of the mediator. Figure 4b presents the experimental data of Fig. 4a in coordinates corresponding to Eq. (11). It can be seen that this equation satisfactorily describes the experimental results. The dimerization constant of reduced MV, estimated according to the segment intercepted on the x axis, is equal to $(2 \pm 1.5) \cdot 10^{-3}$ M, in good agreement with the value found in [11] spectrophotometrically according to the deviation from the Beer–Lambert law.

As is well known, carbon electrodes are inert in the electrochemical oxidation of hydrogen. An investigation of the system hydrogen–hydrogenase–MV–carbon electrode showed that electrooxidation of molecular hydrogen can be accomplished in this sytem under conditions close to reversible. An important peculiarity of the electrode discussed was the possibility of varying the parameters of the bioelectrocatalytic process within a broad range by varying the concentrations of the enzyme and mediator.

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COMPARISON OF THE KINETICS OF THE DISCHARGE OF VARIOUS PROTON DONORS IN ACETONITRILE

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A comparison was made of the kinetic parameters for the discharge of H_3O^+ and CH_3CNH^+ in acetonitrile, and for the discharge of H_3O^+ in water. It was found that the discharge of the ions CH_3CNH^+ and H_3O^+ from acetonitrile solutions was characterized by a practically uniform activation energy, whereas the discharge of H_3O^+ in the two different media, water and acetonitrile, showed substantially different activation energies. Thus the activation energy was determined not by the nature of the bond being broken but by the nature of the solvent.

We showed previously that the process of hydrogen evolution from acetonitrile solutions, and also from aqueous solutions, was subject to the rules of the mechanism of retarded discharge. Acetonitrile is a weakly basic solvent, so that, with the aid of small additions of water, practically all the hydrogen ions can be converted from the solvonium form of the ion to hydroxonium. Thus we could compare the discharges of one and the same proton donors (H_3O^+) in various media, and the discharges of various donors (H_3O^+ and CH_3CNH^+) in one and the same medium, namely acetonitrile.

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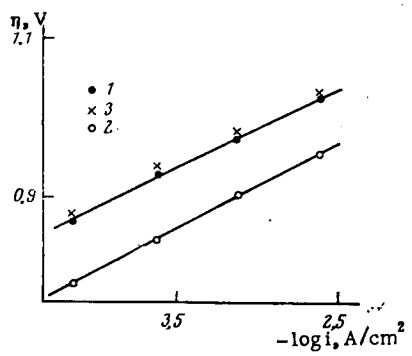

Fig. 1

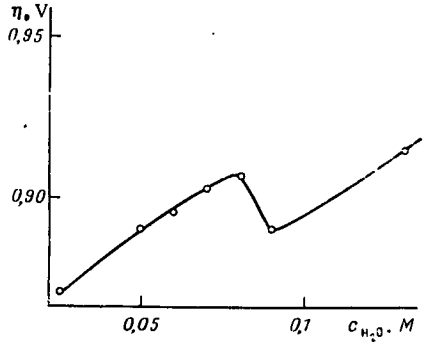

Fig. 2

Fig. 1. The variation of η with log i in a solution of 10^{-1} N $HClO_4$: 1) before boiling in Soxhlet apparatus, 2) after boiling, and 3) solution (2) after addition of 0.24 M H_2O.

Fig. 2. Variation of η with c_{H_2O} in a 10^{-2} N solution of $HClO_4$, i = 10^{-4} A/cm^2.

All the investigations were carried out in solutions of perchloric acid, with and without $LiClO_4$ as supporting electrolyte. Dehydration of the perchloric acid solutions was achieved by boiling of the solution in a Soxhlet apparatus. The drying agent used was molecular sieve 4 Å, previously heated at 400°C in vacuum. Before the solution was dried, the zeolite was washed with pure acetonitrile. The solution, containing $HClO_4$, did not come into direct contact with the zeolite; only acetonitrile vapor, containing water, came into contact with it. The electrolyte was boiled at reduced pressure, at room temperature, so as to avoid hydrolysis of the acidified acetonitrile solution. The absence of hydrolysis products from the solution, which would have distorted the results of the measurements, was monitored by the value of the overvoltage, found after addition to the solvent of water, in a quantity corresponding to that removed in the drying process; it agreed with the overvoltage of the initial solution, before drying (Fig. 1). This result showed that, in the course of the drying, we actually removed the main bulk of the water, so that its residual content was much less than the concentration of acid. The water concentration, after drying, was determined in blank experiments, without acidification of the solution; it amounted to $\leq 5 \cdot 10^{-4}$ M.

Moreover, the data obtained with the dry solution of pure acid agreed well, allowing for the ψ' correction, with the results obtained in solutions not subjected to drying and containing a large excess of $LiClO_4$. As is known from [1], in acetonitrile solution Li^+ is specifically hydrated, and its excess combined practically completely with water existing in the solution. Under these conditions, addition of supplementary water did not affect the overvoltage, i.e., the hydrogen ion was not hydrated.

In electrochemical kinetics, in the change from one solvent to another, the change in solvation energy is compensated for by the induced change in the shift of the equilibrium step of the metal–solvent potential, since the energy level of the initial state does not alter on the whole [2]. Comparing the kinetics of the reaction in various solvents, at a single overvoltage, we made the comparison under isoenergetic conditions and, corresponding to these conditions, the real activation energy did not depend directly on the solvation energy of the real substances. Consequently, the main observed effect was a change in the reorganization energy.

Figure 2 shows the dependence of the overvoltage (η_{H_2}) on the concentration of water in a $5 \cdot 10^{-3}$ N solution of $HClO_4$, at a current density of 10^{-4} A/cm^2. This curve is one of a series of similar curves, obtained under these conditions. In each series of measurements the same portion of solution was treated with increasing quantities of water. Although the depth of the minimum was not very great in absolute terms (10 to 15 mV), the form of the curve was reproducible from one experiment to another.

On the addition of small quantities of water, a considerably more powerful base than acetonitrile, hydroxonium ions were formed and the concentration of acetylnitrilonium (CH_3CNH^+), the main proton donor, decreased. At the same time the total concentration of electrolyte did not change; some of the CH_3CNH^+ ions were replaced by an equal number of substantially less active H_3O^+ ions. The reduction in concentration of discharging ions with a constant total electrolyte concentration led to a corresponding increase in the overvoltage. With a high enough concentration of water, the proportion of H^+ ions, combined with solvent, became vanishingly small, and hydroxonium ions became the main source of protons. Starting at this point, further addition of water led to a

TABLE 1. Values of the Activation Energy and of log K for the Discharge of Ions in Acetonitrile and in Water

Parameters	In CH_3CN*		H_3O^+ in H_2O
	CH_3CNH^+	H_3O^+	
A_0, kcal/mole	18,2±0,4	18,2±0,4	21,7
log K	2,1±0,3	3,2±0,3	4,0

*Number of experimental points: 9 for CH_3CNH^+ and 5 for H_3O^+.

reduction in the overvoltage; because the concentration of H^+ ions combined with water became practically constant, the concentration of the product of the electrode reaction, namely free water, increased. In aqueous solutions the concentration of water was high and practically constant, and normally any changes were not taken into account. However, in nonaqueous solutions these changes were considerable and we had to consider that, in the reaction of discharge of the hydroxonium ion, the reaction products (in the reduced form) were hydrogen and water, so that the full Nernst equation should be written in the form

$$\varphi_e = \varphi_e^\circ + \frac{RT}{F} \ln \frac{x_{H_3O^+}}{p_{H_2}^{1/2} x_{H_2O}}.$$

Accordingly, in determination of the overvoltage, i.e., the potential difference for the current φ and the equilibrium potential φ_e, we obtained a value decreasing with increasing x_{H_2O}. In consequence, the transition from the preferential discharge of CH_3CNH^+ to the discharge of H_3O^+ led to the appearance of a maximum on the curve relating overvoltage and x_{H_2O}.

The hydroxonium ion could exist in acetonitrile both in the form H_3O^+ and in the form of an associate of this ion with one, two, or three molecules of water. The corresponding equilibria were investigated by Kolthoff and Chantooni [3]. Making use of their data, we calculated the concentrations of the various hydrates of hydroxonium, under the conditions of our experiments. It was found that the forms $H_3O^+ \cdot H_2O$ and H_3O^+ predominated in the vicinity of the maximum on the curve. This indicated that the discharged ion was mainly surrounded by acetonitrile molecules. At higher water concentrations there was an increase in the proportion of $H_3O^+ \cdot 2H_2O$ and of $H_3O^+ \cdot 3H_2O$, i.e., the inner coordination sphere of H_3O^+ became more like that prevailing in aqueous solution. Associated with this was a new increase in the overvoltage, so that, with a water concentration of 0.13 M, the overvoltage was only 50 mV less than in water.* Although the mole fraction of water, under these conditions, was about $7 \cdot 10^{-3}$, and the macroscopic properties of the medium had still not altered significantly, yet, thanks to the selective formation of hydrates, the micromedium close to the hydroxonium ion became more "water-like," and this substantially affected the kinetics of its discharge. Thus, in these experiments, there was a clearly defined change in the properties of the medium, with practically no change in the character of the ruptured bond.

A still more pronounced effect of the medium, and of the nature of the ruptured bond, was shown by comparison of the values of the activation energies for discharge of the ions acetylnitrilonium and hydroxonium, in acetonitrile and water. Appropriate data were obtained by investigation of the temperature dependence of the rate of hydrogen evolution, in anhydrous acetonitrile solutions, and in acetonitrile solutions with water concentrations about 0.085 M (this corresponded to a point between the maximum and minimum on the curve of Fig. 2). The data for aqueous solutions were taken from [4]. Temperature curves were recorded over the range 10 to 30°C.

Table 1 shows the values of the activation energies and of the preexponents for the discharge of CH_3CNH^+ and H_3O^+ in acetonitrile and of H_3O^+ in water. The values of the preexponents were recalculated for an identical concentration of H^+ ions, and for an identical mole fraction of the corresponding base, equal to unity (this correction, necessary for the comparison of data, was introduced for H_2O in the discharge of H_3O^+ in acetonitrile). It is evident from Table 1 that discharge of the ions CH_3CNH^+ and H_3O^+ from acetonitrile solutions was characterized by practically uniform activation energies, while the discharge of H_3O^+ in the two different media, water and acetonitrile, had significantly different activation energies. Thus the activation energy was deter-

*However, with the correction for the difference in the mole fraction of water, the overvoltage in this solution was 180 mV less than in pure water.

mined, not by the nature of the ruptured bond, as would be expected in conformity with the model of a gradually stretched bond, but by the nature of the solvent, as would be expected from a quantum mechanical model. Reorganization of the solvent is a unique classical process and completely determines the activation energy.

Since the ions CH_3CNH^+ and H_3O^+ showed different forms and dimensions, then, strictly speaking, they corresponded to different values of the reorganization energy. However, it may be assumed that, in CH_3CNH^+, the charge is centered on the nitrogen atom, but, since the lengths of the bonds O–H and N–H are similar, the electrostatic interactions of the two ions with the medium were similar and the reorganization energies were similar. As for the adsorption energies of the ions, their values were small and their differences could not lead to a substantial difference in the experimentally determined apparent activation energies. Accordingly, we would expect similar values of the activation energy for the discharge of CH_3CNH^+ and H_3O^+ in acetonitrile, and this was confirmed by experiment.

As regards the values of the preexponent, the experimental data agreed in general with the concept that the probability of tunneling was mainly determined by the nature of the ruptured bond. However, it was difficult to make a quantitative comparison of the probabilities of tunneling in the given case, since the ratio of these probabilities differed from the ratio of the experimental values of the real preexponents, by a factor dependent on the difference in entropy of adsorption of the ions HB^+ and of the corresponding molecules B. Since we have no data, enabling us even approximately to estimate the entropy of adsorption in acetonitrile, we can only assert that the preexponents are similar in order of magnitude, but a more precise judgement on their relative values cannot be expressed.

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