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# Bond cleavage in hydroxyl derivatives initiated by electron transfer: electroreduction of 9*H*,9′*H*-bifluorene-9,9′-diol

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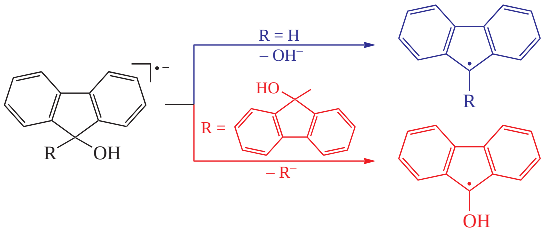
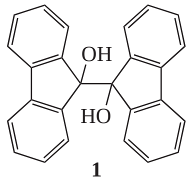
**Cyclic voltammetry, digital simulation and quantum chemical methods were applied to study the electroreduction mechanism of vicinal hydroxyl derivatives using 9*H*,9′*H*-bifluorene-9,9′-diol as an example. Unlike the case of fluoren-9-ol, dissociation of the $C^9$–$C^{9'}$ bond rather than the $C^9$–OH one occurs in radical anion of the substrate, similarly to that in radical cations formed upon oxidation of vicinal hydroxyl derivatives.**



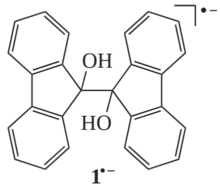
Bond cleavage reactions initiated by electron transfer occur in many chemical[1–7] and biochemical[8–13] processes, which promotes numerous experimental and theoretical studies.[14–16] In particular, dissociation of radical cations formed upon one-electron oxidation of hydroxyl derivatives have been studied rather thoroughly. Oxidation of 1- and 2-aryl substituted alkanols is accompanied by rapid C–C bond cleavage. In the case of aromatic pinacones, the reactions result in the corresponding diaryl ketones.[17–23] Dissociation of a C–C bond initiated by electron transfer was explained as follows:[21,24] its elongation at the radical cation stage is accompanied by a change in the type of the singly occupied molecular orbital (MO) from π to σ*, similarly to the dissociation of the carbon–halogen bond in the radical anions (RAs) of aromatic halo derivatives.[14–16]

Since the antibonding molecular orbital contains an electron, destabilization of C–C bonds should also be observed in RAs formed upon reduction of aryl substituted alkanols. However, the results of the scarce studies[25–29] on the reduction of methanol derivatives containing unsaturated and aromatic substituents in aprotic solvents indicate that not a C–C but a C–OH bond undergoes dissociation in their RAs. Cleavage of a C–OH bond immediately following the electron transfer was assumed[26] even in the case of 9*H*,9′*H*-bifluorene-9,9′-diol **1**, though its electroreduction resulted in fluoren-9-ol **2** and fluoren-9-one **3**. Therefore, we undertook a quantum-chemical study[†] of the reactions of RA $\mathbf{1}^{\bullet-}$ and used cyclic voltammetry (CV)[‡] to study the mechanism of **1** electroreduction.

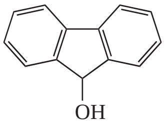
According to the calculations for the potential energy surface (PES), $\mathbf{1}^{\bullet-}$ can exist as a kinetically independent particle, as indicated by the presence of the corresponding minimum on the PES. Comparison between structures of **1** and $\mathbf{1}^{\bullet-}$ shows that formation of the latter [reaction (1)] requires considerable structural



**1**



$\mathbf{1}^{\bullet-}$



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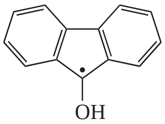
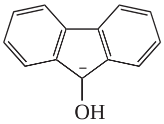
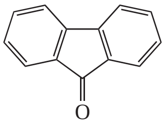


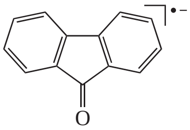
$\mathbf{2}^{\bullet}$



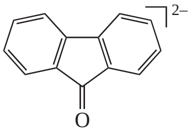
$\mathbf{2}^{-}$



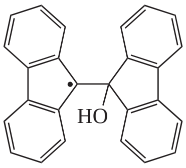
**3**



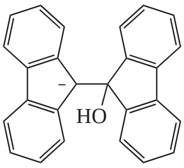
$\mathbf{3}^{\bullet-}$



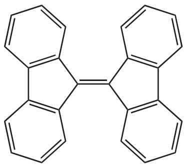
$\mathbf{3}^{2-}$



$\mathbf{4}^{\bullet}$



$\mathbf{4}^{-}$


**5**

$$\mathbf{1} + e^- \longrightarrow \mathbf{1}^{\bullet-} \tag{1}$$

$$\mathbf{1}^{\bullet-} \longrightarrow \mathbf{2}^{\bullet} + \mathbf{2}^{-} \tag{2}$$

$$\mathbf{2}^{\bullet} + \mathbf{2}^{-} \longrightarrow \mathbf{3}^{\bullet-} + \mathbf{2} \tag{3}$$

$$\mathbf{3}^{\bullet-} + e^- \longrightarrow \mathbf{3}^{2-} \tag{4}$$

$$\mathbf{2}^{\bullet} + e^- \longrightarrow \mathbf{2}^{-} \tag{5}$$

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[†] The quantum-chemical calculations of aromatic molecules were carried out in the density functional theory (DFT) framework, using the B3LYP exchange correlation functional and the 6-311++G(d,p) basis set. The effect of solvation was taken into account within the continual theory of reactive field PCM and CSC-PCM using the parameters for DMSO that are close to those for DMF used in the experiment. All quantum-chemical calculations were carried out using the Gaussian-03 and GAUSSIAN-09 software packages.

[‡] The CV study was carried out using an IPC-Pro-MF computer controlled potentiostat (Econics). Polarization curves were recorded using

$$\mathbf{2}^- + \mathbf{2}^- \rightarrow \mathbf{3}^{2-} + \mathbf{2} \tag{6}$$

$$\mathbf{1} + \mathbf{3}^{2-} \rightarrow \mathbf{1}^{\bullet-} + \mathbf{3}^{\bullet-} \tag{7}$$

$$\mathbf{1}^{\bullet-} \rightarrow \mathbf{4}^{\bullet} + \mathrm{OH}^- \tag{8}$$

$$\mathbf{4}^{\bullet} + \mathrm{e}^- \rightarrow \mathbf{4}^- \tag{9}$$

$$\mathbf{4}^- \rightarrow \mathbf{5} + \mathrm{OH}^- \tag{10}$$

changes, in particular, the C–O bond length increases by 0.02 Å and the $C^9$–$C^{9'}$ bond length increases by 0.06 Å, which indicates their destabilization. Analysis of the structure of the singly occupied MO of $\mathbf{1}^{\bullet-}$ allows one to conclude that the higher destabilization of the $C^9$–$C^{9'}$ bond in comparison with the C–O bond is due to the existence of a nodal plane passing through it. Hence, dissociation of this bond in $\mathbf{1}^{\bullet-}$ should give fluoren-9-yl radical $\mathbf{2}^{\bullet}$ and anion $\mathbf{2}^-$ [reaction (2)]. In fact, according to the calculations, this reaction is thermodynamically beneficial and its Gibbs free energy amounts to $\Delta G_2$ = –32 kcal $\mathrm{mol}^{-1}$.

As we have shown previously,[31] dissociation of the C–C bond in the RAs of hydroxyl derivatives can be accompanied by proton transfer between its primary products to give an RA of the carbonyl compound. In the case of **1**, this reaction is also thermodynamically favourable ($\Delta G_3$ = –27 kcal $\mathrm{mol}^{-1}$) and should afford fluoren-9-one RA ($\mathbf{3}^{\bullet-}$) and flouren-9-ol **2** [reaction (3)]. Since the electron affinity of $\mathbf{3}^{\bullet-}$ (2.2 eV) is higher than that of **1** (2.1 eV), at potentials of electron transfer to **1** it should undergo reduction to fluoren-9-one dianion (DA), $\mathbf{3}^{2-}$. Thus, it can be assumed that the electroreduction of **1** involves stages (1)–(4). Furthermore, taking into account that the electron affinity of radical $\mathbf{2}^{\bullet}$ formed by reaction (2) (3.4 eV) is also higher than the electron affinity of **1**, it should be expected that radicals $\mathbf{2}^{\bullet}$ undergo reduction to give the corresponding anions [reaction (5)]. These anions $\mathbf{2}^-$ undergo *trans*-protolysis to afford compound **2** and dianion $\mathbf{3}^{2-}$ [reaction (6)]. Therefore, in addition to reactions (1)–(4), electroreduction of **1** should also be accompanied by reactions (5) and (6). In turn, the resulting DA $\mathbf{3}^{2-}$ can enter a redox reaction with **1** [reaction (7)]. Though the equilibrium of this reaction is shifted to the left ($\Delta G_7$ = 2 kcal $\mathrm{mol}^{-1}$), but due to the fact that its product $\mathbf{1}^{\bullet-}$ undergoes irreversible dissociation [reaction (2)], it should also be taken into consideration. Thus, it could be expected that the electroreduction of **1** should be described by stages (1)–(7).

Notwithstanding the above, the calculation results cannot totally rule out the possibility of elimination of a hydroxide anion from $\mathbf{1}^{\bullet-}$ [reaction (8)] observed[29] in the case of **2**, since this reaction is also exothermal and the value of $\Delta G_8$ = –24 kcal $\mathrm{mol}^{-1}$ even somewhat exceeds the corresponding value (–19 kcal $\mathrm{mol}^{-1}$) for the rapid C–OH bond cleavage in $\mathbf{2}^{\bullet-}$ (*cf.* ref. 29). By analogy with the reduction of vicinal halo[32–34] and nitro derivatives,[35] it can be expected that the radical formed by reaction (8) should be reduced to an anion [reaction (9)] and that this anion should eliminate a hydroxide anion to give 9,9′-bifluorene **5** [reaction (10)].

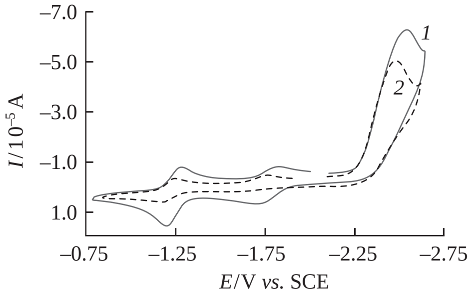

**Figure 1** CV curves of 5 mM solutions of (*1*) **1** and (*2*) **2** on a glass carbon electrode at a potential scan rate of 0.1 V $\mathrm{s}^{-1}$. Supporting electrolyte: 0.1 M solution of $\mathrm{Bu_4NClO_4}$ in DMF.

The CV curve of **1** (Figure 1) contains a chemically irreversible cathodic peak. The potential of this peak is close to that of the similar peak of **2**, but its current is noticeably higher. The anodic branch of the CV curves (*1*) and (*2*) contains oxidation peaks that are related[29] to the oxidation of DA $\mathbf{3}^{2-}$ formed due to protolytic reactions of anionic products of **2** reduction. On the other hand, no peaks whose potentials might correspond to the oxidation of the RA and DA of 9,9′-bifluorene[36] are observed. The latter fact allows one to exclude reactions (8)–(10) from consideration. Thus, based on the results of quantum-chemical calculations and CV data, it may be assumed that the electroreduction mechanism involves reactions (1)–(7) and stages of fluoren-9-ol reduction, as reported previously.[29] In fact, according to Figure 2, the theoretical[§] CV curves obtained for this mechanism are in good agreement with the experimental curves. The ratio between the experimental cathodic current peak of **1** and the corresponding theoretical value in the range of potential scan rates ($v$) from 0.025 to 10 V $\mathrm{s}^{-1}$ is 0.99 ± 0.06. A good match is also observed between the experimental and theoretical plots of the peak current *vs.* the concentration ($C$) of **1** (Figure 3) in the range from $2.5\times10^{-4}$ to $2\times10^{-4}$ mol $\mathrm{dm}^{-3}$. Thus, the suggested mechanism allows one to adequately describe the process of **1** electroreduction in the entire range of potential scan rates and substrate concentrations.

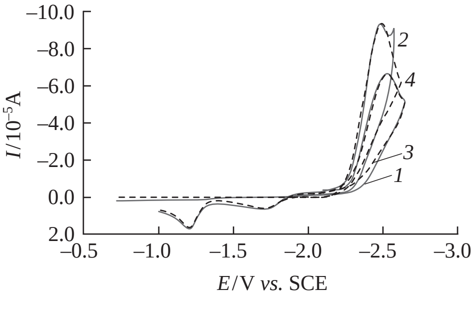

**Figure 2** CV curves of 5 mM solutions of (*1*) **1** and (*2*) **1** in the presence of 50 mM phenol on a glass carbon electrode at a potential scan rate of 0.1 V $\mathrm{s}^{-1}$. Sapporting electrolyte: 0.1 M solution of $\mathrm{Bu_4NClO_4}$ in DMF; theoretical curves for **1** electroreduction mechanisms (*3*) in the absence and (*4*) in the presence of proton donors.

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the three-electrode scheme. A glass-carbon working electrode with a diameter of 1.7 mm was used (active area 2.30 $\mathrm{mm}^2$). A platinum wire spiral and a saturated calomel electrode (SCE) served as the auxiliary electrode and the reference electrode, respectively. The latter was connected with the solution *via* a bridge with a porous ceramic diaphragm filled with the supporting electrolyte (0.1 M solution of $\mathrm{Bu_4NClO_4}$ in DMF). The uncompensated resistance amounted to 830 ± 10 Ω. The solutions being studied were kept in a thermostat at 25 ± 0.5 °C. The solutions were deaerated by passing high purity argon before recording each CV curve. Argon was passed above the solution surface to prevent its contact with air during the experiment. The working electrode surface was polished after each test and the solution was intensely purged with argon. DMF of ‘extra dry’ grade and tetrabutylammonium perchlorate from Acros Organics were used. Diol **1** was obtained as reported.[30]

[§] Digital simulation of CV curves was performed using DigiElch Professional software, v. 4.0 (build 3.008), from ElchSoft. The diffusion coefficients for **1** and its RA estimated using the Stokes–Einstein equation amounted to $5\times10^{-6}$ $\mathrm{cm^2\,s^{-1}}$, assuming that their sizes were two times larger than that of **2** for which this parameter was determined previously.[29] The transfer coefficient ($\alpha$) was assumed to be 0.5. Reactions (2) and (3) were considered as fast and irreversible. The standard potentials ($E^0$), rate constants ($k$) and equilibrium constants ($K$) were determined using the reported procedure.[29] The best match of simulation data with experimental results was achieved using the following values for reactions (1) and (7): $E_1^0$ = –2.45 V, $k_{s1}$ = 0.01 cm $\mathrm{s}^{-1}$, $K_7 = 4\times10^{-9}$, $k_7$ = 12 $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$, as well as the parameters previously found[29] for the other reactions.

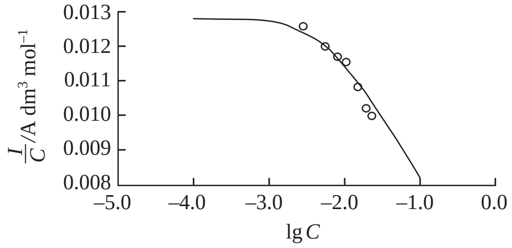
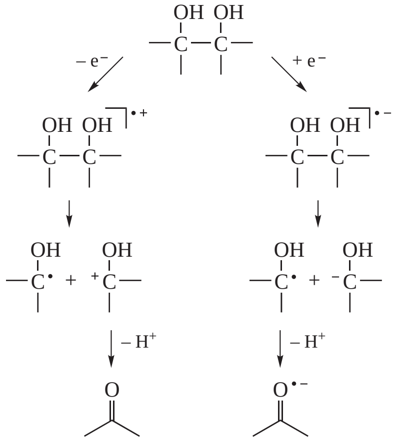


**Figure 3** Cathodic peak current on a glass carbon electrode at a potential scan rate of 0.1 V s$^{-1}$ *vs.* concentration of **1**. Supporting electrolyte: 0.1 M $Bu_4NClO_4$ solution in DMF. Experimental (circles) and theoretical (line) dependences are shown.

The correctness of the suggested mechanism is also supported by the fact that the presence of proton donors (phenol) in the solution increases the cathodic peak current of **1** (Figure 2) to a level corresponding to the reduction by a mechanism involving the protonation of anions **2**$^-$ formed both in the electroreduction of **1** [see reactions (2) and (5)] and in the electroreduction of **2**.[29] As expected, no anodic peaks related to the oxidation of dianion of **2** are observed on the voltammograms of **1** under these conditions.

The results obtained show that the formation of carbonyl compounds both in the oxidation and reduction of vicinal diols is due to the dissociation of the C–C bond initiated by electron transfer, followed by proton elimination from the dissociation product (Scheme 1). In the case of reduction, proton transfer between primary dissociation products can occur.



**Scheme 1**

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