Effect of proton donors on the mechanism of electroreduction of α-radicals of linear and cyclic ethers

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Using laser photoemission, we found two routes of the electroreduction of α-radicals (R_{ads}) adsorbed on a mercury electrode for linear and cyclic ethers in the presence of strong proton donors (BH^+), *i.e.*, by direct one-electron transfer and with the antecedent formation of the metastable complex [R_{ads}·BH^+].

According to laser photoemission data, the irreversible electroreduction[1–4] and electrooxidation[4,5] of radicals adsorbed on an electrode surface (R_{ads}) proceeds *via* two parallel pathways, namely, by the direct one-electron transfer

$$R^+ \longleftarrow e^- - R_{ads} + e^- \xrightarrow{V'_e} R^- \qquad (1)$$

and by the electron transfer on the antecedently formed metastable complex[6] of R_{ads} with a proton donor/acceptor ([R_{ads}·BH^+]/[R_{ads}·BOH^-])

$$R_{ads} + BH^+ \text{ (or } BOH^-) \underset{k_2}{\overset{k_1 = k_0[BH^+] \text{ (or } [BOH^-])}{\rightleftarrows}}$$

$$[R_{ads}\cdot BH^+] \text{ (or } [R_{ads}\cdot BOH^-]) + e^- \xrightarrow{V_e} \text{products} \qquad (2)$$

The second pathway is predominant for radicals containing active functional groups, *e.g.*, carbonyl,[1,2] carboxyl[7(*a*)] and hydroxyl[5] groups, or bifunctional radicals[4,6] ($k_0 = 10^7$–10^{10} dm^3 mol^{-1} s^{-1}; the second group of radicals[6]). Such complexes were not found for hydrocarbon radicals or their halogen derivatives[1] ($k_0 <$ $< 10^3$ dm^3 mol^{-1} s^{-1}; the first group).

To understand the nature of such differences, it seems important to investigate radicals which possess less active functional groups. For example, the reactivity of C–O bonds in ethers is much lower than that of C–O and O–H bonds in aliphatic alcohols.[8] Since the electronic structures and spectrophotochemical characteristics of these two classes of α-radicals are similar,[9] it is likely that their electrochemical behaviour is also similar. Electrode reactions of α-radicals[1,5,10,11] and β-radicals[6,7(*a*),(*b*)] of alcohols were studied in detail by photoemission and other techniques based on non-electrochemical generation of intermediates. There is few data on the electrochemistry of ether α-radicals. Although we found earlier using laser photoemission[3] that the 1,4-dioxane radical belongs to the second group ($k_0 =$ $= 10^7$ dm^3 mol^{-1} s^{-1}), this sole example is probably not typical because 1,4-dioxane is a diether and therefore the radical may be more active than in other ethers, as was observed, *e.g.*, in diols[4] with relation to corresponding aliphatic alcohols.[1,5] Therefore, we decided on more typical radicals of linear and cyclic ethers, namely, radicals of diethyl ether **1**, 1,4-dioxane **2**, tetrahydrofuran (THF) **3**, 2,5-dimethyltetrahydrofuran **4** and tetrahydropyran (THP) **5** (Table 1). Only radicals **1**–**3** were studied previously by the polarography of pulse-radiolysis products[11] and by photomodulated voltammetry.[12]

Radicals were generated according to the following reactions:

$$N_2O\ (H^+) + e^-_{aq} \xrightarrow{k_a} N_2 + OH^- + OH^{\cdot}\ (H^{\cdot}) \qquad (3)$$

$$OH^{\cdot}\ (H^{\cdot}) + RH \xrightarrow[(k_H)]{k_{OH}} R^{\cdot} + H_2O\ (H_2), \qquad (4)$$

where e^-_{aq} is hydrated electron; RH is an aliphatic ether; k_a and k_{OH} (k_H) are the rate constants of reactions (3) and (4), respectively. The generation of radicals **1**–**5** only by reaction (4) is provided by considerable differences in the rate constants k_a for the e^-_{aq} capture by N_2O, H_3O^+ and ether molecules (6×10^9, 2.3×10^{10} and < 10^7 dm^3 mol^{-1} s^{-1}, respectively[13]) (Table 1). The N_2O molecules are main scavengers of e^-_{aq} at pH ≥ 3, and the H_3O^+ cations are main scavengers of e^-_{aq} in more acidic solutions. The measurements at pH no higher than ~2 are difficult to perform because of the appearance of the anodic–cathodic wave of $H^{\cdot}$ near –0.6 V (SCE)[1] and the dark discharge of H_3O^+ on mercury, leading to a deterioration in the signal-to-noise ratio.

The radicals formed in reactions (3) and (4) diffuse to an electrode, become adsorbed on it and participate in electrode

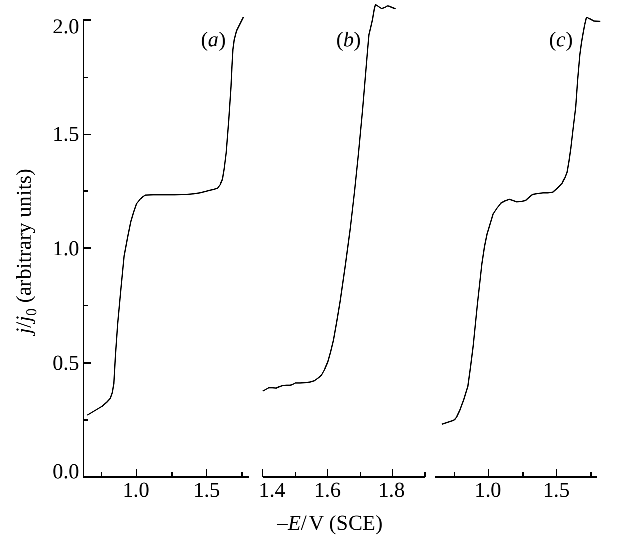

Figure 1 Typical TRWs of radicals at UV illumination of the electrode at various modulation periods: (*a*) radical **5**, t_m = 30 ms; (*b*) radical **4**, t_m = = 300 ms; (*c*) radical **3**, t_m = 30 ms. Stationary mercury electrode. Supporting electrolytes: aqueous buffer solutions with the addition of 0.5 M KCl saturated with N_2O; pH ≥ 5.

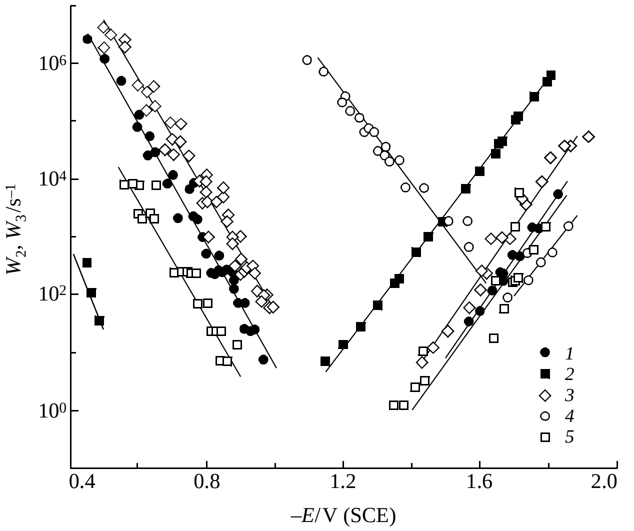

Figure 2 Tafel plots for the rate constants of reduction and oxidation (*1*)–(*5*) of radicals **1**–**5**, respectively. The data for the reduction of radical **2** at pH ≥ 7.0 were taken from ref. 3. The experimental conditions are the same as in Figure 1.

Table 1 Electrochemical properties of linear and cyclic ether radicals and the constants of capture[13] of H atoms and OH radicals by the ether molecules.

α-Radical	k_{OH} (k_H)/dm^3 mol^{-1} s^{-1}	α (β), ±0.05	$(dE/dpH)_{W_3}$ $(dE/d[NH_4^+])_{W_3}$	$-E \pm 0.05$/V at $W_3 = 10^3$ s^{-1}	$-E \pm 0.05$/V at $W_2 = 10^3$
Ethoxyethyl **1**	$(2.9–4.2)\times10^9$ (4.3×10^7)	0.59 (0.61)	0.12 (0.132)	1.74	0.79
1,4-Dioxanyl **2**	$(2.5–3.1)\times10^9$ (10^7)	0.47[a] (0.53)	0.13[a]	1.45	0.38[b]
Tetrahydrofuran-2-yl **3**	4×10^9 $[(3.3–7.2)\times10^7]$	0.55 (0.58)	0.13 (0.114)	1.68	0.87
2,5-Dimethyltetrahydrofuran-2-yl **4**		0.46 (0.63)	0.11 (0.13)	1.83	1.52
Tetrahydropyran-2-yl **5**		0.54 (0.66)	—[c] (0.142)	1.76	0.66

[a] Data from ref. 3. [b] The value was obtained by extrapolation of the Tafel plot to $W_2 = 10^3$ s^{-1}. [c] The reduction wave of radical **5** is overlapped by the dark discharge of H_3O^+ at pH < 3.5.

reactions to generate photocurrent *j*. The values of *j* were obtained by the measurements and numerical Fourier transformation of signals from a photoelectrochemical cell illuminated with modulated light at the period $t_m = 1.0–0.001$ s. This results in the voltammetric time-resolved wave (TRW) of a radical. The position of the half-wave $E_{1/2}$ on the *E* axis depends on t_m and the type of R and is controlled by the competition between the characteristic time of irreversible reduction/oxidation of R_{ads} with the rate constants W_3/W_2 and the electrode illumination time. At $E = E_{1/2}$, $W = kt_m$, where $k = 5.31$ or 10.88 for $W = W_3$ or W_2, respectively. Thus, the measurements of W_3 values can be performed in the range $5–5.8\times10^3$ s^{-1}. In the range $3\times10^3–6\times10^6$ s^{-1}, the values of W_3 were determined from measurements of the kinetics of emitted charge $Q = f(t)$.[†] Typical TRWs for the oxidation and reduction of the radicals are presented in Figure 1. The experimental details were described elsewhere.[1–7]

It is well known that $H^\cdot$ and $OH^\cdot$ radicals are reactive and hence non-selective agents. Therefore, in addition to α-radicals, the formation of β-radicals or, moreover, γ-radicals in the case of THP, by reaction (4) cannot be excluded *a priori* (such possibilities were repeatedly discussed in the literature). However, the TRWs of radicals **1**–**5** demonstrated the electroreduction or electrooxidation of only one type of intermediates. Consequently, under the experimental conditions, the fraction of β- and γ-radicals does not exceed 5%, similarly to the EtOH–N_2O system.[1,5]

Figure 2 shows the Tafel functions lg $W_{2,3}(E)$ for radicals **1**–**5** at pH varied from weakly acidic to strongly basic values. It can be seen that all of the functions are similar and have similar slopes (Table 1); *W* is independent of pH in the specified range. This fact is indicative of the similarity of mechanisms of electrode processes. Direct electron transfer *via* reaction (1) is predominant, *i.e.*, the reduction of R_{ads} to carbanions (analogously to the radicals of alcohols, hydrocarbons and their halogen derivatives[1,5,10]) and the oxidation to carbocations (as in the cases of methyl, ethyl[1] and carboxyalkyl radicals[7(*a*)]).

The lg $W_3(E)$ functions plotted for radicals **1**–**5** are shifted to more positive *E* values on the addition of NH_4^+ ions and at pH ≤ pH*, where pH* is a threshold value which is characteristic of each of the radicals, *e.g.*, pH* ~ 3.3 for radical **3** (Figure 3). The $(dE/dpH)_{W_3}$ and $\{dE/d(-lg[NH_4^+])\}_{W_3}$ values obtained by cross-section of the Tafel plots at W_3 = const (Table 1) are close to the corresponding values of $(2.3RT/F)/\alpha$. This fact characterises the electroreduction as a first-order reaction with respect to [BH$^+$]. Thus, with increasing [BH$^+$], a transition to the quasi-reversible reduction of the complex $[R_{ads}\cdot BH^+]$ occurred in all of the radicals. Simultaneously the observed rate constant was a linear or exponential function of [BH$^+$] or *E*, respectively. In contrast to radical **2**, the slopes of the Tafel plots for radicals **1** and **3**–**5** remained unchanged even at minimum [BH$^+$]. Thus, the transition to the discharge, which is limited by the rate of complex formation, occurs at observed constants higher than W_m, *i.e.*, at $k_1 \geq W_m \approx 10^7$ s^{-1} (Figure 3). Consequently, the value of k_0 lies between $10^7–10^{10}$ and $10^9–10^{10}$ dm^3 mol^{-1} s^{-1} for the complexes with NH_4^+ and H_3O^+ ions, respectively. In terms of the model[6] it is possible to determine the difference of overvoltages $\Delta\eta$ for radicals **1**–**5** and their complexes[‡] with BH$^+$. For BH$^+$ = H_3O^+, this difference decreased as the Tafel plot was shifted towards the cathodic region from ~1.0 (radical **2**) to ~0.45 V (radical **1**); for BH$^+$ = NH_4^+, $\Delta\eta$ is ~0.2–0.3 V, and the above correlation does not occur. Previously,[14–17] a much lower efficiency of NH_4^+ ions as proton donors, as compared with H_3O^+, was found in the bulk protonation of NO_3^{2-} and $CO_2^{\cdot-}$ and in the electroreduction of stable anions.

An analysis of the experimental results (Table 1) and a comparison with published data demonstrate that the position of Tafel plots for radicals **1**–**5** on the *E* axis correlates with the redox potentials of pairs[§] $E^0_{(R/R^+)}$, *e.g.*, $E^0_2 >> E^0_1$, E^0_3 (ref. 12), as well as with the rates of anodic methoxylation of ethers in the presence of solid polymer electrolytes[19] and, generally, with the structure and reactivity of the corresponding molecules. For example, the insertion of an additional CH_2 group into a cyclic ether molecule facilitates the electrooxidation, and the replacement of this group by an electronegative O atom leads to considerable inhibition of the process.[18] The Tafel plot of the electroreduction is analogously shifted by *ca.* 0.40 V on the replacement of an O atom in radical **2** with a CH_2 group (radical **5**). As in the case of the parent cyclic ether molecules,[18] the reduction rate of the radicals substantially increased (Figure 2) after the insertion of additional electronegative substituents (O atoms), and it was somewhat inhibited due to appearance of additional electropositive (CH_2 or Me) groups (Table 1). This effect is most pronounced for structurally similar radicals, *e.g.*, the shifts of

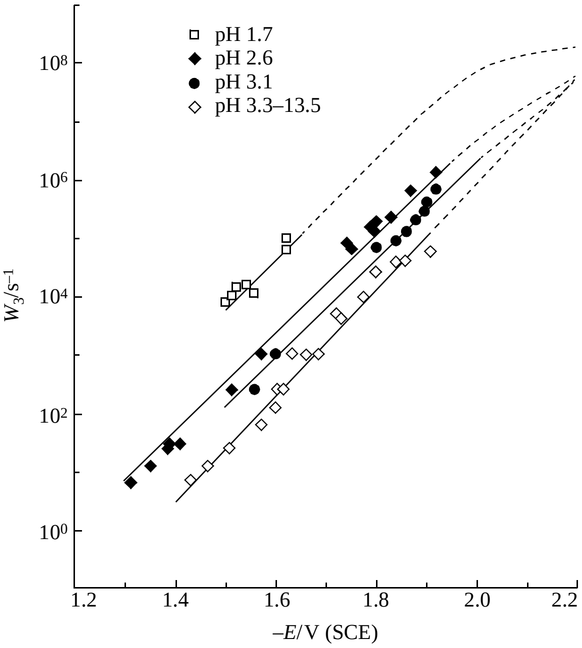

Figure 3 Typical relationship between W_3 and H_3O^+ concentration. Radical **4**; the experimental conditions are the same as in Figure 1. Dashed lines show the calculations of $W_3(E, \text{pH})$ in terms of the model.[6]

[†] With the use of laser photoemission, radicals were generated at distances of ~(10–100) Å from the electrode; this allowed us to measure *W* up to the maximum values $W_m \approx 10^7$ s^{-1}.

[‡] The maximum values of k_0 and k_2 are diffusion-controlled constants of ~10^{10} dm^3 mol^{-1} s^{-1} and the reciprocal of the lifetime ~10^{12} s^{-1} for a collisional complex. The following averaged *k* values were chosen for the calculation: $k_0 = 7\times10^9$ dm^3 mol^{-1} s^{-1} and $k_2 = 10^{11}$ s^{-1}.

[§] The correspondence between the differences in the redox potentials of intermediates and the Tafel plots for their electroreduction was postulated previously.[1]

the Tafel plots are ~0.25±0.03 V for radicals **2** and **5** and ~0.15±0.03 V for radicals **3** and **4**.

Thus, the α-radicals of linear and cyclic ethers can form complexes with proton donors at the rate constants of 10^7–10^{10} s^{-1}, which depend on the nature of BH^+ only slightly. In contrast, the reduction overvoltages for the $[R_{ads}\cdot H_3O^+]$ and $[R_{ads}\cdot NH_4^+]$ complexes are substantially different. The electrochemical properties of adsorbed α-radicals of ethers and alcohols, *i.e.*, the mechanisms and rates of electrode processes, were found to be similar. In both cases, the electrode reactions are described by the model,[6] *i.e.*, electron transfer proceeds by the two parallel pathways: directly to R_{ads} or to the antecedently formed metastable complex of R_{ads} with a proton donor or acceptor. The rate of electron transfer to the adsorbed radicals correlates with the structure and reactivity of the parent ether molecules.

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