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ELECTROCHEMICAL HYDROGEN EVOLUTION AND KINETIC ISOTOPE EFFECT

By

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Abstract

It has been considered the relationship between the isotope effect (separation factor) of electrochemical hydrogen evolution and the set of reaction steps. On that basis has been shown the possibility of the isotope effect analysis in solving of many problems of hydrogen evolution kinetics: elementary act of a reaction, stepwise mechanism of molecular hydrogen formation, influence of ψ_1-potential on the kinetics, problems associated with the nature of intermediates and proton donors.

Professor Horiuti was the first to use hydrogen isotopes for investigation of the reaction mechanism at the hydrogen electrode. In his lecture at the Japan-Soviet Seminar in Sapporo in October 1974 he gave a vivid picture of the initiation of this direction of research early in the thirties.[1] Since then Horituti and his School have carried out numerous studies in which a number of problems of the mechanism of hydrogen evolution reaction were investigated by the isotope exchange and the kinetic isotope effect methods (for literature, see *e.g.* refs. 2) and 3). These methods gained unversal recognition and have been used at many electrochemical laboratories.

In this communication the authors wish to demonstrate the existing techniques of applying the data on the kinetic isotope effect (KIE) to solution of the problems of electrochemical hydrogen evolution kinetics and primarily to examine the relationship between the isotope effect and the set of reaction steps. This will lead to the parameters influencing KIE and thus assess the potentialities of the method under consideration.

The isotope effect is characterized by the separation factor defined by the relation

$$S=\left(\frac{C_T}{C_H}\right)_{\text{solution}}\Big/\left(\frac{C_T}{C_H}\right)_{\text{gas}} \qquad (1).$$

where $C_T(C_H)$ is the concentration of heavy (light) isotope in gas or in solu-

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tion. We shall only consider the case where the concentration of one of the isotopes is much less than that of the other. This case, which is always met when a protium-tritium mixture is used, allows simplification of the KIE data analysis, as well be evident in what follows.

Many principles of electrochemical kinetics have been established on the basis of the studies of hydrogen evolution at mercury, where the process consists in a sequence of two irreversible steps : discharge and electrochemical desorption. Here proton removal from solution and its transfer to gas follow the reactions :

$$H_3O^+ + e \rightarrow H_a + H_2O\,;\ i_H \qquad (2),$$

$$H_a + H_3O^+ + e \rightarrow H_2 + H_2O\,;\ i_{H-H} \qquad (3),$$

Here i are the rates of corresponding reactions. In the presence of the heavy isotope in solution the following reactions take place :

$$H_2TO^+ + e \rightarrow T_a + H_2O\,;\ i_T \qquad (4),$$

$$H_a + H_2TO^+ + e \rightarrow HT + H_2O\,;\ i_{TH} \qquad (5),$$

$$T_a + H_3O^+ + e \rightarrow HT + H_2O\,;\ i_{HT} \qquad (6).$$

Strictly speaking, account should also be taken of the reactions involving two heavy isotope atoms, such as $HT_2O^+ + e$ or $T_a + H_2TO^+ + e$, but at $C_T \ll C_H$ the probability of two or more heavy atoms participating in a reaction is negligible. The heavy isotope concentration being small, we can write for the total transfer of H into gas :

$$j_H = 2i_{HH} \qquad (7)$$

and for the condition of the steady-state concentration of adsorbed H atoms :

$$i_H = i_{HH} \qquad (8)$$

since the removal of H_a from the surface as the result of the reaction (5) is negligible compared with the reaction (3). Transfer of the heavy isotope to gas takes the form :

$$j_T = i_{TH} + i_{HT} \qquad (9).$$

The conditions of the steady-state concentration of the intermediate (T_a) are similar to (8), $i_{TH} = i_T$, *i. e.*

$$j_T = i_T + i_{HT} \qquad (10).$$

Taking into account (7), (8) and (10), we have for the heavy isotope concentration in gas :

$$\frac{j_T}{j_H}=\frac{i_T}{2i_H}+\frac{i_{HT}}{2i_{HH}} \qquad (11).$$

Since j_T/j_H is equal to the tritium/protium concentration ratio in gas, we obtain from (I):

$$2S^{-1}=\frac{i_T C_H}{i_H C_T}+\frac{i_{HT} C_H}{i_{HH} C_T} \qquad (12),$$

where C_H and C_T are the isotope concentrations in electrolyte. Since in aqueous solution the H_3O^+ concentration is usually much less than the H_2O concentration, C_H and C_T are approximately equal to the isotope concentrations in water. The rate of discharge with participation of tritium may be represented as the product of the reaction rate constant (K_T) and the tritium concentration in hydroxonium ions (C'_T): $i_T=K_T C'_T$. Similar transformations involving the remaining quantities in (12) give:

$$2S^{-1}=\left(\frac{K_T}{K_H}+\frac{K_{HT}}{K_{HH}}\right)\cdot\left(\frac{C'_T C_H}{C'_T \cdot C_T}\right) \qquad (13).$$

The concentration ratio in the right hand side of (13) is nothing but the separation factor of the isotope exchange reaction between water molecules and hydroxonium ions (K_{ex}):

$$H_3O^+ + HTO \rightleftarrows H_2TO^+ + H_2O \qquad (14).$$

Representing the true kinetic separation factors of the steps as the ratio of the rate constants of reactions involving different isotopes: $S_d=K_H/K_T$ and $S_{ed}=K_{HH}/K_{HT}$, we can write in the final form:

$$S=\frac{2\,K_{ex}\,S_d\,S_{ed}}{S_d+S_{ed}} \qquad (15)$$

The material balance equation and the fact that the step rates had the same order in respect to both isotope species sufficed for derivation of this equation.[4] No use was made here either of the dependences of the process rate on potential as it was done in ref. 5) or of the models of an elementary act of proton transfer.

As it follows from the derivation, Eqn. (15) is valid for any surface coverages with intermediate, *i. e.* for any ratio of the rate constants of two irreversible steps. The same approach may be used in considering the isotope effects in the case of other reaction mechanisms. Below in the Table are given the formulae for differentmechan isms obtained in the same manner, which are valid regardless of the polarization curve shape and the surface coverage with adsorbed hydrogen. It follows from Eqn. (15) that KIE depends both on the discharge step (S_d) and on electrochemical desorption (S_{ed}) This results from removal of isotopes from solution along parallel route whereas in the kinetic reaction scheme these two steps are successive. Herein lies the difficulty of interpreting KIE data in the case under consideration. At present we cannot separate quantitatively the effects in individual steps. But at the same time this circumstance is of advantage in that KIE contains some information on the electrochemical desorption step generally not obtainable by electrochemical measurements.

A different picture presents itself if the electrochemical desorption step is reversible:

$$H_2O+H_a+e \rightleftarrows H_2+OH^- \qquad (16).$$

The presence of the heavy isotope in solution gives:

$$HTO+H_a+e \rightleftarrows HT+OH^- \qquad (17).$$

Let us consider the ratio of the equilibrium constants of these reactions:

$$\frac{K_{16}}{K_{17}}=\frac{[H_2]\cdot[HTO]}{[HT]\cdot[H_2O]} \qquad (18).$$

Evidently, this equation describes the isotope exchange reaction equilibrium

$$HT+H_2O \rightleftarrows H_2+HTO \qquad (19)$$

The equilibrium constant of this reaction is known and equal to 6.19.[6] By definition (I) the separation factor is the ratio of the relative isotope concentrations in electrolyte ($[HTO]/2\,[H_2O]$) and in evolving gas ($[HT]/2\,[H_2O]$), *i.e.* the right hand side of the equation represents the separation factor. Thus due to the electrochemical desorption equilibrium, the separation factor is equal to the equilibrium constant of the reaction (19). The kinetic isotope effect, which can occur during the nonequilibrium discharge step, does not affect the isotope composition of evolving hydrogen because the discharge rate is much less than those of the forward and back directions of the electrochemical desorption step which is in equilibrium.

If the hydroxonium ion takes part in the equilibrium electrochemical desorption step, then since there is equilibrium (14) in aqueous solution, the isotope equilibrium between water molecules and hydrogen is not disturbed. Thus regardless of whether it is H_2O or any other proton donor being in isotope equilibrium with water which is discharged and irrespective of the cathode material and its potential, KIE must be equal to 6.2 as long as electrochemical desorption is in equilibrium. If the protium-deuterium system is used, equilibrium similar to (19) will cause KIE equal to 3.18.[6] The data on the isotope effect available for a large group of metals[*)] show that this value does not coincide with the experimental S values for acid and alkaline solutions and does not represent the limiting value which S would tend to approach with decreasing overvoltage. Thus even a simple analysis of the hydrogen evolution kinetic scheme from the standpoint of the isotope effect

TABLE

	Mechanism	Isotope effect	$\partial S/\partial \varphi$	
I	$H_3O^+ + e \rightarrow H_a + H_2O$ $H_2O^+ + H_a + e \rightarrow H_2 + H_2O$	$\frac{2}{S} = \frac{1}{S_d K_{ex}} + \frac{1}{S_{ed} K_{ex}}$	+	
II	$H_3O^+ + e \rightarrow H_a + H_2O$ $H_2O + H_a + e \rightarrow H_2 + OH^-$	$\frac{2}{S} = \frac{1}{S_d K_{ex}} + \frac{1}{S'_{ed}}$	$K_{ex} S_d \ll S'_{ed}$	+
			$K_{ex} S_d \gg S'_{ed}$	○
III	$H_2O + e \rightarrow H_a + OH^-$ $H_3O^+ + H_a + e \rightarrow H_2 + H_2O$	$\frac{2}{S} = \frac{1}{S'_d} + \frac{1}{S_{ed} K_{ex}}$	$K_{ex} S_{ed} \gg S'_d$	○
			$K_{ex} S_{ed} \ll S'_d$	+
IV	$H_2O + e \rightarrow H_a + OH^-$ $H_2O + H_a + e \rightarrow H_2 + OH^-$	$\frac{2}{S} = \frac{1}{S'_d} + \frac{1}{S'_{ed}}$	○	
V	$H_3O^+ + e \rightarrow H_a + H_2O$ or $H_2O + e \rightarrow H_a + OH^-$ $H_2O + H_a + e \rightleftharpoons H_2 + OH^-$	$S_{H/T} = 6.2$ $S_{H/D} = 3.8$	○	
VI*	$H_3O^+ + e \rightarrow H_a + H_2O$ $2\,H_a\,(\rightleftarrows)\,H_2$	$S = K_{ex} S_d$	+	
VII*	$H_2O + e \rightarrow H_a + OH^-$ $2\,H_a\,(\rightleftarrows)\,H_2$	$S = S'_d$	○	
VIII	$H_2O + e \rightleftharpoons H_a + OH^-$ $H_3O^+ + H_a + e \rightarrow H_2 + H_2O$	$\frac{2}{S} = \frac{1}{S_{TH} K_{ex}} + \frac{1}{S_{HT} K_{ad}}$	+	
IX	$H_2O + e \rightleftharpoons H_a + OH^-$ $H_2O + H_a + e \rightarrow H_2 + OH^-$	$\frac{2}{S} = \frac{1}{S'_{TH}} + \frac{1}{S'_{HT} K_{ad}}$	○	
IX**	$H_2O + e \rightleftharpoons H_a + OH^-$ $2\,H_a \rightarrow H_2$	$S = K_{ad} S_r$	○	

* The KIE is independent of the degree of the reversibility of the recombination step.

** The separation factor in the recombination step (S_r) is the ratio of the rate constants of the reactions: $H + H \rightarrow H_2$ and $H + T \rightarrow HT$.

[*)] See, *e.g.* ref. 7—10.

and the experimental KIE values suggest that on many cathode materials electrochemical desorption is a non-equilibrium process. So far it has not been possible to obtain such direct proof by conventional electrochemical measurements*).

The Table lists the expressions for experimentally observed isotope effect for the hydrogen evolution mechanisms frequently discussed in literature. Most of these expressions were first obtained by J. O'M. Bockris and S. Srinivasan.[5] It is clear from the Table that in the cases in which water molecules are proton donors, the separation factor (K_{ex}) resulting from isotope exchange (14) disappears from the corresponding expressions. In the Table the expressions for the equilibrium steps take account of the participation of water molecules; their substitution by the hydroxonium ion will not affect the expression for S since there exists equilibrium (14) in solution. This fact was pointed out earlier when considering the Mechanism V. In the cases where there is equilibrium between atomic hydrogen and solution bulk (Mechanisms VIII-X) the expression for S contains the quantity K_{ad}, which represents the separation factor of the isotope exchange reaction

$$H_2O + T_a \rightleftarrows HTO + H_a \qquad (20).$$

And finally in order to explain the quantities contained in the Table it should be pointed out that S_{HT} and S_{TH} (Mechanisms VIII, IX) are the ratios between the rate constant of the reaction (3) and those of the reactions (6) and (5), respectively. The separation factor values in the steps involving water molecules are marked with primes to distinguish them from the values referring to the steps involving the hydroxonium ion.

As can be seen from the Table, the observed isotope effect is defined both by the kinetic isotope effects of individual steps (S_i) and by the isotope effects caused by the equilibrium steps K_{ex}, K_{ad}. The quantities S_i can be represented as the product of S_i^E — the component of the isotopic effect determined by the difference in the zero levels of the isotope-substituted molecules in intial and final states and $S_i^{\varkappa}$ — the component completely determined by the difference in the tunneling probabilities of light and heavy isotopes. The quantities S_i^E and K_{ad} can be estimated with a sufficiently high precision if the zero energies of the corresponding proton bonds are known. Quantitative estimation of $S_i^{\varkappa}$ requires the use of certain models of an elementary act of proton transfer and at present does not seem to be

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*) In the case of mercury, the irreversibility of electrochemical desorption along with the KIE data confirms the nonequilibrium character of the ratio between the ortho- and paraforms of the hydrogen evolved as the result of cathodic process in acid solutions.[11]

reliable since it requires knowledge of a number of parameters, which in their turn cannot be evaluated accurately enough. An elementary act model, however, even though it cannot lead to a reliable quantitative estimate of the isotope effect, can give a qualitative picture of the dependence of the isotope effect on the reaction conditions (such as potential, metal or proton donor nature). This makes it possible to use the KIE data for verification of the models. This approach was used by the authors[8,9] in comparing two models of an elementary act of proton transfer : the gradual covalent bond stretching model based on Horiuti and Polanyi's work[12] and the quantum-mechanical model developed by Dogonadze and coworkers.[13] The comparison could only be carried out with the use of the KIE data obtained for the cathodes with the hydrogen evolution mechanism known.

Another sphere of KIE application is investigation of the kinetic reaction scheme. The simplest case of using KIE in this investigation is based on the influence of the multistep character of the hydrogen evolution reaction on the isotope effect. Let us assume that there are reasons to believe that near a certain potential a change in the hydrogen evolution mechanism occurs. This assumption can be independently confirmed by measuring the isotope effect. It is unlikely that the same separation factor should correspond to two different mechanisms of the molecular hydrogen formation. Therefore, near this potential the monotonic dependence of S on potential should be disturbed. If no peculiarities in the isotope effect behaviour in the potential range of interest are observed, this can mean that the step or steps responsible for the isotope effect have not changed and do not define the overall reaction rate. This suggestion can be very useful in interpreting the reaction mechanism.

Investigation of KIE of metals of mercury type (Hg, Ga, Pb, Tl amalgam)[8,9] in which hydrogen evolution is due to irreversible discharge and electrochemical desorption steps, revealed two main regularities : 1. The separation factor decreases with increasing negative potential drop in the Helmholtz layer if hydroxonium ions are proton donors. If, however, it is water molecules which are donors, the separation factor does not depend on potential. 2. The separation factor increases with increasing energy of the atomic hydrogen bond with metal. In terms of the quantum-mechanical model of an elementary act of proton transfer[13], the first dependence can be explained as follows : increase of the negative potential drop between metal and the plane in which the discharging positively charged H_3O^+ ion is localized leads to its ever increasing attraction to metal surface and this decreases the distance of the quantum-mechanical jump of proton from its state in H_3O^+ to the state H_a. Decrease of this distance means increase of the tunneling probability, *i.e.* it levels the difference in the tunneling probability for the nuclei of different hydrogen isotopes or, which is the same, decreases the separation factor in the discharge step. In the case of a neutral water molecule discharge, the change of the potential drop does not affect virtually the position of the proton center, and as the result, S_d does not change. This reasoning leads to similar conclusions for the electrochemical desorption step as well (S_{ed}).

The concepts developed on the basis of the elementary act theory and their experimental corroboration for the Mechanisms I, II and IV*) allow a suggestion to be made about the nature of the dependence of S on potential for other hydrogen evolution mechanisms : it depends on participation of H_3O^+ or H_2O in the step determining KIE (this is not necessarily the rate-determining step of the hydrogen evolution process). Hence directly ensures the possibility of using KIE data for settling the question which is the proton donor — H_3O^+ or H_2O. The character of the dependence of S on potential to be expected for different mechanisms : decrease of S with increasing negative potential ($\partial S/\partial\varphi > 0$) or its practical constancy ($\partial S/\partial\varphi \approx 0$) is indicated in the Table. These dependences are presented under the assumption that the adsorption energy does not vary with potential.

The dependence of KIE on the adsorption energy of atomic hydrogen (E_{MH}) is explained as follows. Increase of E_{MH} means a stronger proton localization, *i.e.* a lesser tunneling probability. This increases the difference in the behaviour of light and heavy hydrogen isotopes, *i.e.* it enhances KIE in both steps. This is true for the KIE component depending on the tunneling probability ($S_I^{\neq}$). The activation component of KIE S_I^E decreases with increasing E_{MH} if H_a is the product of the step. If, however, H_a is an initial reagent, S_I^E rises with rising E_{MH}. Besides $\partial K_{ad}/\partial E_{MH} < 0$. Due to the above circumstances, in the general case it is not possible to determine the dependence of KIE on E_{MH}. In practice examination of the dependence of KIE on metal nature is complicated by the $S(\varphi)$ dependence in the case if H_3O^+ ions are proton donors. We managed to avoid this difficulty because there was no reason to suppose the existence of a significant difference in the electric double layer structure at the metals studied (Hg, Ga, Pb, Tl amalgam) and the S values were compared at the same surface charge, *i.e.* in the presence of the same force acting on the discharging H_3O^+ ion.[7]

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*) Mechanism IV is the hydrogen evolution mechanism from alkaline solutions at metals with high overvoltage and Mechanisms I and II are the most likely hydrogen evolution mechanisms from acid solutions at low and medorate overvoltage at the same metals.[14]

In the case if water molecules are donors, determination of the dependence of KIE on metal nature is considerably simplified since $\partial S/\partial \varphi = 0$. The coincidence of the sign of $\partial S_i^{\neq}/\partial \varphi$ predicted by the elementary act model with the experimentally observed $\partial S/\partial \varphi > 0$ in the case under consideration shows that the activation components S_i^E (metals of the type of mercury and Mechanisms I, II and IV) do not play an important role. It is not possible to make any predictions about other mechanisms and metals with a much larger E_{MH}. But knowledge of the dependence of single KIE components on E_{MH} facilitates using KIE data for interpretation of the reaction mechanism.

Thus it can be stated with sufficient reliability that, for instance in the case of Mechanism X, KIE will not remain constant with changing E_{MH} due to complete compensation of the changes of K_{ad}, S_r^E and $S_r^{\neq}$ since the character of the dependence of K_{ad} and S_r^E on E_{MH}, on one hand, and of the tunneling probability, *i.e.* $S_r^{\neq}$ on the other hand, is obviously different. Therefore, when for Mechanism X an assumption is made about a significant change of adsorbed hydrogen energy with potential (*e.g.* an isotherm of Temkin's type), the dependence of S on potential serves as a criterion of the validity of this assumption. The constancy of S in a wide potential range invalidates the assumption that $\partial E_{MH}/\partial \varphi \; 0$. An example of the employment of the dependence of S on E_{MH} is its use for proving that H_a is formed as an intermediate during decomposition of alkali metal amalgams.15) It was found that S changes when passing from simple amalgams (Hg-alkali metal) to complex ones (Hg-Ga-alkali metal). Since there is no justification for supposing that there should be change in the mechanism of the reaction as a whole, the only reason of the change of S must be that of E_{MH}.

Recently a thorough analysis of the mechanisms listed in the Table was made in connection with the discussion of the KIE data obtained for hydrogen evolution from acid solutions at iron, chromiun and manganese.16) It was found that all the mechanisms considered could not explain unambiguously the experimental data and thus a chemical mechanism of the hydrogen molecule formation as the result of a reaction of electronegative metal with water was suggested.

In conclusion, it would be relevant to mention another application of KIE bearing no relation to investigation of the stepwise nature of reactions. Measurement of S at mercury in acid solutions containing various specifically adsorbed ions showed KIE to be a unique function of the potential drop in the Helmholtz layer and at given value of the later does not depend on immidiatly overpotential, equilibrium potential of the electrode, ψ_1-potential and electrolyte composition.[8] This allows KIE to be used for determining the contribution of ψ_1-potential to the change in the hydrogen evolution kinetics observed when other factors are present at the same time. Such investigation, in particular, was carried out for elucidation of the role of the ψ_1-effect in hydrogen evolution from acid concentrated salt solutions.[17]

Thus, the KIE method can be applied in solving a great variety of problems of the hydrogen evolution kinetics: elementary act of a reaction, stepwise mechanism of molecular hydrogen formation, influence of ψ_1-potential on the kinetics, problems associated with the nature of intermediates and proton donors. Undoubtedly, the method is not independent in the sense that its data must be supplemented by the results of other methods. But strictly speaking, this is true for any experimental method.

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