Communications

Synthesis of a Vinylene-Bridged Ferrocene−Hydroquinone Complex and Its Unusual Structural Change Originated by Proton-Coupled Electron Transfer

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Quinonoid compounds are one of the most versatile redox active organic molecules.[1] The covalently and noncovalently linked donor−acceptor systems including these molecules are of particular interest with regard to the study of proton-coupled intramolecular electron transfer[2] and photoinduced charge separation.[3] The quinonoid compound linked to ferrocene complex by a π-conjugated spacer is a useful model which provides insight into proton-coupled intramolecular electron transfer, since the redox potentials of the two molecules are similar and the redox potential of the quinonoid compound can be readily controlled by the external perturbation, such as by protonation[1,2,4] and solvation.[5] The sensitivity to the external field leads to significant change in the optical, structural, and magnetic properties, accompanied by an intramolecular electron transfer. We here report the synthesis of a novel vinylene-bridged ferrocene−hydroquinone complex, 2-(2-ferrocenylvinyl)hydroquinone, **1**, the change into a novel allene and quinonoid structure by two-electron oxidation, and the proton response of the oxidized form including an intramolecular electron transfer.

Compound **1** was synthesized by Wittig coupling with ferrocenylmethyltriphenylphosphonium bromide and 2,5-ditosylbenzaldehyde,[6] followed by deprotection of the tosyl group. The drastic decrease of the UV−vis absorption band of **1** at 342 nm and the increase of the band at 312 nm were observed in intensity in methanol upon stepwise addition of $[\text{Fe}(\eta^5\text{-}C_5H_4Cl)_2]^+PF_6^-$, as a 1-electron oxidizing agent, under nitrogen. The spectral change was completed by the addition of 2 equiv of $[\text{Fe}(C_5H_4Cl)_2]^+PF_6^-$, indicating that **1** undergoes 2-electron oxidation (Figure 1a).

The oxidized compound, **3**, was isolated from the methanol solution and purified by preparative thin-layer chromatography. In the ^{1}H NMR spectrum of **3** in acetone-d_6, two doublets at δ 6.88 and 7.02 ppm derived from the vinylene protons of **1**
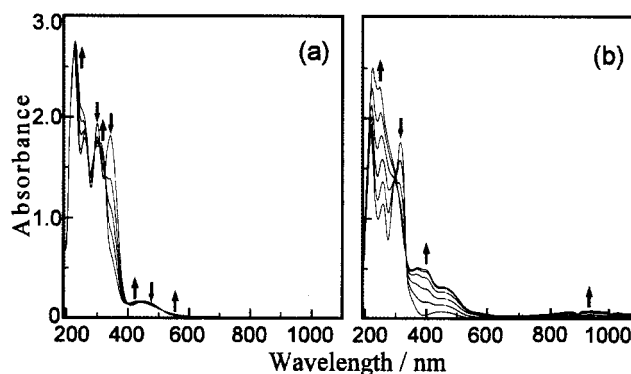

Figure 1. (a) UV−vis−near-IR absorption spectral change of **1** (1.2 mM) in methanol upon stepwise addition of 0−2.0 equiv of $[\text{Fe}(C_5H_4Cl)_2]^+PF_6^-$. Light path length is 1 mm. (b) UV−vis−near-IR absorption spectral change of **3** (1.2 mM) in acetonitrile upon stepwise addition of 0−100 equiv of CF_3SO_3H. Light path length is 1 mm.

disappeared and a new singlet appeared at 6.67 ppm (Figure 2S, Supporting Information). One of the two singlets at 7.60 and 7.81 ppm due to nonequivalent hydroxy protons of **1** was not detected in **3**, and the remaining singlet at 8.00 ppm immediately disappeared by H/D exchange upon addition of D_2O. The molecular ion peak of **3** (m/z 318) indicated the loss of two hydrogen atoms from **1** (m/z 320) in composition, on the basis of the FAB mass spectra. This indicates that significant structural change of one hydroxy group and the vinylene group of **1** occurred by 2-electron oxidation and 2-proton elimination to form **3**. A new ^{13}C NMR signal as a quaternary carbon appeared in lower field position at 131.6 ppm with disappearance of the signal due to one of the two vinylene carbons of **1** (Figure 3S, Supporting Information). The ferrocenyl structure was maintained without the oxidation-induced significant change into a fulvene-like structure,[7] according to the NMR signals. The IR spectrum of **3** exhibited weak bands around 1900 cm^{-1} ascribable to C−C stretching of an allene structure. On the basis of these spectra, **3** is assigned to 6-(ferrocenylvinylidene)-4-hydroxycyclohexa-2,4-dien-1-one with a novel structure including an allene and a carbonyl group, as shown in Scheme 1. Compound **3** is considered to be a structural isomer of both 2-(2-ferrocenylvinyl)-*p*-benzoquinone and 2-(ferrocenylethynyl)hydroquinone. It is of substantial interest that the oxidation of **1** favors the release of two

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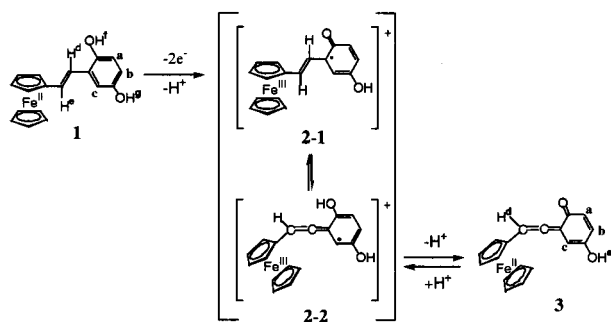
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Scheme 1

hydrogen atoms—one from the vinylene and one from the hydroxy group—to disintegrate the ordinarily stable aromatic structure of **1**.[8]

A proposed formation mechanism of **3** is shown in Scheme 1. The oxidation of **1** initially occurs at the ferrocenyl site to form a ferrocenium state of Fe(III), because the reversible redox wave due to the ferrocenyl site is observed at the potential $E^{0'} = 0.10$ V vs Ag/Ag$^+$ more positive than the potentials of irreversible oxidation waves due to the hydroquinone site ($E_{p,a} = 0.60$ and 1.00 V) in acetonitrile and the redox potential of the oxidizing agent [Fe(C$_5$H$_4$Cl)$_2$]$^+$PF$_6^-$ (0.44 V vs Ag/Ag$^+$) is located between the potentials of the ferrocenyl and the hydroquinone sites.[9] The strong electron-withdrawing effect of the ferrocenium moiety causes the immediate elimination of a proton. The proton elimination from the hydroquinone moiety and the vinylene moiety followed by further 1-electron oxidation resulted in formation of semiquinone radical intermediates, **2-1** and **2-2**, respectively. The structural change between **2-1** and **2-2** likely occurs through the proton exchange between the carbonyl oxygen and the allene carbon, which are located nearby. A further proton-elimination reaction from the vinylene carbon of **2-1** or from the hydroxy group of **2-2** affords the stable compound **3**, where the iron center is reduced. It is considered that the deprotonation of **2-1** is less likely than that of **2-2**, and that the structural change between **2-1** and **2-2** plays an important role in the formation mechanism of **3** including the allene and quinonoid structure.

An interesting proton response was indicated by the UV−vis−near-IR absorption spectral change of **3** in aprotic media, such as acetonitrile, upon stepwise addition of CF$_3$SO$_3$H (0−100 equiv), as shown in Figure 1b. The new intense bands appearing at 400 and 456 nm of which molar extinction coefficients, ϵ's, are estimated at 4.0×10^3 and 2.5×10^3 M^{-1}cm^{-1}, respectively, are appreciably similar to those of the free semiquinone radical,[1,10] and the weak shoulder band at 600 nm with $\epsilon = 350$ M^{-1} cm^{-1} can be attributed to the $^2E_{2g} \rightarrow {}^2E_{1u}$ transition of the ferrocenium ion.[11] The ESR spectrum of the frozen solution of the product at 6.4 K exhibited a well-resolved signal ($g_{\parallel} = 3.97$, $g_{\perp} = 1.64$) assignable to a ferrocenium cation including paramagnetic Fe-(III) nuclei (Figure 4S, Supporting Information).[12] The appearance of the ferrocenium state of Fe(III) from diamagnetic **3** results in

generation of an odd number of electrons, that is, generation of a semiquinone radical through an intramolecular electron transfer. The semiquinone radical could not be detected in the ESR spectrum, probably due to fluctuation of the electron spin states, that is supported by the significant broadening of the axial signal of the ferrocenium moiety. These facts indicate that the diamagnetic **3** can be converted to the paramagnetic semiquinone−ferrocenium compound **2-1** through the protonation to **3**. Note that a broad absorption band was observed at 1000 nm in the near-IR spectrum of **2-1**, which may be due to LMCT to the Fe-(III) center—i.e., photoinduced valence tautomerization[13] between the Fe(III) center and the semiquinone. It has been mentioned that radical complexes exhibit long-wavelength bands due to low-lying transitions originating from the singly occupied molecular orbitals (SOMO).[14]

Two protonation sites exist in **3** to form **2-1**. The protonation to the allene carbon leads to the direct formation of **2-1** via an intramolecular electron transfer from the ferrocenyl to the quinonoid site. The protonation to the carbonyl oxygen of the quinonoid site forms **2-2** and requires the structural change into **2-1** from the allene to the vinylene bonding. On addition of 100 equiv of CF$_3$SO$_3$H at once, a transient UV−vis absorption spectrum was observed and gradually changed to that of **2-1** (Figure 5S, Supporting Information). This implies a two-step transformation and supports the idea that the transient species is produced by the protonation to the carbonyl oxygen. Intriguingly, when **1** was oxidized by 2 equiv of [Fe(C$_5$H$_4$Cl)$_2$]$^+$PF$_6^-$ in acetonitrile as an aprotic solvent, the observed UV−vis−near-IR absorption spectrum at room temperature and the ESR spectrum at 6.9 K were quite similar to those of the protonated form of **3**. This suggests that the radical intermediate **2-1** is stabilized in the aprotic media. The addition of methanol into the acetonitrile solution of **2-1** caused the UV−vis−near-IR absorption spectral change into that of **3**. This means that protic solvent assists the proton elimination from **2-1**, and supports the consideration that the intermediate **2-1** should be included in the formation process of **3** from **1** in methanol.

In summary, we observed an unusual structural change of a vinylene-bridged ferrocene−hydroquinone compound, **1**, by 2-electron oxidation and 2-proton elimination in protic media. The oxidation product, **2**, which includes an allene and a quinonoid structure, exhibited a unique proton response, leading to exchange of the magnetic property.

Supporting Information Available: Synthetic procedures and characterization data for **1** and **3**; ^{1}H and ^{13}C NMR spectra of **1** and **3** (Figures 2S and 3S); an ESR spectrum of **3** treated with the acid (Figure 4S); and UV−vis−near-IR spectral change of **3** with the acid (Figure 5S). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Our preliminary calculation using semiempirical PM3 minimization indicated that **3** was thermodynamically less stable than 2-(2-ferrocenylvinyl)-*p*-benzoquinone and 2-(ferrocenylethynyl)hydroquinone by 18.3 and 10.5 kcal mol^{-1}, respectively.

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