ISOTOPIC EFFECT IN ELECTRODE PROCESSES

É. D. German, R. R. Dogonadze,
A. M. Kuznetsov, V. G. Levich, and Yu. I. Kharkats

UDC 541.138

An explanation of the isotopic effect by consideration of the hydrogen ion transfer processes within the framework of theories of absolute reaction rates encounters certain difficulties [1]. According to this theory the isotope effect is determined by the difference between the zero-point energy of the proton ε_H^0 and the triton * ε_T^0 in the ground state

$$\frac{k_H}{k_T} = c \exp \frac{\varepsilon_H{}^0 - \varepsilon_T{}^0}{kT}, \tag{1}$$

where the preexponent is determined by the ratio of the masses of the reacting particles and may vary between the limits $1 < c < \sqrt{3}$. Experimental values for the isotopic effect may be markedly different from the values of k_H/k_T calculated from Eq. 1. To explain the experimental values in such cases an assumption is usually introduced that tunnelling occurs and that there is a change in bond frequency in the transient state. However, as Krishtalik and Tsionskii show in [2, 3], the concept of the theory of absolute reaction rates, even though the stated assumptions are attractive, is not in agreement with the experimental observations on the variation of the electrochemical separation factor for hydrogen isotopes S with the nature of the metal. Comparison of the separation factors on different metallic electrodes shows that with different metals the values of S obtained at the same energy differences of the initial and final states do not agree, as would be expected from the Khoriuch-Polyani theory which is based on the transition complex method taking into account the tunnelling effect. A quantum mechanical theory is given in [4] for the discharge of hydrogen ions on metals with a high overvoltage. It is interesting to consider the isotopic effect within the framework of this theory.

According to [4] the probability of the transfer of a proton from the ion AH^+ to an electrode at a distance R (Fig. 1) may be written in the form:

$$W(R) = \frac{\omega_0}{2\pi} \varkappa(R) e^{-\frac{E_a}{kT}}, \tag{2}$$

where ω_0 is the characteristic dielectric relaxation frequency of the polar solvent in which the reaction takes place, $\varkappa(R)$ is the transmission coefficient, and E_a is the activation energy. The activation energy E_a has been calculated in [4, 5]. For simplicity, we consider below the isotopic effect in the normal region ($|\Delta I| < E_S$), where E_S is the reorganization energy of the solvent, and $-\Delta I$ is the heat of reaction. Generalization to the barrierless and activationless regions causes difficulties in principle. According to [4] the activation energy in the normal region has the form:

$$E_a = \frac{(E_S + \Delta I)^2}{4E_S}. \tag{3}$$

---

* To be specific, we shall consider the isotope effect arising during proton/triton exchange. Extrapolation to the case of proton/deuteron exchange is obvious.

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 6, No. 3, pp. 350-354, March, 1970. Original article submitted May 5, 1969.

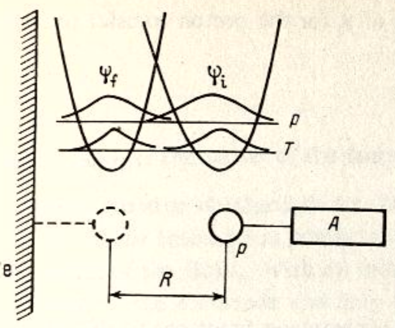

Fig. 1

To obtain the rate constants for the proton transfer reaction it is necessary to average Eq. (2) for the probability of proton transfer at a given distance R for the various possible values of this distance, i.e.,

$$k=\int W(R)f(R)\,dR, \tag{4}$$

where f (R) is the probability of the reagent approaching the electrode at a distance R. We shall consider the reaction, without investigating the diffusion limitations, when the reacting particles are able to "collide with the electrode" repeatedly before proton transfer occurs. Since the transfer takes place over very small distances, the function f(R) may be given as

$$f(R)=\exp\left[-\frac{U_0(R)}{kT}\right], \tag{5}$$

where $U_0(R)$ is some short-range, repulsive potential determined by quantum forces.

Since we shall be interested below in the isotopic effect as a function of the electrical field E, it is necessary to add to the short range potential U_0 (R) and to $\Delta I_{H,\,T}$ the electrostatic energy eER + const. From Eqs. (2)-(5) it is not difficult to obtain the following expression for the isotopic effect

$$\frac{k_H}{k_T}=\frac{\int \varkappa_H(R)\exp\left[-\frac{U_0(R)+eER/2}{kT}\right]dR}{\int \varkappa_T(R)\exp\left[-\frac{U_0(R)+eER/2}{kT}\right]dR}$$
$$\times\exp\left[-\frac{E_S{}^H-E_S{}^T}{4kT}-\frac{\Delta I_H-\Delta I_T}{2kT}-\frac{(\Delta I_H)^2}{4E_S{}^H kT}+\frac{(\Delta I_T)^2}{4E_S{}^T kT}\right]. \tag{6}$$

It follows from Eq. 6, that the isotopic effect may be determined by different factors. The term, $(\Delta I_H - \Delta I_T)/2kT$, in the exponent index, includes the zero vibration energy of a proton and triton in the initial and final states, and can be expressed as

$$(\varepsilon_{iH}{}^0-\varepsilon_{fH}{}^0-\varepsilon_{iT}{}^0+\varepsilon_{fT}{}^0)\,/\,2kT. \tag{7}$$

For the discharge of hydrogen isotopes on mercury the multiplier in the isotopic effect, corresponding to this term, is equal to 2.3. A comparison with experimental results shows that it is insufficient to calculate this multiplier alone in order to explain the absolute value of the isotopic effect.

To estimate the contribution to the isotopic effect of the terms

$$\exp-\frac{E_S{}^H-E_S{}^T}{4kT}\quad\text{and}\quad\exp-\left(\frac{(\Delta I_H)^2}{4E_S{}^H kT}-\frac{(\Delta I_T)^2}{4E_S{}^T kT}\right) \tag{8}$$

it is also necessary to know the values of E_S^H and E_S^T. At the present time it is only possible to calculate the theoretical order of magnitude of E_S. It is possible, however, to give a qualitative reason for the relative roles of these terms in the isotopic effect. Since the solvent reorganization energy E_S is a function of the charge redistribution during the reaction, the difference between E_S^H and E_S^T can only be connected with the different degree of localization of the wave functions of a proton and a triton. Analysis shows that the value is evidently not large. In every case the contribution of these terms, along with that of the previous term, to the isotopic effect are independent of the electrical field. It should be noted that the structure of the last exponential cofactor in Eq. (6) is essentially different from that of the corresponding multiplier in the equation based on the theory of reaction rates, where the motion of the proton is considered as classical. Equation (6) is based on the assumption that the motion of the proton is essentially of a quantum nature [4].

Equation (6) indicates that the relation of kH/kT to the field is contained only in the first cofactor. It should be noted that in adiabatic reactions ($\varkappa_H = \varkappa_T = 1$) the isotopic effect is independent of the field. Therefore, we shall assume that the reactions are nonadiabatic ($\varkappa_H < \varkappa_T < 1$). The value of $\varkappa$ for the proton transfer reaction has been calculated in [4], and has the form:

$$\varkappa = \frac{\left| \int \psi_f^* V \psi_i \, dv \right|^2}{\hbar\omega_0 \sqrt{\frac{E_S kT}{4\pi^3}}} = \frac{L^2}{L^2_{\text{crit}}} < 1, \tag{9}$$

where the matrix element $L = \int \psi_f^* V \psi_i \, dv$ is determined by the overlap of the wave functions of the proton in the initial and final states, and V is the interaction potential of the proton with the electrode.

The function $\varkappa(R)$ was calculated by using the proton wave functions at different potentials (for example, for a Morse type potential, and a parabolic potential). Below we give the form of $\varkappa_H(R)$ and $\varkappa_T(R)$ for a parabolic potential:

$$\varkappa_{p,T}(R) = \text{const} \cdot \exp(-\alpha_{p,T} R^2), \tag{10}$$

where $\alpha_{p,T} = \frac{m_{p,T}}{\hbar} \frac{\omega_i^{PT} \omega_f^{PT}}{\omega_i^{PT} + \omega_f^{PT}}$ and $\alpha_p = \sqrt{3}\,\alpha_T$, a ω_i, ω_f

are the vibration frequencies of the proton and triton in the initial and final states. We note that, since the transmission coefficients $\varkappa_{H,T}(R)$ decrease rapidly with increasing distance (R), and $U_0(R)$ increase rapidly with decreasing R, the proton transfer effectively takes place over a narrow range of R, i.e., it is characterized by definite values of the transfer distance R^*

$$\int \varkappa_{H,T}(R) \exp - \frac{U_0(R) + eER/2}{kT} dR$$

$$\approx \varkappa_{H,T}(R^*_{H,T}) \exp - \frac{U_0(R^*_{H,T}) + eER^*_{H,T}/2}{kT} \Delta R^*, \tag{11}$$

where the value of $R^*_{H,T}$ is determined by the equation

$$2\alpha_{H,T} R^*_{H,T} + \left(U_0'(R^*_{H,T}) + \frac{eE}{2} \right) \Big/ kT = 0. \tag{12}$$

The values of $R^*_{H,T}$ depend on the actual form of the potential $U_0(R)$ and are functions of the electrical field. It is obvious, moreover, that always $R^*_H > R^*_T$, i.e., the transfer of the heavy isotope always takes place at a closer distance. If, over a short range of R, $U_0(R)$ is approximated by the quadratic potential $U_0 = [(\gamma/2)](R-b)^2$, where γ and b are parameters characterizing the form of the potential, then it follows from Eq. (12) that

$$R_p^{*E} = b \frac{\left(1 - \frac{eE}{2\gamma b}\right)}{\left(1 + \frac{2kT\alpha_p}{\gamma}\right)}, \qquad R_T^{*E} = b \frac{\left(1 - \frac{eE}{2\gamma b}\right)}{\left(1 + \frac{2kT\alpha_p\sqrt{3}}{\gamma}\right)}. \tag{13}$$

Substituting the expressions obtained for R^{*E}_H and R^{*E}_T in Eqs. (11) and (6), we find after simple calculations, the following expression for the isotopic effect as a function of the electric field E:

$$\left(\frac{k_H}{k_T}\right)_E = \left(\frac{k_H}{k_T}\right)_0 e^{-\frac{eEba_p}{2\gamma}(\sqrt{3}-1)}, \quad (14)$$

where $(k_H/k_T)_0$ is the value of the isotopic effect in the absence of a field ($E = 0$).

The expression obtained shows that the isotopic effect decreases with increasing electric field, while the steeper the change in the interaction potential between the particles and the electrode (the larger the value of γ), the smaller the influence of the field. With an increase in the electrical field E the ion from which the proton is transferred is drawn closer to the electrode and may fall into a region of steeper repulsive potential. In this case the variation of k_H/k_T with E is not represented by Eq. (13), but it may be shown that the isotope effect, which initially decreased exponentially with field strength, will change more slowly, and an effect similar to saturation sets in, when the field strength ceases to affect the ratio k_H/k_T. The analysis given above for k_H/k_T as a function of the field strength is in qualitative agreement with the experimental data for the isotope separation factor as a function of field strength. At the present time it is difficult to make a quantitative comparison, since the experimental values measured represent the over-all effect of all the process stages [2].

The authors express their gratitude to L. I. Krishtalik for helpful discussions.

LITERATURE CITED

1. R. P. Bell, The Proton in Chemistry, New York (1959).
2. L. I. Krishtalik and V. M. Tsionskii, Élektrokhimiya, 5, 1188 (1969).
3. L. I. Krishtalik and V. M. Tsionskii, Élektrokhimiya, 5, 1019 (1969).
4. R. R. Dogonadze, A. M. Kuznetsov, and V. G. Levich, Electrochim. Acta., 13, 1293 (1968).
5. R. R. Dogonadze, A. M. Kuznetsev, and V. G. Levich, Élektrokhimiya, 3, 739 (1967).