The β-hydroxyethyl radical as a model system for two-pathway electroreduction in the presence of proton donors

Alexander G. Krivenko, Alexander S. Kotkin and Vladimir A. Kurmaz*

Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 096 515 3588; e-mail: kurmaz@icp.ac.ru

The mechanism of electrode reactions of the β-hydroxyethyl radical has been found experimentally to depend on pH, and a general kinetic scheme of organic radical electroreduction is suggested which includes two parallel pathways of electron transfer, either to adsorbed radical R_{ads} or to its metastable protonated complex $[R_{ads}\cdot BH^+]$; the competition between these pathways is determined by the capacity of R_{ads} for complex formation, the concentration of the proton donor, and electron transfer rates to R_{ads} and $[R_{ads}\cdot BH^+]$.

The problems of electron transfer in electrochemical systems have received much attention.[1] Two-electron electrochemical reduction (subsequently called electroreduction or reduction) of electroactive depolariser A may be represented by the following sequence of one-electron steps:[2]

$$\mathrm{A} \underset{W_2}{\overset{W_1}{\rightleftarrows}} \mathrm{IS} \underset{W_4}{\overset{W_3}{\rightleftarrows}} \mathrm{B} \qquad (1)$$

where IS is an intermediate and W_3 and W_2 are its electroreduction and electrooxidation rate constants, respectively. If A is an organic depolariser, *e.g.*, an organic halide, IS is usually a radical which is adsorbed on the electrode surface.[2] It has been demonstrated previously by the laser photoemission method[2] (LPE) that the dependence of W_3 on the electrode potential E for organic radicals follows the slow discharge equation with a transfer coefficient α *ca.* 0.5 at W_3 within $1\text{–}10^7$ s^{-1}. According to refs. 2–6, W_3 does not depend on the concentration of proton donors BH^+ for certain radicals (linear ether and α-hydroxy alkyl radicals; alkyl, aryl and their halogen derivatives, *i.e.* group I), whereas W_3 is proportional to $[BH^+]$ for group II (α-radicals of cyclic ethers and glycols; β-radicals of alkylcarboxylic acids; HCO·).

The nature of these differences is not clear. Therefore, it seems important to perform a comparative study of the electrochemistry of radicals which have the same (or similar) chemical composition but differ in structure, *e.g.* in the localisation of the free valence. The α- and β-hydroxyethyl radicals were chosen for the study (radicals **I** and **II**, respectively). The former has been thoroughly studied by photoemission methods,[6,7] but the electrochemistry of radical **II** has not been studied in detail before, see refs. 2 and 8. We generated radical **II** by the reaction of solvated electron e^-_{aq}[†] with an acceptor, namely, 2-chloro- or 2-bromoethanol XCH_2CH_2OH (X = Cl, Br):

$$XCH_2CH_2OH + e^-_{aq} \xrightarrow{k_a} XCH_2CH_2OH^{\cdot -} \xrightarrow{k_d} \cdot CH_2CH_2OH\cdot + X^- \qquad (2)$$

where $k_a = 6.4\times10^8$ dm^3 mol^{-1} s^{-1} for X = Cl.[9‡] Radical **I** is formed upon elimination of an H-atom by an OH radical from the α-carbon of ethanol. The OH radical is generated from aqueous solutions of N_2O by a process such as reaction (2).

The radicals formed by a dissociative electron transfer[1] reaction (2) diffuse to an electrode and are adsorbed on it and are involved in electrode reactions to yield photocurrent j. The values of j were obtained by recording and digital Fourier-transformation of the signal from a photoelectrochemical cell at 1.0–1100 Hz frequencies ν of electrode illumination. The position of the voltammetric wave on the E axis is determined by a competition between the irreversible reduction of a radical with rate constant W_3 and the duration of electrode illumination. W_3 is derived from $W_3 = 5.31\nu$ at $E = E_{1/2}$ under the same experimental conditions as those which provide the measurement of W_3 values in the range $5\text{–}5.8\times10^3$ s^{-1}. The values of W_3 in the range $3\times10^3\text{–}6\times10^6$ s^{-1} were determined by measurement of the kinetics of emitted charge $Q(t)$. The experimental setup and measurement technique have been described in detail elsewhere.[2–4]

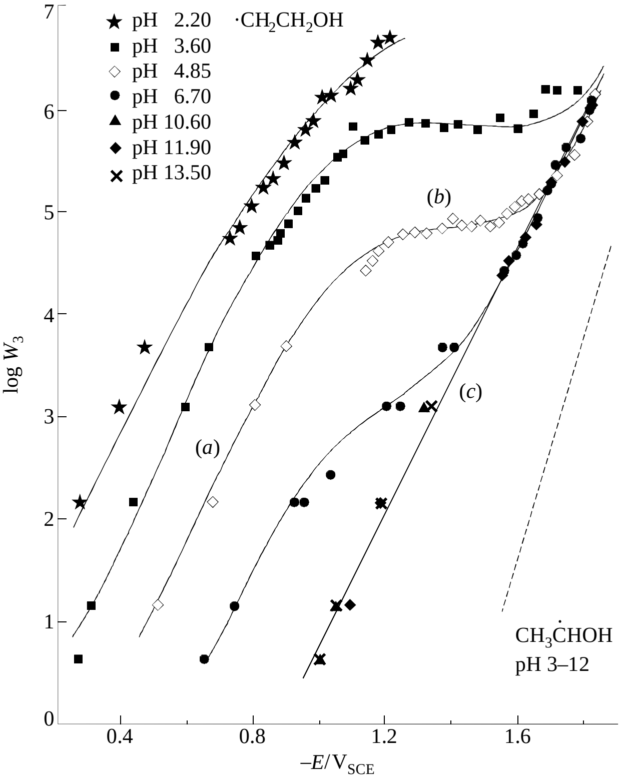

Figure 1 $W_3(E)$ dependences for the radicals **I** (dashed line, data from refs. 6 and 7) and **II** (solid lines) at various pH. 0.045–0.27 M 2-chloroethanol or 0.01 M 2-bromoethanol are used as acceptors. Stationary mercury electrode. Supporting electrolytes are aqueous buffer solutions with the addition of 0.5 M KCl.

The electrochemical behaviour of α- and β-hydroxyethyl radicals was found to differ fundamentally. W_3 does not depend on pH in the range 3–12 for radical **I**,[6] whereas the $W_3(E)$ dependences for radical **II** are different in acidic and basic solutions and consist of three characteristic sections (Figure 1). The first (*a*) and third (*c*) sections follow the equation of slow discharge with a transfer coefficient α of *ca.* 0.4, while W_3 decreases in the first section of the curve as pH increases. These sections are separated by an intermediate second section (*b*), where W_3 hardly depends on E; the lower the pH the higher the position of this region on the *Y*-axis. All three sections (*a*)–(*c*) are most pronounced at low-acid pH values.

W_3 decreases in the first section as pH changes from acidic to low-basic values (Figure 2); the slope of $(dE_{W_3 = 10\ s^{-1}}/d\mathrm{pH})$ dependence (0.14±0.02 V) at pH ≤ 8.1 is close to the corre-

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[†] e^-_{aq} are generated by the LPE method at distances of *ca.* 10–100 Å from the electrode by its irradiation with a UV-laser pulse (λ 337 or 265 nm).

[‡] k_d values for such reactions are usually ≥ $10^8\text{–}10^9$ s^{-1}, see ref. 10.

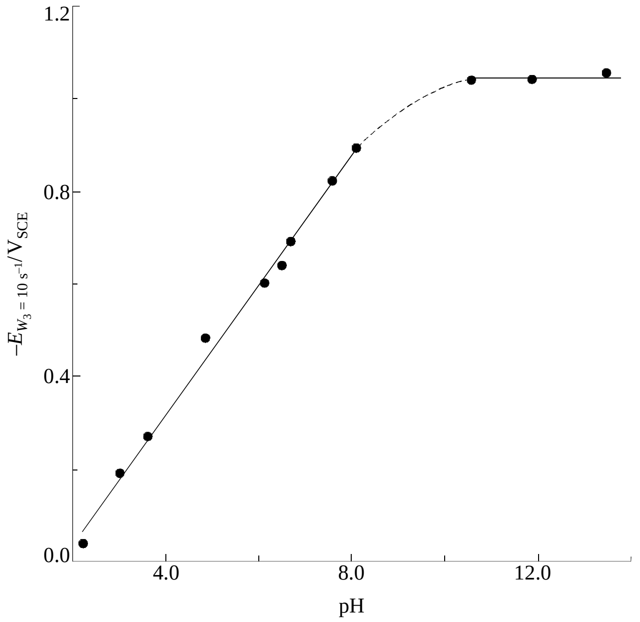

Figure 2 E, pH-dependences obtained by a cross-section method from $W_3(E)$ plots for radical **II** at $W_3 = 10$ s^{-1}.

sponding $(2.3RT/F)/\alpha$ value that characterises electroreduction as a first-order reaction with respect to BH^+ concentration.

Similar $W_3(E, \text{pH})$ dependences were observed earlier for electroreduction of H atoms,[11] bromate anions,[2,12] radicals of 1,4-dioxane[3] and dihydroxyethyl radicals.[4] We believe that their shape is evidence for two parallel electron transfer pathways. The first one involves electron transfer to R_{ads} with the formation of an R^- carbanion (W_3 does not depend on $[BH^+]$). The second pathway involves electron transfer with a preceding chemical step, which is the formation of a metastable complex of the radical with a proton donor $[R_{ads}{\cdot}BH^+]$.[3,4] The general scheme of the process may be written as follows:

$$R_{ads} \xrightarrow{V'_e} R^- \xrightarrow{k_{pr}} RH \qquad (3)$$

$$R_{ads} + BH^+ \underset{k_2}{\overset{k_1}{\rightleftarrows}} R_{ads}H^+ \xrightarrow{V_e} \text{products} \qquad (4)$$

where V'_e and V_e are the rate constants of electron transfer to R_{ads} and to a metastable complex $[R_{ads}{\cdot}BH^+]$, and k_1, k_2 are rate constants of its formation and dissociation, respectively; k_{pr} is the rate constant of R^- protonation. The lifetime of the carbanions is very small[13] in aqueous solutions for simple organic radicals, which makes electron transfer irreversible. The W_3 value measured by the LPE method is described by the following expression in terms of this scheme (see, *e.g.*, refs. 2 and 4):

$$W_3 = \frac{k_1 V_e}{k_1 + k_2 + V_e} + V'_e;\ k_{pr} >> W_3;\ k_1 = k_0[BH^+] \qquad (5)$$

Let us consider the dependence of W_3 on E and pH and compare it with the experimental results.

(*a*) Strongly acidic solutions, not too negative potentials: $k_1 \geq k_2$; V_e, and $W_3 = V_e$. Apparently, this case cannot occur because the dark H_3O^+ discharge makes the measurements impossible at the required BH^+ concentrations.

(*b*) Moderately acidic solutions, the same E: $k_2 > k_1$; V_e; $W_3 = (k_1/k_2)V_e$. Quasi-reversible complex discharge. W_3 is proportional to $[BH^+]$ and depends on E as an exponent [section (*a*) of the $W_3(E, \text{pH})$ dependences at pH < 6.7, Figures 1, 2].

(*c*) Low-acidic and neutral solutions: $V_e > k_1, k_2$; $W_3 = k_1$. The limiting step is complex formation. $W_3 \propto [BH^+]$ but does not depend on E [section (*b*) of $W_3(E, \text{pH})$ dependences, Figures 1, 3). It follows from equation (5) that the potential of transfer E_{QC} from a 'quasi-reversible discharge' to that controlled by a chemical step is defined by $V_e \cong k_2$ and does not depend on pH; this is also observed experimentally (Figure 1).

(*d*) Neutral and basic solutions, more negative potentials. $V'_e > k_1$; $W_3 = V'_e$. The rate of electron transfer to R_{ads} is higher than that of complex discharge [section (*c*) of $W_3(E, \text{pH})$ dependences; it is observed in the electroreduction of radical **I** as well as in the electroreduction of radical **II** at pH > 10, Figure 1].

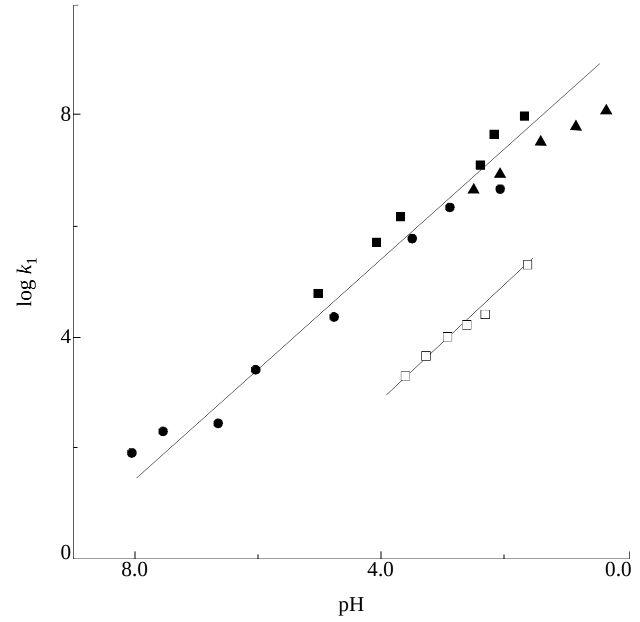

Figure 3 k_1, pH-dependences obtained in terms of kinetic scheme (3)–(4) for radical **II** (●), the radical of 1,4-dioxane[3] (□), H-atoms[11] (▲) and dihydroxyethyl radical[4] (■).

In this model, the particular method of electroreduction [*i.e.* (*b*), (*c*) or (*d*)] at the given E and pH is determined both by the difference in overvoltages of electroreduction of R_{ads} and $[R_{ads}{\cdot}BH^+]$ and the free energy $\Delta_f G^0$ of complex formation, where $\Delta_f G^0 \propto \log(k_1/k_2)$. For example, only the reduction of $[H_{ads}{\cdot}BH^+]$ is observed for H atoms, since their direct electroreduction to H^- is energetically unfavourable. And *vice versa*, reduction of radicals of group **I** occurs only through the first pathway, probably due to their relatively low capacity for complex formation. The value of k_0 may be a quantitative characteristic of such ability and is determined by the extrapolation of the k_1, pH-dependence (Figure 3) to pH = 0. This is close to the diffusion-controlled rate constant for the H atom,[11] for radical **II** and for the dihydroxyethyl radical[4] and equals $(6\text{–}8)\times10^9$ mol^{-1} s^{-1}, whereas k_0 for the 1,4-dioxane radical[3] is somewhat lower, $(1.5\text{–}2.0)\times10^7$ mol^{-1} s^{-1}. For radicals of group **I** $k_0 < (10^3\text{–}10^2)$ mol^{-1} s^{-1}. Assuming that k_2 constants for the complex decay are similar in both groups, this implies that for radicals of groups **I** and **II** the $\Delta_f G^0$ values differ by no less than 0.4–0.45 eV.[§]

The reason for such differences may lie in the structural features of the radicals. Probably, the free valence is blocked upon adsorption of radicals of group **I**, and formation of the $[R_{ads}{\cdot}BH^+]$ complex is hindered. However, if a radical is bifunctional, the reactivity is provided by the second active centre, *e.g.*, the remote functional group (radicals of group **II**). This may lead to differences in the products of reactions (3) and (4), as is the case in redox reactions of α- and β-radicals of aliphatic alcohols and ethers with ions of variable valences, see ref. 14 and references therein. Conjugated elimination of active groups with the formation of an olefin in such reactions is more characteristic of β-radicals.[14]

Thus, the model suggested is in accordance with the experimental results. This approach may be applied to the description of electroreduction of stable compounds, with the only difference that the respective intermediates are formed not only on the electrode surface but in the bulk of the solution.

[§] In this case the E_{QC} values define the respective positions of $W_3(E)$ dependences for reduction of complexes of BH^+ with various radicals.

This work was supported by the Russian Foundation for Basic Research (grant no. 97-03-32265).

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Received: Moscow, 29th December 1997
Cambridge, 11th February 1998; Com. 8/00174J