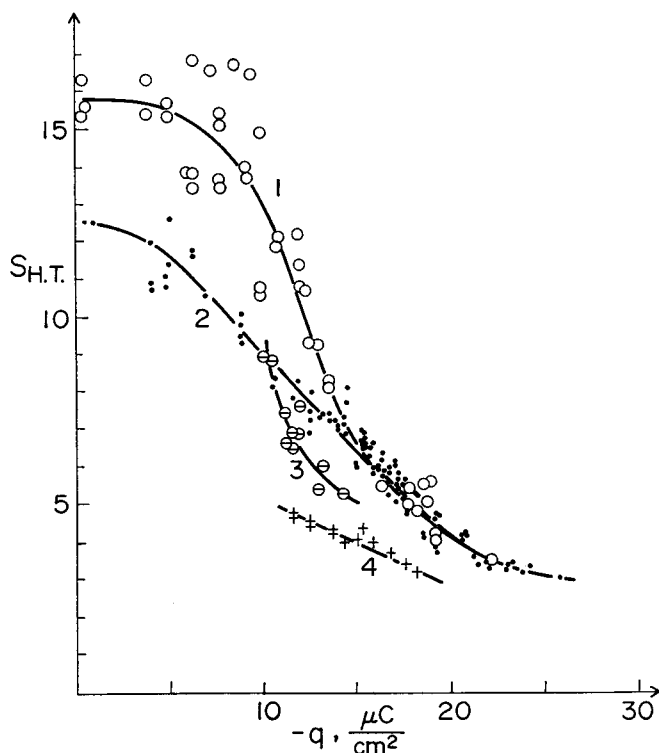
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Fig. 4. Dependence of the separation factor on the charge of the electrode surface in acid solution (according to the data of refs. (13) and 21)): 1) Ga, 2) Hg, 3) Pb, 4) Tl amalgam 40.6 at. %.

In the light of this conclusion the decrease of S with rising potential is explained by better overlapping of the wave functions of the initial and final states due to the approach of the hydroxonium ion to the electrode under the action of electric field. The validity of this explanation is clear if we compare the isotope effect in acid and alkaline solutions. In the latter the prpton donor is the uncharged water molecule which, naturally, is attracted to the electrode much less than the H_3O^+ ion. Its distance from the electrode practically does not vary with the potential and therefore the dependence of the isotope effect on potential is absent (Fig. 4)[13,21].

In the O–H bond stretching model there is no essential difference between the H_3O^+ and H_2O discharges: in both cases with increasing overvoltage, the potential barrier decreases and tunneling would be expected to become easier. As can be seen from Fig. 5, at the same activation energy values in acid and alkaline solutions, essentially different dependences
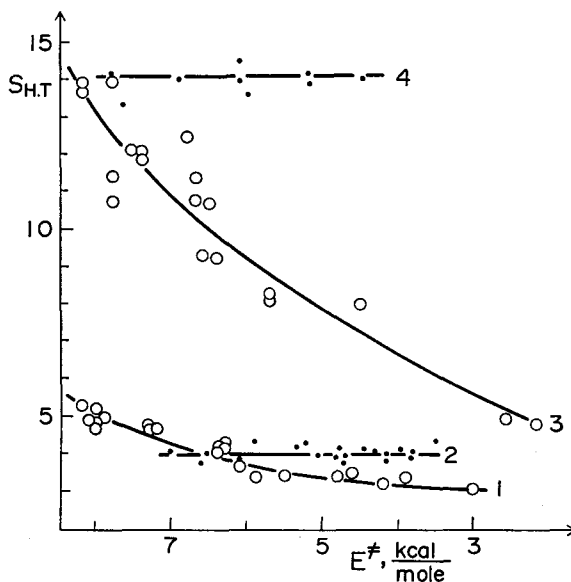
Fig. 5. Dependecs of the separation factor on the activation energy
1) Hg, acid[13,19] ; 2) Hg, alkali[13,31] ; 3) Ga, acid[13,21] ; 4) Ga, alkali[21].

of S on potential are observed.   This points to the absence of a direct connection between the activation energy and the probability of proton tunneling.

Christov[22] pointed out the fact that at certain barrier parameters along the proton coordinate the region optimum for tunneling lies at a constant distance from the top of the barrier and hence the tunneling probability does not depend on the activation energy.   In the bond stretching model this fact could account for the constant value of S in alkaline solutions, but, on one hand, there is no evidence that the real barrier parameters fit these conditions and, on the other hand, by these additional assumption it is imposible to explain the data given earlier on the barrierless and activationless processes and on the influence of the cathode metal nature.

The above explanation of the dependence of S on potential presumes that with increasing electric field, the preexponential factor for hydrogen ion discharge should increase.   In investigation of the temperature dependence of the rate of this reaction in the usual, rather narrow, potential range this effect was so slight that it could be ascribed to experimental error (a weak tendency to the change of the preexponential factor was observed[11]). However, it was proved[23] that at a silver cathode in the potential range of 1 V, the preexponential factor increases by at least two orders.

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A much weaker, as compared to the H_3O^+ ion, attraction of water molecules to the electrode should lead to a greater distance between the initial and final localizations of proton and, as a consequence, to lesser tunneling probobility. This conclusion is completely confirmed by experiment : the ratio of the tunneling probabilities for H_3O^+ and H_2O, found from the preexponential factors valus is[11] for Ga $10^{5.6}$ and the In–Ga alloy $10^{4.8}$.

Another approach to the investigation of the mechanism of an elementary act of hydrogen evolution consists in using a medium with the properties essentially different from those of water. As such medium we chose an aprotonic weakly basic solvent acetonitrile. In anhydrous acetonitrile the hydrogen overvoltage in acid solution is by ~ 150 mV lower than in water[*]. The hydrogen evolution process occurrs in accordance with the usual relationships of the slow discharge of hydrogen ions (dependence on the H^+ ion concentration in the presence of salt excess, the dependence on the salt concentration at constant H^+ concentration).

When small amounts of water are added, which is a much stronger base than acetonitrile, hydroxonium ions are formed and the concentration of acetonitrilonium ions, which are the main proton donors, decreases. This leads to corresponding increase of the overvoltage (see Fig. 6). At sufficiently high water concentration, the contribution of the H^+ ions bound with solvent becomes negligible and the hydroxonium ions become the main source of protons. Starting from this moment, further addition of water leads to decrease of overvoltage, for the concentration of the H^+ ions bound with water becomes practically constant, whereas the concentration of the electrode reaction product-free water- increases. This fact is responsible for the appearance of a maximum on the curve in Fig. 6.

The hydroxonium ion can exist in acetonitrile both as H_3O^+ ion and as an associate of this ion with one, two or three water molecules (the last mentioned form is predominating in aqueous solutions). The corresponding

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*) All investigations were carried out in $HClO_4$ solutions ; $LiClO_4$ was used as supporting electrolyte. We used perchloric acid because according to ref. (24), in this solvent it is practically the only strong acid. The $HClO_4$ solutions were dehydrated by boiling in the Soxhlet apparatus, the vapors being kept in contact with a molecular sieve 4 A. To avoid hydrolysis, solutions were boiled at room temperature (under reduced pressure) and direct contact of the molecular sieve with solution was eliminated. The absence in solutions of the hydrolysis products, distorting the results of measurements was controlled from the overvoltage value, found after addition of water to the solution in the same amount as was removed during drying. It coincided with the overvoltage in the initial solution before drying. The residual water is estimated as being $\lesssim 5 \times 10^{-4}$ mole/ℓ, *i. e.* much less than the acid concentration. The measurements were performed at the dropping mercury electrode.
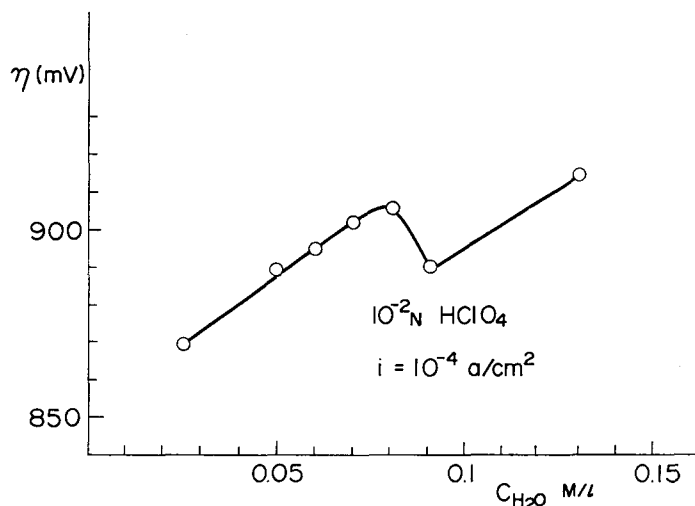
Fig. 6. Dependece of hydrogen overvoltage (at $\log i = -4.0$) in acetonitrile in 0.01 N $HClO_4$ on H_2O concentration.

equilibria were studied by KOLTHOFF and CHANTOONI[25]. Using their data, we calculated the concentrations of various hydroxonium hydrates under our experimental conditions. It proved that in the vicinity of the maximum of the curve of Fig. 6 $H_3O^+ \cdot H_2O$ and H_3O^+ are the prevailing forms. This means that the discharging ion is surrounded mainly by acetonitrile molecules. However, at a larger water concentration the amount of $H_3O^+ \cdot 2H_2O$ and $H_3O^+ \cdot 3H_2O$ increases, *i. e.* the first coordination sphere of H_3O^+ becomes more and more smear to that present in the aqueous solution. This gives rise to a new increase in the overvoltage, so that at the water concentration 0.13 mole/ℓ it is only by 50 mV lower than in water. Through under these conditions the mole fraction of water is only 7×10^{-3} and the macroscopic properties of the medium can not change significantly as yet, owing to selective formation of hydrates, the micromedium near the hydroxonium ion becomes "waterlike" and this affects strongly the kinetics of its discharge. Thus, in these experiments the effect of the change in the properties of the medium becomes quite pronounced with the nature of the breaking bond remaining practically unchanged.

The influence of the medium and of the nature of the breaking bond show up even more clearly when we compare the values of the preexponential factors and of the activation energies of the acetonitrilonium and hydroxonium ions discharge in acetonitrile and water. These data were obtained by studying the temperature dependence of the hydrogen evolution

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TABLE

	CH_3CNH^+ in CH_3CN	H_3O^+ in CH_3CN	H_3O^+ in H_2O
A_0	18.2	18.2	21.9
$\log K$	2.1	3.2	3.4

rate in anhydrous acetonitrile solutions and in acetonitrile solutions at the water concentration 0.085 mole/ℓ (this corresponds to a point between the maximum and the minimum of the curve) and also in aqueous acid solutions. In the Table all the values of the preexponential factors are recalculated for the same H^+ ion concentrations and for equal mole fractions of the corresponding conjugated base equal to unity (this correction, necessary for comparison of the data, is introduced for H_2O in the case of H_3O_+ discharge in acetonitrile.

As is clear from the Table, the discharge of the CH_3CNH^+ and H_3O^+ ions from acetonitrile solutions is characterized by significantly different preexponential factor values and practically the same activation energies, whereas the H_3O^+ ions discharge in two different media, water and acetonitrile, by practically the same preexponential factors and different activation energies. Thus, it proved that the preexponential factor is determined mainly by the nature of the breaking bond (N–H or O–H), while the activation energy by the nature of the solvent (acetonitrile or water). This conclusion is in complete agreement with prediction of the theory of DOGONADZE *et al.*, according to which the activation energy is determined by the reorganization of the medium and the preexponential factor by the probability of proton tunneling. But in terms of the bond stretching model both the preexponential factor and the activation energy are determined by the nature of the breaking bond, so that other relationships would be expected to be valid *viz.* similar activation energy values for the H_3O^+ ions discharge in acetonitrile and water, and different A_0 for the CH_3CNH^+ and H_3O^+ discharge in acetonitrile.

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