Acid−Base Equilibrium between Phenoxyl−Nitronyl Nitroxide Biradical and Closed-Shell Cation. A Magnetic pH Sensor

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Spin-crossover, which means the switching between two species or phases with different magnetic properties, have been focused much attention, especially in developing a novel functionality for magnetic materials.[1] In relation to the recent advances in the studies on organic ferromagnets,[2] molecule-based spin-crossovers may be also an attractive target in organic chemistry, but a few related phenomena such as the photo-isomerization of a carbene[3a] and the spin isomerism of a non-Kekulé molecule[3b] are known only under matrix-isolated conditions.

An alternative model for spin-crossover molecules may be given for a cross-conjugated unsymmetrical biradical with donor−acceptor characters ($D^\bullet - A^\bullet$); if the singlet zwitterionic state ($D^+ - A^-$) is energetically close to the triplet biradical state,[4] a large difference between them in dipole moments or acid−base properties may bring about a novel reversed relative stability by their intermolecular interaction. Typically, when the zwitterionic state may be stabilized in acidic media by forming $D^+ - AH$ species, the spin-state may be controlled by changing pH of solutions.

Recently, we could prepare a cross-conjugated phenoxyl−nitronyl nitroxide biradical, 2-(3′,5′-di-*tert*-butylphenyl-4′-oxy)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide, **2**, by the PbO₂ oxidation of the corresponding phenol-substituted radical **1**.[5] In contrast to the triplet biradical structure of **2** as confirmed by ESR spectroscopy,[6] the one-electron oxidation of **1** in acetonitrile led to the generation of the corresponding closed-shell cation (**3**), which was silent on ESR. We report here an acid−base pair of **2** and **3** with different spin multiplicities, both of which satisfies the requirement of kinetic stability in solutions (Scheme 1), representing a novel pH sensor responding by the change of magnetic property.

As reported before,[5] the PbO₂ oxidation of a phenol-substituted nitronyl nitroxide radical ($D^\bullet - AH$, **1**) led to the formation of diradical **2** almost quantitatively, which was stable in solution and could be isolated as a powder. The redox properties of **1** and **2** were investigated by cyclic voltammetry in acetonitrile containing 0.1 M *n*-Bu₄NBF₄ as a supporting electrolyte. The voltammogram of **1** showed a reversible couple at +0.71 V vs SCE (Figure 1a). While the oxidation of **2** occurred at +1.00 V vs SCE, the reduction of **2** showed a reversible peak at −0.05 V vs SCE (Figure 1e). Thus, all of the intermediates generated by the redox reactions of **1** and **2**, such as closed-shell cation ($D^+ - AH$, **3**), cation radical ($D^+ -$

Scheme 1
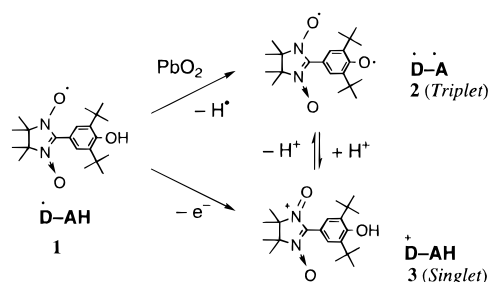
$A^\bullet$, **4**), and anion radical ($D^\bullet - A^-$, **5**), were shown to persist during the voltammetric analyses.

The absorption spectrum of **1** in acetonitrile showed maximum absorption bands at 283, 322, 365, and 615 nm,[5] and those of **2** were observed at 318, 359, and 604 nm (solid line in Figure 2B). On the other hand, the chemical one-electron oxidation of **1** with Cu(ClO₄)₂ (E_{red} = +1.0 V vs SCE)[7a] or NO⁺BF₄⁻ (E_{red} = +1.3 V vs SCE)[7b] in acetonitrile resulted in almost complete conversion of **1** but the formation of **2** was not identified by absorption spectrum. Instead, an alternative product was formed which showed the maximum absorption at 334 nm (solid line in Figure 2A). A similar absorption spectrum could be obtained by the controlled potential electrolysis (+0.9 V vs SCE, ~1 *F*/mol) of **1** in acetonitrile containing 0.1 M *n*-Bu₄NBF₄. According to the cyclic voltammogram of **1**, the product at λ_{max} = 334 nm was assigned as the closed-shell cation **3** generated by the removal of unpaired electron from the nitronyl nitroxide, which does not deprotonate the phenol proton under the neutral conditions.

The interconversion between **2** and **3** was successfully observed by the addition of acid or base. Spectral changes upon the addition of pyridine to the solution of **3** prepared from **1** and Cu(ClO₄)₂ are shown as dashed lines in Figure 2A. The clear isosbestic points observed at 322, 355, and 362 nm indicate the quantitative nature of the transformation (**3** → **2**). The absorption spectrum of **2** was also obtained by the electrolysis of **1** followed by the deprotonation of **3** with pyridine. The reverse transformation, i.e., the protonation of biradical **2** by acids leading to the formation of cation **3**, could be followed by the changes in absorption spectra upon the addition of trifluoroacetic acid to the solution of **2** (dashed lines in Figure 2B), indicating the equilibrated acid−base pair (**2** and **3**) with different spin multiplicities.

The interconversions were also observable by cyclic voltammetry in acetonitrile solutions. When 10.0 mM pyridine was added to the solution of **1**, the oxidation peak at +0.7 V became irreversible and the formation of **2** was identified by the appearance of its redox peak at +1.0 V (Figure 1d). The formation of **2** decreased with decreasing basicity of pyridines on the order of pyridine (pK_a^B = 12.3)[8a] > 3-chloropyridine (pK_a^B = 9.0,[8b] Figure 1c) > 4-cyanopyridine (pK_a^B = 7.0,[8c] Figure 1b). The voltammogram of **2** (Figure 1e) was also affected by the presence of acids. When 10.0 mM acetic acid (pK_a = 22.3, Figure 2f) was added,[9] the oxidation peak of **2** at +1.0 V remained but the reversible cathodic couple at −0.05 V vs SCE became irreversible, indicating that acetic acid is not stronger acid than **3** but can protonate the anion radical **5** to yield **1**. With a stronger acid such as trifluoroacetic acid (pK_a

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(6) The hyperfine coupling constant in toluene is $a_N \approx$ 3.7 G (2N) at room temperature and the zero-field splitting parameters at 77 K are |*D*/*hc*| = 0.107 cm⁻¹ and |*E/hc*| ≈ 0.5 See Supporting Information for the ESR spectra.

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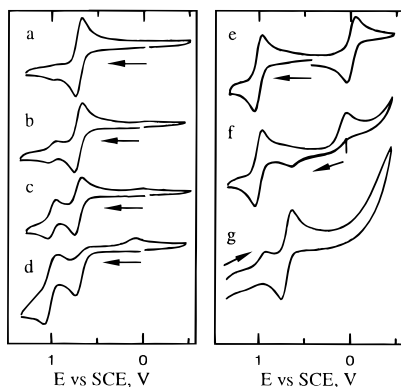
Figure 1. Cyclic voltammograms of 1.0 mM **1** in the absence (a) and presence of 10.0 mM (b) 4-cyanopyridine, (c) 3-chloropyridine, or (d) pyridine, and those of 1.0 mM **2** in the absence (e) and presence of 10.0 mM (f) acetic acid or (g) trifluoroacetic acid in acetonitrile containing 0.1 M *n*-Bu$_4$NBF$_4$ at sweep rate = 1 V/s.
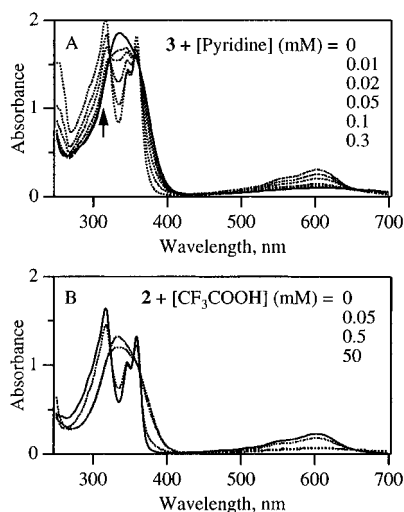
Figure 2. Absorption spectra of ca. 0.05 mM of (A) **3** and (B) **2** in acetonitrile. Dashed lines show the spectral changes upon the addition of (A) pyridine and (B) trifluoroacetic acid.

$\approx$ 13,[10] Figure 1g), in accordance with the spectroscopic observation, the formation of cation **3** was proved by the appearance of the reduction peak at +0.7 V vs SCE.

The equilibrium constants (K) for **3** with various substituted pyridines were determined from spectral changes upon the addition of pyridines to the 0.05 mM **3**·BF$_4$$^-$ solution[11] at 0 °C,[12] and the pK_a values for the equilibrium between **3** and **2** at 25 °C were obtained according to pK_a(**3**) = pK_a^{B}(pyridines) +

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(10) (a) The pK_a value of CF$_3$CO$_2$H in acetonitrile was estimated from the pK_a in dimethyl sulfoxide (3.45)[10b] and a typical difference in acidities (9.7 pK_a unit) of carboxylic acids in DMSO and in MeCN.[9] (b) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

(11) The oxidant-free solution of **3**·BF$_4$$^-$ was prepared by the oxidation of **1** with equimolar of NO + BF$_4$$^-$ followed by the removal of NO• by passing argon gas.

(12) The cation **3** decomposed slowly in acetonitrile at room temperature but was stable for over several hours at 0 °C.
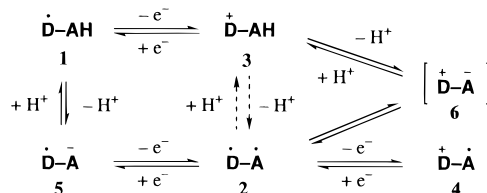

Table 1. Reaction of Cation **3** with Substituted Pyridines

substituent	pK_a^{B}(pyridines)^a	K^b	pK_a(**3**)^c
4-CN	8.0	$(9.8 \pm 0.2) \times 10^{-4}$	10.8
3-Cl	9.0	$(5.1 \pm 0.6) \times 10^{-2}$	10.2
3-F	9.4	$(9.8 \pm 0.6) \times 10^{-3}$	11.2
		average	10.7 ± 0.5

^{a} pK_a^{B} values of substituted pyridines in acetonitrile at 25 °C.[8]
^{b} Equilibrium constants for the reaction of **3** + Py $\rightleftarrows$ **2** + PyH$^+$ at 0 °C. ^{c} pK_a values of **3** at 25 °C.

Scheme 2

(273.15/298.15) log(K). As listed in Table 1, the resulting pK_a(**3**) of 10.7 ± 0.5 is in good agreement to the observed effects of acids or bases on cyclic voltammetry.

The unexpectedly high acidity of **3**, which is intermediate between those of common phenols (pK_a = 19−27)[13] and phenol radical cation (pK_a $\approx$ 1)[14] and is as high as that of picric acid (pK_a = 11),[13] may be explained by assuming that the actual conjugate base of **3** is a singlet zwitterion **6** (D$^+$−A$^-$) rather than **2**. As shown in Scheme 2, the transition (**6** → **2**) gains an additional stabilization energy due to the exothermic electron transfer from A$^-$ to D$^+$, where a large energy gap of ca. −1.0 eV ($\approx$−16.9 pK_a unit) is estimated from the Weller expression, $E_{1/2}$(**5/2**) − $E_{1/2}$(**2/4**) + $e_0^2/\epsilon a$.[15] The protonation of triplet **2** to singlet **3** may take place either via **6**, which may exist in equilibrium with **2**, or at the singlet−triplet surface crossing point.[16]

In summary, the acid−base pair (**2** and **3**) with different spin multiplicities can be prepared independently by the oxidation of the parent phenol **1**, and they are shown to be interconvertible in solution, which may provide a basis for novel magnetic switching devices or sensors for pH monitoring.

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(13) Kolthoff, I. M.; Chantooni, M. K., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 4621.

(14) (a) The acidity of phenol radical cation in MeCN was calculated from the difference between oxidation potentials of phenol and phenoxide (2.1 and 0.55 V vs Ag/AgI, respectively)[14b] and pK_a of phenol (27).[13] (b) Bordwell, F. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 1736.

(15) (a) Weller. A. *Z. Physik. Chem. NF* **1982**, *133*, 93. (b) The value of $e_0^2/\epsilon a$ = 0.06 eV is applied, which corresponds to the Coulombic energy of organic ion pair in acetonitrile at separation distance of 7 Å.

(16) (a) Berson, J. A. *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. I, p 346. (b) We are thankful to a reviewer for the consideration on this point.