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Direct Observation of Cation Radicals of a Diarylethene during Oxidative Ring-opening Reaction

Kenji Matsuda,*[1,2] Satoshi Yokojima,[3] Yoshihisa Moriyama,[1] Shinichiro Nakamura,[3] and Masahiro Irie*[1]
[1]*Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University,*
744 Motooka, Fukuoka 819-0395
[2]*PRESTO, JST*
[3]*Mitsubishi Chemical Group Science and Technology Research Center, Inc. and CREST, JST,*
1000 Kamoshida-cho, Yokohama 227-8502

(Received May 8, 2006; CL-060544; E-mail: kmatsuda@cstf.kyushu-u.ac.jp, irie@cstf.kyushu-u.ac.jp)

The ESR spectrum of a diarylethene was measured during electrochemical oxidative ring-opening reaction of the closed-ring isomer. The spectrum was simulated by UB3LYP/cc-pVTZ method to reveal that the spectrum contains the cation radicals of both the open- and closed-ring isomers. By comparing the calculated spectrum with the experimental one, the ratio between the cation radical of the open- and the closed-ring isomers was determined to be 4:1.

Diarylethene is a well-known class of photochromic compounds and regarded as one of the most promising materials for the optoelectronic application.[1] Apart from their excellent photochromic performance, the electrochemical behavior of diarylethene derivatives also attracts considerable attention. The electrochemical reactions are being used for molecular switching and can be potentially applied to molecular-scale electronic switches. Although the electrocyclic reaction of radical ions is a relatively classic issue,[2] revisiting this issue by using diarylethene is meaningful. The electrochemical cyclization of fulgides[3] and cycloreversion[4] and cyclization[5] reactions of diarylethenes have been reported. Very recently Feringa's group,[6] Coudret's group,[7] and our group[8] reported on detailed study of the oxidative electrocyclic reaction of diarylethenes. Although the characterization of the intermediate is very important to understand the reaction, direct observation of the reaction intermediates by ESR spectroscopy has not yet been accomplished.

Judging from the experimental results as well as theoretical calculation of several diarylethene derivatives, we have found that the diarylethene derivatives undergo oxidative cyclization reactions when the radical cations of the closed-ring isomers are more stable than the open-ring isomers and also that the diarylethenes undergo oxidative cycloreversion reactions when the radical cations of the open-ring isomers are more stable than the closed-ring isomers. **1a** is the representative example of the latter case and **2a** is the representative example of the former case (Figure 1).

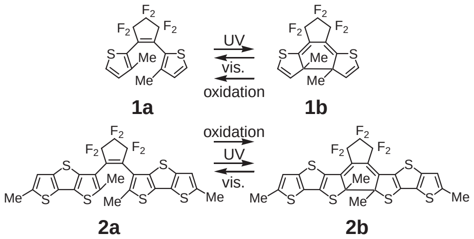

Figure 1. Electrochromic diarylethenes.

We have also reported that during the electrolysis of **1b**, a new band ($\lambda_{\max} = 667\,\text{nm}$) appeared and the new band was assigned as the cation radical of **1b**. This intermediate was also observed by γ-radiolysis of **1b** in 1-chlorobutane matrix. In this communication, direct observation of the reaction intermediates by ESR upon electrochemical oxidation will be reported. The quantum chemical calculation was carefully performed to reveal the nature of the intermediates.

The molecule studied is 1,2-bis(3-methyl-2-thienyl)perfluorocyclopentene **1a**.[9] After irradiation with UV light, the photogenerated closed-ring isomer **1b** was separated using HPLC in the dark. The X-band ESR spectrum under electrolysis of the isolated pure **1b** was measured in dichloromethane solution (Figure 2). The working and reference electrodes were Au and the counter electrode was Pt. The supporting electrolyte was tetrabutylammonium perchlorate. The electrolysis was performed at 1.1 V (vs Au reference electrode). At this potential, only the closed-ring isomer was oxidized. The observed spectrum was the 9-line hyperfine-coupled signal centered at $g = 2.0072$.

To determine whether the origin of this spectrum is the mono-cation radical intermediate in the oxidative ring-opening reaction, the high-level quantum chemical spectrum simulation was performed. The isotropic hyperfine coupling constants (hfcc) were calculated according to the calculated spin density on each atom. The geometry optimization and the calculation of the isotropic hfcc based on the optimized structures were performed by the unrestricted B3LYP hybrid density functional method[10] with the cc-pVTZ basis set[11] in Gaussian 03.[12] To avoid the analysis of the full potential energy surface, which is almost impossible for this size of molecule with the accuracy

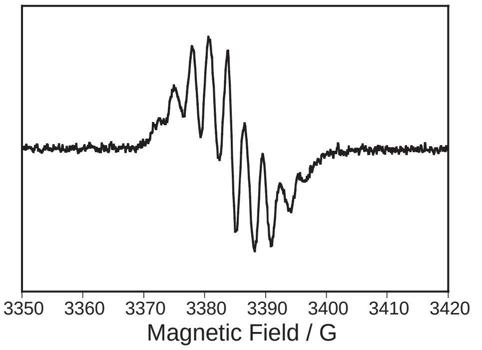

Figure 2. ESR spectrum of **1b** under electrolysis (+1.1 V vs Au reference electrode) measured in dichloromethane (1×10^{-3} M) at room temperature; microwave frequency and power: 9.53 GHz, 5 mW; modulation amplitude: 1 G.

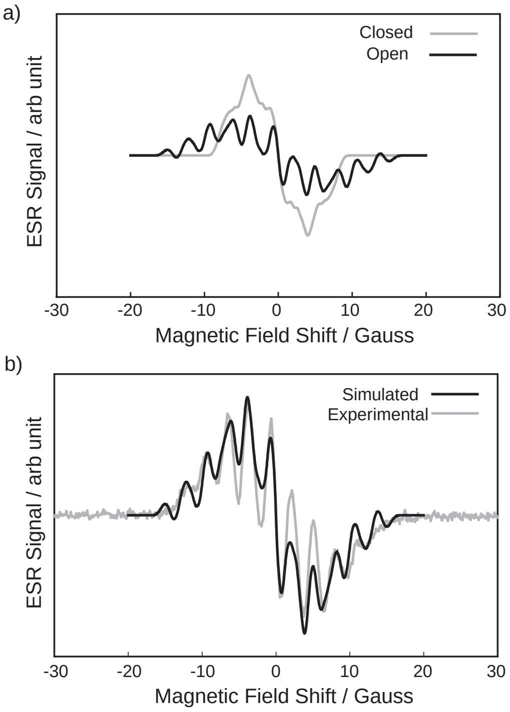

Figure 3. a) Simulated ESR spectra of $\mathbf{1a}^{+\bullet}$ (black line) and $\mathbf{1b}^{+\bullet}$ (gray line). b) Experimental (gray line) and simulated (black line) ESR spectra of **1b** under electrolysis. The simulated ratio between $\mathbf{1a}^{+\bullet}$ and $\mathbf{1b}^{+\bullet}$ was 4:1.

required for the ESR calculation, we used the C_2 symmetric structure to approximately take into account the averaging over the puckering motion of the diarylethene.

The ESR spectrum can be reproduced by the superposition of the two spectra, $\mathbf{1a}^{+\bullet}$ and $\mathbf{1b}^{+\bullet}$. The peak spacing of the calculated spectrum of $\mathbf{1b}^{+\bullet}$ is significantly smaller than the apparent experimental peak spacing. Additionally, the sum of the absolute values of the hfcc, which gives the total spectral width of the ESR spectrum, is 17.4 gauss, which is much smaller than the experimental value of 32 gauss. On the other hand, the sum of the absolute value of the hfcc of $\mathbf{1a}^{+\bullet}$ is 31.6 gauss, which is consistent with the experimental spectrum. The calculated spectrum of $\mathbf{1a}^{+\bullet}$, however, fails to reproduce the overall shape (Figure 3a). Even though the calculation of ESR spectra is very sensitive to the choice of basis sets and to a slight change of the structure,[13] the spectral features are unaffected as long as a large basis set is used. Therefore, it is required to postulate the superposition of $\mathbf{1a}^{+\bullet}$ and $\mathbf{1b}^{+\bullet}$ to explain the experimental ESR spectrum. By superimposing the two spectra, the experimental spectrum was reproduced. When the $\mathbf{1a}^{+\bullet}$:$\mathbf{1b}^{+\bullet}$ ratio is 4:1, the simulated spectrum agreed well with the observed spectrum (Figure 3b).

By assuming the steady-state approximation, the ratio of 4:1 between $\mathbf{1a}^{+\bullet}$ and $\mathbf{1b}^{+\bullet}$ means that the apparent first-order kinetic constant between $\mathbf{1b}^{+\bullet} \rightarrow \mathbf{1a}^{+\bullet}$ and $\mathbf{1a}^{+\bullet} \rightarrow \mathbf{1a}$ is 4:1. The possibility of the equilibrium between two states is excluded from the calculated energy gap (14.62 kcal/mol).[8] Although the conversion from $\mathbf{1b}^{+\bullet}$ to $\mathbf{1a}^{+\bullet}$ is a monomolecular reaction, the conversion from $\mathbf{1a}^{+\bullet}$ to **1a** is a bimolecular reaction which requires the collision with the electron donor. Therefore, the reaction from $\mathbf{1b}^{+\bullet}$ to $\mathbf{1a}^{+\bullet}$ was faster than the reaction from $\mathbf{1a}^{+\bullet}$ to **1a**. Because the energy gap between $\mathbf{1a}^{+\bullet}$ and **1a** is larger than the energy gap between $\mathbf{1b}^{+\bullet}$ and **1b**, **1b** can serve as an electron donor. The reduction of $\mathbf{1a}^{+\bullet}$ to **1a** can reoxidize **1b** to $\mathbf{1b}^{+\bullet}$, which indicates the possibility of the chain reaction.

The absorption spectra of the cation radicals $\mathbf{1a}^{+\bullet}$ and $\mathbf{1b}^{+\bullet}$ were calculated by SAC-CI/6-31G//UB3LYP/cc-pVTZ method for the optimized geometry with C_2 symmetry which was used to calculate the hfcc. SAC-CI calculation was performed at Level One.[14] For sulfur atoms, 6-31G(d) basis set was used. The calculated absorption maxima for $\mathbf{1a}^{+\bullet}$ is 752 and 855 nm and for $\mathbf{1b}^{+\bullet}$ was 662 nm. The observed absorption spectrum during electrochemical oxidation showed a peak at 667 nm and a tail up to 800 nm. This result also supports that both the cation radicals are involved in the reaction.

In conclusion, the ESR spectrum measurement under electrolysis and its quantum chemical simulation revealed that both cation radicals of the open- and the closed-ring isomer are involved in the reaction and that the conversion from the cation radical of the closed-ring isomer to the cation radical of the open-ring isomer is a rather fast reaction.

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