MECHANISM OF HYDROGEN EVOLUTION ON IRON, CHROMIUM, AND MANGANESE

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It is shown on the basis of data for the protium–tritium kinetic isotope effect and of observed kinetic features of hydrogen evolution on iron, chromium, and manganese in acidic solutions that the full set of experimental data is hard to explain with the aid of the "traditional" mechanisms of hydrogen evolution. A scheme of hydrogen evolution is put forward which consists of a chemical reaction between water and the metal surface leading to formation of a hydrogen molecule and to metal oxidation. Removal of the oxidized form from the surface is the process governing overall reaction kinetics; it is accomplished either by electrochemical reduction during cathodic hydrogen evolution or by metal ions passing into the solution during chemical metal dissolution.

In [1] we published results obtained when measuring the protium–tritium kinetic isotope effect (KIE) during hydrogen evolution on Fe, Cr, and Mn in acidic solutions. Hydrogen evolution on these metals has several common features: their ability to dissolve according to a chemical mechanism [2-4]; identical KIE during cathodic hydrogen evolution and during the hydrogen evolution attending chemical dissolution of the metals; and independence of the KIE on electrode potential.* Considering all these observations we were able to suggest in [1], (i) that the process yielding molecular hydrogen is the same in the cathodic reaction and in chemical dissolution, and (ii) that the mechanisms of hydrogen evolution on these metals also are the same.

In the literature, attention has been focused on kinetic studies of cathodic hydrogen evolution on iron cathodes from acidic solutions. Multistep schemes comprising the discharge of H_3O^+ ions and subsequent recombination or electrochemical desorption are discussed for this process, and different versions are suggested for the rate-determining step. Without going into detailed analysis of these multistep schemes and of the experimental data from which they were proposed, we shall see how these schemes agree with the results for the KIE. This can be done since the KIE depends, not only on the energy characteristics of the reactants but also on the specific multistep scheme producing the H_2 molecules. The separation factors (S) to be expected for the hydrogen isotopes in multistep processes have been analyzed in [5, 6].

Let us first examine the case where the discharge step is followed by reversible electrochemical desorption. It has been shown in [5, 7] that such a multistep process always should yield S equal to the equilibrium constant of isotope exchange between gaseous hydrogen and water, i.e., 6.2. Actually the S-values found on the metals studied in [1] are substantially higher (12 for Mn, 16 to 18 for Fe, and 10 to 12 for Cr). Thus, hydrogen evolution on these metals cannot be described with the aid of mechanisms comprising reversible electrochemical desorption.

Previously we investigated the KIE during hydrogen evolution on gallium and mercury [8, 9], where one finds the sequence of irreversible steps: discharge and electrochemical desorption. In this case the KIE is governed by both steps [5, 6]. It was shown that S remains practically constant in the case of H_3O^+ discharge at low charge densities of the electrode surface ($< |-5| \mu C/cm^2$), but decreases at more negative charge densities (up to $-25 \mu C/cm^2$). This was explained by suggesting that with increasing negative charge density the discharging H_3O^+ ions are pulled somewhat closer to the electrode surface. This results in a decreasing proton jump distance and leveling of the tunneling difference of the isotopes, i.e., S decreases. The constancy of the KIE at low charge densities most likely is to be explained by weakness of the attraction forces.

* On Mn, the behavior of the KIE could only be traced in buffer solutions (pH ~ 2) where, as on Fe and Cr in H_2SO_4, the KIE does not change with potential. Measuring the KIE on Mn in H_2SO_4 as a function of potential proved to be impossible owing to the high rate of self-dissolution.

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Let us assume that on Fe, Cr, and Mn one has the sequence of irreversible steps: discharge and electrochemical desorption involving the H_3O^+ ion. However, on these metals the KIE does not depend on electrode potential. This could be explained, either in terms of low surface charge density or in terms of a charge density remaining constant over the potential range examined. Reliable data for the potential of zero charge are available for Fe only (−0.7 V vs nhe [10]). No data exist for electrode charge density at the potentials which are of interest to us, but it seems unlikely that the surface charge would remain constant or small in absolute value over a wide range of potentials quite far from the potential of zero charge (−0.28 to −0.45 V is the region where the KIE was measured on Fe). It is unlikely, therefore, that the slow discharge–slow electrochemical desorption mechanism is realized on the metals discussed. For the same reasons one can reject the mechanisms: slow discharge followed by recombination and equilibrium discharge followed by slow electrochemical desorption. The point is that, as shown in [5], the value of S resulting with such sequences of steps is governed by the slow reaction step. The H_3O^+ ion being the most likely proton donor in hydrogen evolution with acidic solutions, it becomes difficult to explain the fact that S is independent of potential.

Let us consider the scheme of hydrogen evolution consisting of reversible discharge and slow recombination. One must suggest that the adsorption energy (E) of atomic hydrogen depends on electrode potential if one wants to explain the experimental Tafel slopes (~ 120 mV on Fe [11] and Cr [12]) in terms of this mechanism. It follows from [5] that for this scheme, the S-value to be observed is determined by the constant (K) of the isotopic equilibrium $H_2O + Ta \rightleftharpoons HTO + Ha$ and by the kinetic isotope effect in the irreversible recombination step (S_{rec}), i.e., $S = K S_{rec}$. Since the KIE observed does not depend on potential, while K and S_{rec} certainly are functions of bond energy, one must suggest that $d \ln K/dE = -d \ln S_{rec}/dE$. Such compensation appears unlikely, since K only depends on the zero-point energy difference of bonds M−H and O−H, while S_{rec} should directly depend, in addition to the zero-point energies of the M−H bond, on purely kinetic parameters such as the transfer coefficient and the tunneling probability. The latter basically is a function of E, but the form of the functional dependence differs from the Arrhenius exponential characterizing the effect of the zero-point energies. If one still assumes that the changes in K and S_{rec} are strictly compensating, so that the KIE is independent of the bond energy of atomic hydrogen, then S should also be independent of the metal. It follows that substantial inconsistencies are encountered when one attempts to explain the entire set of experimental data (the Tafel slopes, independence of the KIE on potential, dependence of the KIE on the metal) in terms of the reversible discharge–slow recombination mechanism.

One two-step scheme with which one could explain that the KIE does not depend on potential is the following sequence of irreversible reactions:

$$H_3O^+ + e \rightarrow H_a + H_2O,$$
$$H_a + H_2O + e \rightarrow H_2 + OH^-. \qquad (1)$$

Here the H_3O^+ ion is proton donor in the first step; this is necessary in order to explain the effect of H_3O^+ concentration on the overall reaction kinetics. The involvement of water in the second step is less likely, since proton detachment from water is less advantageous energetically than detachment from the H_3O^+ ion. This two-step combination is more likely in the case of hydrogen evolution on mercury acidic solutions, where electrochemical desorption in all likelihood is activationless [13]. However, one could explain in terms of such a mechanism that the KIE does not change with potential. In scheme (1), in fact, the measurable S is determined by the relation: $2/S = 1/S_{dis} + 1/S_{des}$, where S_{dis} and S_{des} are the separation factors in the discharge and electrochemical desorption step, respectively [6]. We had assumed that the step of H_a removal involves a neutral H_2O molecule; therefore, the KIE in this step should not depend on electrode potential, just as is true in hydrogen evolution on mercury and gallium in alkaline solutions [9]. Further, for the overall effect, S, not to depend on potential, one must suggest that the KIE in the discharge step, which does depend on potential, is much larger than the KIE in the desorption step ($S_{des} \ll S_{dis}$). In this case $S \simeq 2S_{des}$, and there is no dependence of the KIE on potential.

For chemical metal dissolution one must write down a scheme of hydrogen evolution which comes as close as possible to the sequence of steps (1), since the KIE does not change as one goes from chemical metal dissolution attended by hydrogen evolution to electrochemical hydrogen evolution [1]. Such a scheme could for example be the sequence of the following irreversible steps:

$$M + H_3O^+ \rightarrow M^+ + H_a + H_2O,$$
$$M^+ + H_2O + H_a \rightarrow H_2 + M^+ + OH^-. \qquad (1')$$

Here, the formation of H_2 molecules occurs in almost the same way as in scheme (1). A change of mechanisms similar to that from (1) to (1') had already been encountered when going from cathodic hydrogen evolution on Hg and Hg–Ga alloys in alkaline solutions to hydrogen evolution on account of chemical dissolution of alkali metals from these electrodes [14, 15]. Cathodic hydrogen evolution from alkaline solutions is known to be accomplished according to the mechanism

$$\begin{aligned} H_2O+e &\rightarrow H_a+OH^-, \\ H_2O+H_a+e &\rightarrow H_2+OH^-. \end{aligned} \qquad (2)$$

For the case of chemical amalgam decomposition we have suggested that hydrogen evolution is accomplished according to the following mechanism [15]:

$$\begin{aligned} H_2O+M &\rightarrow H_a+M^++OH^-, \\ H_2O+H_a+M &\rightarrow H_2+M^++OH^-. \end{aligned} \qquad (2')$$

It was found, however, that the KIE changes as one goes from the electrochemical to the chemical process. We attributed this change encountered when going from (2) to (2') to the change in proton jump distance caused by the metal atom (or ion) appearing as a reactant. By analogy to the change of mechanism from (2) to (2'), a change in KIE should also be expected when replacing (1) by (1'). In reality, however, the KIE are the same in chemical dissolution and in cathodic hydrogen evolution on Fe, Cr, and Mn. Different KIE should arise in these two mechanisms for any of the schemes of hydrogen evolution discussed above when the change from electrochemical to chemical process is associated with changes analogous to those from (1) to (1') or from (2) to (2').

Thus, the independence of S on potential and the observation that the change from electrochemical to chemical hydrogen evolution is not attended by a change in KIE on Fe, Cr, and Mn [1] while it is sensitive to the change in mechanism on mercury [14] and mercury–gallium alloys [15], cannot be explained in a consistent way in terms of the traditional two-step mechanisms of hydrogen evolution on the metals examined. Of course, one cannot in principle rule out the possible accidental coincidence of KIE for electrochemical and chemical hydrogen evolution on one of these metals, but the accidental coincidence of the KIE for the different mechanisms on three metals is unlikely.

Independence of the KIE on potential in our opinion indicates that the H_2 molecule is formed directly from a water molecule on the metals being discussed here, despite the fact that the process occurs in acidic medium. Identical KIE in hydrogen evolution via the chemical and electrochemical mechanism demand that the elementary acts of molecular hydrogen formation be identical in the two cases. On the other hand, the reaction must involve the H_3O^+ ion. This is necessary in order to explain the reaction orders with respect to H_3O^+ ions found in the chemical mechanism [3, 4].*

In [2-4], the following scheme is reported as one possible mechanism of chemical metal dissolution:

$$n\,H_2O+M \rightarrow M(OH)_n+n/2H_2, \qquad (3'a)$$

$$M(OH)_n+n\,H_3O^+ \rightarrow M^{+n}+2n\,H_2O. \qquad (3'b)$$

If one assumes that the process

$$n\,H_2O+M \rightarrow M(OH)_n+n/2H_2, \qquad (3a)$$

$$M(OH)_n+n\,H_3O^++ne \rightarrow M+2n\,H_2O \qquad (3b)$$

takes place during cathodic hydrogen evolution, then it is obvious that the demands which are to be made upon the mechanism of hydrogen evolution with respect to the KIE data and which were formulated above are fully satisfied. The KIE does not change as one goes from the chemical (3') to the electrochemical (3) mechanism, since there is no change in the elementary act of molecular hydrogen formation; and the KIE does not depend on potential, since the reaction governing the KIE involves a neutral water molecule, so that the proton jump distance should not change with surface charge density.

The reality of the mechanism where water molecules are formed by chemical oxidation of the metal surface is supported indirectly by experiments on water adsorption on metals (in particular Fe [18, 19]) from the gas phase. In these experiments the metal surface is oxidized (atomic oxygen or OH groups become ad-

* The data for the effect of acid concentration on the electrochemical process are contradictory [16, 17].

sorbed), while molecular hydrogen appears in the gas phase. It was shown in [20] that one of the intermediate steps of surface oxidation during water adsorption from the gas phase is the formation of OH radicals on the surface.

Optical methods were used in [21, 22] to study the Fe/electrolyte interface. By comparing the conclusions drawn by the authors of these papers with our ideas as to surface coverage with OH radicals (or with the compound MOH) one comes to the following picture for the potential dependence of water interaction with the iron surface, which we believe to be free of contradictions: at potentials more negative than −1.0 V (vs nhe) the interaction of the water molecules in all likelihood is weak, and has no effect on the proton bond energy in H_2O. A potential shift in the positive direction (−0.9 to −0.7 V) causes weakening of the H−OH bond because of stronger interaction between the metal and the water oxygen. This results in increasing acidity of the adsorbed water [21]. In the region of positive surface charge densities (the zero-charge potential of iron is −0.7 V [10]), the Fe−O bond becomes so strong that detachment of one proton from H_2O becomes possible and the surface is primarily covered with OH radicals. (This is the potential range, from −0.31 to −0.5 V, where the KIE was measured [1].) At more positive potentials the formation of dehydrated forms of surface oxide right up to Fe_2O_3 becomes possible on the surface [22].

Considering the KIE data, one probably must expect a similar water adsorption picture on chromium and manganese.

Let us see what are the conditions under which the mechanism being proposed will satisfy the kinetic data for hydrogen evolution on the metals being discussed. The step of hydrogen formation is the same in schemes (3) and (3'). Its rate, i_a, is proportional to the number of sites, $1-\theta$, not taken up by the oxidized form $M(OH)_n$: $i_a = K_a(1-\theta)$. The rate of removal of the $M(OH)_n$ from the surface can be written as $i_b = K_b\theta$ and $i_b' = K_b'\theta$ for schemes (3'b) and 3b), respectively; here, K_b and K_b' include the concentrations of H_3O^+ ions, while K_b in addition contains the dependence of the rate of the electrochemical process of (3) on electrode potential. The two processes (3) and (3') proceed simultaneously; therefore, under steady-state conditions we have

$$\theta = \frac{K_a}{K_a + K_b + K_b'}. \tag{4}$$

It had been shown in [2-4] that the rate of hydrogen evolution on Fe, Mn, and Cr represents the sum of rates of the chemical and electrochemical process ($i_b + i_b'$); the rate of the chemical process does not depend on the rate of the electrochemical process (which changes with electrode potential). But the two processes have a common intermediate, $M(OH)_n$; therefore, i_b and i_b' will only be unrelated in the case where the degree of coverage by $M(OH)_n$ as defined by relation (4) is close to unity, i.e., when $K_a \gg K_b + K_b'$. This implies that the formation of H_2 molecules and simultaneous surface oxidation are a process with high rate constant, while removal of $M(OH)_n$ from the surface is the rate-determining step of processes (3) and (3'); the metal may (3'b) or may not dissolve (3b).

It follows from [1] that the KIE is higher on Fe than on Mn and Cr. In terms of the hydrogen evolution mechanism being suggested, two explanations can be given for metal-dependent KIE. According to one explanation, the KIE should depend on the metal when adsorbed atomic hydrogen is formed as an intermediate. In this case, increasing M−H bond energy results in higher KIE [8]. With n = 1, reaction (3a), (3'a) can then be written as the two steps

$$M + H_2O \rightleftharpoons H_a + MOH, \tag{5a}$$

$$M + H_2O + H_a \rightarrow H_2 + MOH. \tag{5b}$$

This multistep scheme is consistent with relation (4), provided the coverage with Ha is much smaller than unity or atomic hydrogen and the OH group adsorb independently.

One cannot say whether step (5a) is an equilibrium step or not,* but (5b), like the process as a whole, must be a nonequilibrium step; were it not, then the experimental separation factor would be 6.2, and constant, as in the case where electrochemical desorption is an equilibrium step [7]. Another possible explanation for KIE influenced by the nature of the metal is that of a dependence of KIE on proton jump distance [8]. This quantity can depend on the properties of the metal surface, since species adsorbed on the surface are involved in the formation of molecular H_2. It is obvious that in addition to scheme (5) one can suggest other multistep

* A case will be examined below where equilibrium must be suggested to exist in this step.

versions of chemical H_2 formation, but an unambiguous choice between them is not possible with the available data.

The independence of the KIE on potential in our opinion implies that the M−H bond energy is constant over the potential range studied. Above, when analyzing the mechanism comprising slow recombination, we discussed the case where the effects of bond energy on different KIE components were mutually compensated, but this possibility seems unlikely, both for the case discussed above and for the schemes of H_2 formation involved in the mechanism (3) and (3') suggested here.

When writing down reaction (5) we assumed that n = 1. It appears unlikely that several H_3O^+ ions would be involved in the elementary step [and at the same time several electrons, too, in reaction (3b)]. With n = 1 and an MOH coverage close to unity, reaction

$$MOH+H_3O^++e\rightarrow M+2H_2O \tag{5c}$$

determining the rate of electrochemical process (3b) makes the mechanism under discussion similar to the mechanism comprising the step of slow H_3O^+ discharge; the reaction rate in both mechanisms depends identically on the ψ'-potential, solution pH, and electrode potential. In this way one can explain the slopes of the polarization curves (100 to 120 mV on Fe [11] and Cr [12]) and the effect of solution composition on kinetics [16]. However, a somewhat different explanation holds in the case where the cathodic process is inhibited by the addition of iodide to the solution (see, e.g., [16]). Previously this effect had been attributed to the change in M−H bond energy occurring upon I^- adsorption. In our case one can use a similar suggestion relating to an effect of I^- adsorption on the M−OH bond, or the suggestion that the total number of OH groups on the surface that can take part in the reaction decreases upon iodide adsorption.

Singly charged metal cations are produced according to scheme (3') with n = 1:

$$MOH+H_3O^+\rightarrow M^++H_2O, \tag{5'c}$$

but all three metals are known to dissolve yielding doubly charged cations. The singly charged cations of the metals discussed here are reactive enough to rapidly reduce H_2O molecules:

$$M^++H_2O\rightarrow M^{2+}+H_a+OH^- \tag{5'd}$$

or hydroxonium ions:

$$M^++H_3O^+\rightarrow M^{2+}+H_a+H_2O. \tag{5'e}$$

Atomic hydrogen should enter the reactions yielding molecular H_2, and hence should influence the KIE. However, steps like (5'd) and (5'e) do not exist in the electrochemical process terminating in step (5c), and the KIE found in the chemical and electrochemical process are the same; one must suggest, therefore, that (5a) is an equilibrium step. In this case the effect of reactions (5'd) and (5'e) on the isotopic composition of adsorbed hydrogen should be fully leveled by equilibrium (5a). On the whole, the KIE will be governed by the constant of isotopic equilibrium $H_a + HTO \rightleftharpoons H_2O + T_a$ and by the kinetic isotope effect in step (5b), just as in the two-step mechanism of equilibrium discharge and slow electrochemical desorption discussed in [5]. At MOH coverages close to unity, reactions of the type of

$$M^++MOH+H_3O^+\rightarrow M^{2+}+2H_2O \tag{5'f}$$

which do not require equilibrium in step (5a) are possible in addition to reactions (5'd) and (5'e), since they do not produce atomic hydrogen. Without reporting the analysis of the corresponding kinetic equations we point out that the order of the chemical reaction of metal dissolution with respect to H_3O^+ ions will be two when (5'c) is an equilibrium step and is followed by the irreversible step (5'e) or (5'f). A reaction order of zero will result when water molecules are involved instead of H_3O^+ in step (5'c), and this is followed by step (5'd). The other possible versions yield first order. It is basically possible, too, that M^{2+} formation follows two parallel reaction pathways; this gives rise to fractional orders. The following reaction orders with respect to H_3O^+ ions are observed experimentally: 2 for Mn dissolution [4], 1 for Cr dissolution [3], and about 0.4 for Fe dissolution [3].

We note in conclusion that the set of steps suggested for the formation of H_2 molecules and M^{2+} cations certainly is speculative. It shows, however, that all of the experimental data can be explained on the basis of the concept developed above, viz., that hydrogen is produced from water and the metal surface. Moreover, such a reaction takes place, both in chemical metal dissolution and in cathodic hydrogen evolution from acidic

solutions. But traditional ways of describing cathodic hydrogen evolution do not succeed in giving a consistent explanation for available data in the case of the above metals.

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