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Prospects for the determination of thermodynamic and kinetic parameters of electrode reaction intermediates by laser photoemission

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The method of voltammetric time-resolved waves (TRW) based on a comparative analysis of experimental and simulated curves of photoemissionally generated intermediates was used to determine the thermodynamic and kinetic properties of the R/R$^-$ redox pairs for the benzyl $\mathrm{PhCH}_2^{\cdot}$ and benzhydryl $\mathrm{Ph_2CH}^{\cdot}$ radicals.

Interest in the redox properties of intermediates including free radicals R in liquid media is stimulated by their ability to determine the direction and efficiency of electrode processes, *e.g.*, in organic electrochemistry.[1] The thermodynamic characteristics of redox pairs R/R$^-$ and R/R$^+$ can be determined from standard potentials E^0, *e.g.*, pK and BDE values.[2–4] The standard potentials of intermediates obtained by various methods are available.[2–11] However, the main drawbacks of many experimental methods consist in their insufficient versatility and the influence of side processes leading to the inconsistency of measured values with thermodynamic characteristics. Therefore, the experimental values should be corrected depending on the life times of intermediates and the rates of their electrode reactions. It is possible to determine the values of E^0 for R/R$^-$ redox pairs by traditional electrochemical methods such as voltammetry only in rare cases when the rate of the first electron transfer to an organic halide is much higher than that of the second.[12] The relative stability of intermediates is a necessary condition for the majority of methods for E^0 measurements[3,8,10] and a more powerful method of indirect reduction[9(a),(b)] requires the knowledge of the full reorganization energy of intermediate self-exchange.

Laser photoemission (LPE) can be used to overcome such difficulties; in particular, the method of voltammetric time-resolved waves (TRW) of photoemission-generated intermediates was proposed.[13] The values of E^0 were determined by this method for a number of organic and inorganic intermediates in aqueous and aprotic solvents.[4–7,11] An analysis[5(c),7] demonstrated a similarity between E^0 and the half-wave potentials $E_{1/2}$, measured under conditions of the TRW method, *i.e.*, intermediate generation in a thin near-electrode layer is followed by an equilibrium establishment at the electrode between adsorbed intermediates (radicals) $\mathrm{R_{ads}}$ and products X of their reduction/oxidation. However, for the development of a complete kinetic model for an electrode process, it is also necessary, along with E^0, to know the rate constants of redox reactions W^0 and the dependence of rate constants W_R of electrode reactions of intermediates on the potential $W_\mathrm{R} = f(E)$ within a sufficiently broad range and their activation energies E_a, as well as the times of bulk decay of an intermediate τ_R and a product of its reduction/oxidation τ_X in a given solvent. All these values can also be determined by TRW.

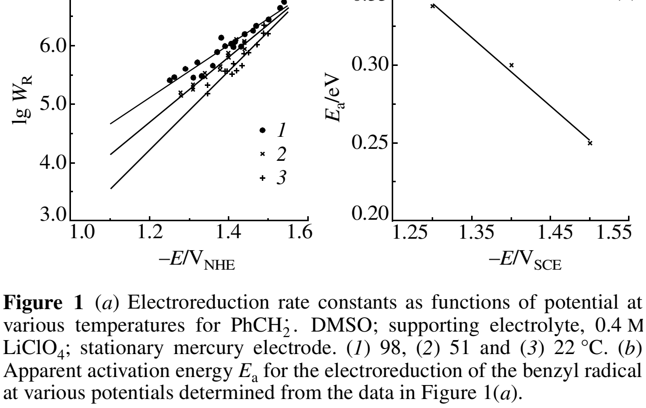

Figure 1 (*a*) Electroreduction rate constants as functions of potential at various temperatures for $\mathrm{PhCH}_2^{\cdot}$. DMSO; supporting electrolyte, 0.4 M $\mathrm{LiClO_4}$; stationary mercury electrode. (*1*) 98, (*2*) 51 and (*3*) 22 °C. (*b*) Apparent activation energy E_a for the electroreduction of the benzyl radical at various potentials determined from the data in Figure 1(*a*).

The long-lived benzyl $\mathrm{PhCH}_2^{\cdot}$ and benzhydryl $\mathrm{Ph_2CH}^{\cdot}$ key organic radicals[14] were chosen for the study. The redox potentials of their R/R$^-$ pairs were reliably determined by various methods,[2] and τ_R and τ_X parameters may substantially differ.[14]

The set of R transformations, generated by photoemission current I_P, can be represented by the following scheme:

$$\begin{tikzcd} {} & \mathrm{R} \arrow[l, "\tau_\mathrm{R}"'] \arrow[r, shift left, "\kappa_\mathrm{R}"] & \Gamma_\mathrm{R} \arrow[l, shift left, "W_\mathrm{d}"] \arrow[r, shift left, "W_\mathrm{R}"] & \Gamma_\mathrm{X} \arrow[l, shift left, "W_\mathrm{X}"] \arrow[r, shift left, "W'_\mathrm{d}"] & X \arrow[l, shift left, "\kappa_\mathrm{X}"] \arrow[r, "\tau_\mathrm{X}"] & {}, \\ I_\mathrm{P} \arrow[ur] \end{tikzcd} \qquad (1)$$

where κ_R, κ_X, W_d and W'_d are the rate constants of adsorption and desorption, respectively; W_R and W_X are the rate constants of electrode reactions, and Γ_R and Γ_X are the surface concentrations of adsorbed intermediates (radicals) $\mathrm{R_{ads}}$ and products X, respectively. A decrease in the surface concentration of stable reagents is compensated by their diffusion from the bulk of a solution during the diffusion-controlled discharge. However, R and X discharge occurs at their zero bulk concentrations and competes with desorption accompanied by the decay of intermediates.

The kinetic equations for surface and bulk concentrations of reagents n_R and products n_X take the form

$$\begin{aligned} \frac{d\Gamma_\mathrm{R}}{dt} &= \kappa_\mathrm{R} n_\mathrm{R}(0) - (W_\mathrm{R} + W_\mathrm{d})\Gamma_\mathrm{R} + W_\mathrm{X}\Gamma_\mathrm{X}; \\ \frac{d\Gamma_\mathrm{X}}{dt} &= \kappa_\mathrm{X} n_\mathrm{X}(0) + W_\mathrm{R}\Gamma_\mathrm{R} - (W_\mathrm{X} + W'_\mathrm{d})\Gamma_\mathrm{X}. \end{aligned} \qquad (2)$$

Bulk concentrations obey the diffusional equations

$$\begin{aligned} \frac{\partial n_\mathrm{R}}{dt} &= D_\mathrm{R}\frac{\partial^2 n_\mathrm{R}}{dx^2} - \frac{n_\mathrm{R}}{\tau_\mathrm{R}} + \frac{I_\mathrm{P}}{x_0}e^{-x/x_0}f(t); \\ \frac{\partial n_\mathrm{X}}{dt} &= D_\mathrm{X}\frac{\partial^2 n_\mathrm{X}}{dx^2} - \frac{n_\mathrm{X}}{\tau_\mathrm{X}}, \end{aligned} \qquad (3)$$

where D_R and D_X are the diffusion coefficients of reagents and products, respectively; $I_\mathrm{p}f(t)$ is the impulse of intermediate generation in the near-electrode layer with a characteristic length of x_0.[4] The boundary conditions determine the continuity of reagent and product streams on the interface (Scheme 1):[†]

$$\begin{aligned} D_\mathrm{R}\left(\frac{\partial n_\mathrm{R}}{dx}\right)_{x=0} &= \kappa_\mathrm{R} n_\mathrm{R}(0) - W_\mathrm{d}\Gamma_\mathrm{R}, \\ D_\mathrm{X}\left(\frac{\partial n_\mathrm{X}}{dx}\right)_{x=0} &= \kappa_\mathrm{X} n_\mathrm{X}(0) - W_\mathrm{d}\Gamma_\mathrm{X}. \end{aligned} \qquad (4)$$

The solution of nonstationary diffusional equations (2)–(4) were analysed[7] based on ref. 15. A number of parameters of Scheme 1 are estimable. The values of Γ_R and Γ_X are controlled in the photoemission measurements, and they are equal to 10^{10}–10^{11} particle per cm^2. Such an estimation as κ_R, κ_X ~ $D/l \approx$ $\approx 10^2$ cm s^{-1} is valid for the rate constants of adsorption if the

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[†] The absence of such boundary conditions led[5(c)] to a decrease of requirements to the time interval of measured TRWs, which are necessary for the unambiguous interpretation of experimental data, and caused a partial loss of information at their treatment.

Table 1 Thermodynamic and kinetic properties of benzyl and benzhydryl radicals in DMSO, DMF and acetonitrile.

$R^\cdot$	E_s ($E = E^0$)/eV	W^0/s^{-1}	$-\Delta G^0_{a(R)} \pm 0.02^a$/eV	$\tau_R \times 10^4$/s	$\tau_X \times 10^4$/s	$-E^0$ ($-E_{1/2}$)/V_{SCE}		
						DMSO	DMF	Acetonitrile
$PhCH_2^\cdot$	0.34±0.01^a 0.433,^{c} 0.733^g 0.925^e	(2–6)×10^3 ^{a} 4×10^6 ^{e}	0.45	0.05–0.15^a (11–15)±0.3^f 0.1–0.001^i	5–15^a 0.2^e ~0.0001^i	1.35±0.03^a (1.36)^b	(1.37)^b 1.40^c 1.215^e	(1.35)^b (1.45)^d ~1.42^e
$Ph_2CH^\cdot$	0.33±0.015^a 0.703^e	(1–3)×10^4 ^{a} 2.8×10^7 ^{e}	0.39	50–150^a (16–20)±0.2^f 0.1–0.001^i	500–1500^a 0.033^e	0.97±0.02^a (1.07)^b	(1.12)^b 1.07^c 1.107^e	(1.16)^b (1.14)^d (1.115),^{f} (1.130)^h

[a] This study, DMSO + 0.4 M $LiClO_4$. [b] Ref. 5(*a*), the illumination period $t_m = 2\times10^{-6}$ s; supporting electrolyte 0.1 M Et_4NClO_4. [c] Ref. 9, ±0.05 V, supporting electrolyte 0.1 M $TBABF_4$ (acetonitrile). [d] Ref. 3(*b*), ±0.05 V, supporting electrolyte 0.1 M Bu_4NClO_4, the illumination period $t_m = 2\times10^{-2}$ s. [e] Ref. 5(*b*), supporting electrolyte 0.1 M Et_4NClO_4 (DMF) and 0.1 M Bu_4NPF_6 (acetonitrile), the illumination period $t_m = 10^{-3} - 3\times10^{-6}$ s. [f] Ref. 8(*d*), ±0.05 V, supporting electrolyte acetonitrile + 0.1 M Bu_4NClO_4, the illumination period $t_m = 2\times10^{-2}$ s. [g] Ref. 9(*c*), quantum-chemical simulation. [h] Ref. 8(*d*), ±0.05 V, supporting electrolyte acetonitrile + 0.1 M Bu_4NClO_4, the illumination period $t_m = 10^{-2}$ s. [i] Ref. 8(*e*), supporting electrolyte 0.1 M Bu_4NClO_4 (acetonitrile). [a,b,c,e] Hg electrode. [e,f,h] Au electrode. [i] Glassy carbon or Hg-electrode.

diffusion coefficient D of intermediates is ~ 5×10^{-6} cm^2 s^{-1} and the diffusional jump l is $(2–3)\times10^{-8}$ cm. For κ_R and W_d, using the detailed equilibrium principle,[4] we can derive

$$\frac{\kappa_R}{W_d} = \frac{\Gamma_0}{N_0}\exp\left(-\frac{\Delta G^0_{a(R)}}{k_B T}\right). \qquad (5)$$

We can obtain from (5) that W_d is $10^2–10^4$ s^{-1} at standard values of the parameters ($\Gamma_0 = 10^{14}$ cm^{-2}, $N_0 = 6.4\times10^{20}$ cm^{-3}) and the typical standard adsorption free energy of organic radicals $-\Delta G^0_{a(R)} \approx -(0.3–0.4)$ eV.[4] $W'_d >> W_d$ since $-\Delta G^0_{a(R)}$ for radicals is sufficiently lower than the standard adsorption free energy of carbanions $-\Delta G^0_{a(R^-)}$. The value of $\Delta\Delta G^0_a$ was determined[7] for the redox pair $CF_3^\cdot/CF_3^-$ ($\Delta\Delta G^0_a = 0.3\pm0.06$ eV), and the difference in the standard free energies of adsorption of organic acids and their anions is equal to 0.1–0.15 eV, which may serve as its lower estimation [$\Delta\Delta G^0_a = -(\Delta G^0_{a(R)} - \Delta G^0_{a(R^-)})$] (see, *e.g.*, ref. 16 and references therein). The parameter τ_X is relatively controllable, and it can range from $10^0–10^{-7}$ s in aprotic solvents[7,8] to $10^{-8}–10^{-10}$ s in aqueous solutions.[4]

The previously developed procedure[13] was improved to obtain TRWs. TRWs were recorded by the measurements and numerical Fourier transformation of signals from a photoelectrochemical cell illuminated with modulated light with a period of $t_m = 1.0–10^{-3}$ s. Converting from the repetition frequency to frequency Ω was achieved using the relation $\Omega = 5.31t_m^{-1}$. A program package was elaborated to expand an effective Ω range, and that allows the recording of TRWs within the range $\Omega \sim (4–5)\times10^4$ s^{-1}. This enables us to determine $E_{1/2}$ on the highest harmonics of modulation frequency, up to 10th. The values of $W_R = f(E,T)$ were determined for irreversible electroreduction ($E < E^0$) from the kinetics of the electrode charge during electrode reactions of R_{ads}. The experimental procedure was described elsewhere.[4,17] The transition from $W_R(E)$ to $E_{1/2}(\Omega)$ dependences is based on the coincidence of $E_{1/2}$ and the potential, where $W_R = \Omega$ for a given Ω at the irreversible electroreduction of R_{ads} with an accuracy of 0.01 V. The precision of $E_{1/2}$ determination is no worse than ±0.005 V.[5(b)]

The radicals R were generated by the dissociative electron transfer[17]

$$RX + e_s^- \xrightarrow{k_a} RX^{\cdot-} \xrightarrow{k_d} R^\cdot + X^-, \qquad (6)$$

where e_s^- is a solvated electron, RX is $PhCH_2Cl$ or Ph_2CHCl, k_a is the rate constant of its capture by an acceptor, and k_d is the dissociation rate constant of an anion radical. The values of k_a for $PhCH_2Cl$ and Ph_2CHCl are $(1.6–4.5)\times10^9$ and 9.5×10^8 dm^3 mol^{-1} s^{-1}, respectively,[18] *i.e.*, they exceed the rate constant of e_s^- capture by a solvent by more than an order of magnitude. This provides an increase in the signal by a factor of 3–4 in comparison with the background signal on the addition of 0.08–0.2 M of acceptors.

The experiments were carried out in DMSO because it is much more stable than DMF and, especially, acetonitrile[19] with respect to the action of strong bases such as carbanions. The life times of benzyl and benzhydryl carbanions are considered to change oppositely to pK_a values of respective CH acids, consisted of 35 and 32.2 in DMSO;[19] 51.2 and 43.1 in acetonitrile,[3(b)] while τ_X is usually ≤ 10^{-3} s[19(b)] in this solvent.

The $W_R(E,T)$ functions are presented in Figure 1(*a*) for the irreversible reduction of the benzyl radical at $E < E_{1/2}$.[‡] They follow the equation of slow discharge with the transfer coefficient $\alpha \sim 0.45$ at $t = 22$ °C, as well as other organic radicals ($\alpha \sim 0.5\pm0.05$).[4] Similar functions were also obtained for the benzhydryl radical. Apparent activation energies E_a for various E values were found from these data to estimate the reorganization energy E_s of outer-sphere electron transfer by quadratic Marcus equation[1] ($E_s = 4E_a$ at $E = E^0$). The values of E_s are 0.32–0.35 eV in DMSO, which is close to the published data[6] for a number of alkyl radicals (E_s is 0.34–0.38 eV).

The TRWs of benzyl and benzhydryl radicals obtained on a mercury electrode in DMSO–$LiClO_4$ solutions are similar to those described previously[4,5(a),(b),6,7]. No serious differences were found in the wave forms and their location on the E-axis at transition to DMF and acetonitrile, the use of LiCl as a supporting electrolyte or the replacement of a Hg electrode with Au. The experimental and simulated $E_{1/2}(\Omega)$ functions for the radicals are represented in Figure 2(a),(b). They are plotted in the lg Ω–$E_{1/2}$ coordinates. Figure 2 demonstrates a satisfactory coincidence of experimental data and numerical simulation in each case, even in spite of complex character of the dependence and significant range of Ω change. Hence it follows that the necessary interval of Ω change has to override all transition region from reversible to irreversible reduction, *i.e.*, not to be less than 5–7 orders (Ω is $1–10^7$ s^{-1}) to obtain reliable results. It is possible to measure $W_R(E)$ and E_a in this case, to determine τ_R, τ_X and $-\Delta G^0_{a(R)}$ and to estimate the standard potentials of redox pairs R/R$^-$ on the basis of these data with the precision better than ±0.04 V (Table 1).

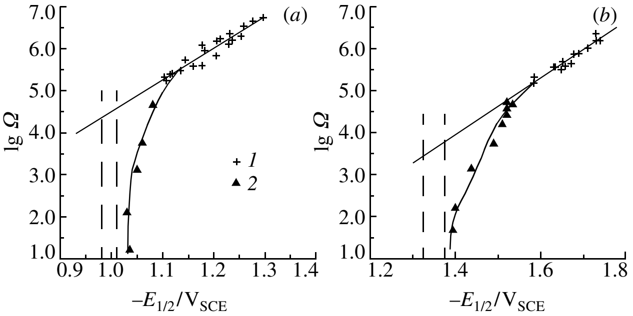

Figure 2 The comparison of the experimental $E_{1/2}$–Ω relation with the numerical simulation. DMSO; supporting electrolyte, 0.4 M $LiClO_4$; stationary mercury electrode; 22 °C. (*1*) The data of kinetic measurements; (*2*) TRWs. The areas of E^0 dispersion are depicted by vertical dotted lines: the deviation of E^0 to anodic direction from the most positive $E_{1/2}(\Omega)$ values is systematic in nature and may consist of 0.025–0.075 V for systems with such parameters.[7] (*a*) The radical $Ph_2CH^\cdot$. The parameters of calculation: $W_d = 10^4$ s^{-1}; $W'_d = 10^7$ s^{-1}; $\tau_R = 10^{-4}$ s and $\tau_X = 1$ s. (*b*) The radical $PhCH_2^\cdot$. The parameters of numerical simulation: $W_d = 10^4$ s^{-1}; $W'_d = 10^8$ s^{-1}; $\tau_R = 10^{-5}$ s and $\tau_X = 10^{-3}$ s.

[‡] Note that the maximum of the measured W_R values was *ca.* 5×10^6 s^{-1} and, consequently, $k_d \geq 10^7$ s^{-1} for both ion radicals, and similar values may be considered as typical for such systems.[20] For instance, k_d value for the anion radical $ClC_6H_4Me^{\cdot-}$ was estimated to be[20(b)] 7.6×10^9 s^{-1}.

The results of measurements and the simulated parameters of Scheme 1 were tabulated together with published data. It follows from Table 1 that the available thermodynamic and kinetic characteristics of the radicals are consistent with those determined in this work. Hence, the proposed method of the time-resolved voltammetric waves can be promising not only for their determination but it provides necessary thermodynamic and kinetic information on a studied intermediate over a broad range of temperatures and observation times.

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