Notes

Bull. Korean Chem. Soc. **1994**, Vol. 15, No. 10 909

lar reaction field of the complex, the positive charge is centered on Ru. All the surrounding atoms can be treated as having the same negative charges and may manifest the equal electric field effects.

The term σ_c has been widely interpreted in terms of a solute-solvent collision complex.[16] The term collision complex is meant to imply a short-lived orientation of the solvent molecule(s) that has been brought about by dipole-induced dipole, dipole-quadrupole, or other weak chemical association, which can be related to the dipole moment. Figure 2 shows the plot for the dipole moment(μ) versus the chemical shift difference of the $6'_1$ bipyridyl proton for the *cis*-[Ru^{II}(bpy)$_2$(*p*-tert-butylpy)(OH$_2$)]$^{2+}$ complex against D$_2$O solvent(δ). Although there is a deviation for (CD$_3$)$_2$CO solvent, linear relationship has been observed. Linearity between molecular dipole moment and solvent shift of the methyl protons has been observed in some organometallic compounds of the type (CH$_3$)$_n$SnX$_{4-n}$ (X=Cl, Br, and I).[17]

In conclusion, we find that the change in the nature of the ligand L in the series of *cis*-[Ru^{II}(bpy)$_2$(*p*-tert-butylpy)(L)]$^{2+}$ complexes can be easily detected from the chemical shift data of $6'_1$ bipyridyl proton. Those results can be very useful to understand the reaction mechanism(s). The migration of the chemical shift of the $6'_1$ bipyridyl proton possibly suggests the existence of specific solute-solvent interaction. The formation of Ru^{II}-OH$_2$$^{2+}$ complex from the reaction of [Ru^{IV}(bpy)$_2$(*p*-tert-butylpy)(O)]$^{2+}$ complex with solvents like CHCl$_3$, CH$_2$Cl$_2$, or THF indicates that this reaction can be useful as an example of electrocatalytic application.[18] The principle involved is for the case where Ru^{IV}=O^{2+} is the active oxidant of a substrate S and the products of the redox reaction are the oxidized substrate S$_{ox}$ and Ru^{II}-OH$_2$$^{2+}$. In the electrocatalytic schemes, the catalyst redox couple is oxidatively regenerated at the electrode in a net electrocatalytic shuttle mechanism.[19] Catalytic application of these reactions is now in progress.

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Spectroelectrochemical Study of the Dimerization of Methylviologen Cation Radical in the Diffusion-limited Region

Chongmok Lee*, Chiwon Kim, Myung Sun Moon, and Joon Woo Park

Department of Chemistry, Ewha Womans University, Seoul 120-750, Korea

N,N'-disubstituted-4,4'-bipyridinium ions (vilogens) are very attractive materials for the purpose of electron-transfer reagent[1] in photochemical solar energy conversion,[2] herbicides,[3] and electrochromic display.[4] One of viologens that is encountered most frequently in literatures is N,N'-dimethyl-4-4'-bipyridinum dication (methylviologen, MV^{2+}) salt. Most of the reported applications has been focused on methylviologen cation radical (MV$^{\cdot+}$) which can be electrogenerated from the colorless MV^{2+} with equilibrium electrode potential of -0.69 V *vs* SCE.[15a] MV$^{\cdot+}$ is also known to dimerize in aqueous media as Eq. (1).[1,5-11]

$$2MV^{\cdot+} \rightleftharpoons (MV^{\cdot+})_2 \tag{1}$$
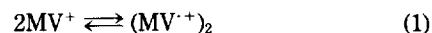
$$K_D = [(MV^{\cdot+})_2]/[MV^{\cdot+}]^2 \tag{2}$$

where K_D is the equilibrium constant for monomer-dimer equilibrium. The formation of dimers should affect further reactions where MV$^{\cdot+}$ participate. Quantitative studies for dimerization were performed by absorption spectroscopy using chemical reduction method.[6,7] There are several reports dealing with dimerization of viologens. Some reports[1,5-9] used 365 and 560 nm bands as those of dimer, which are
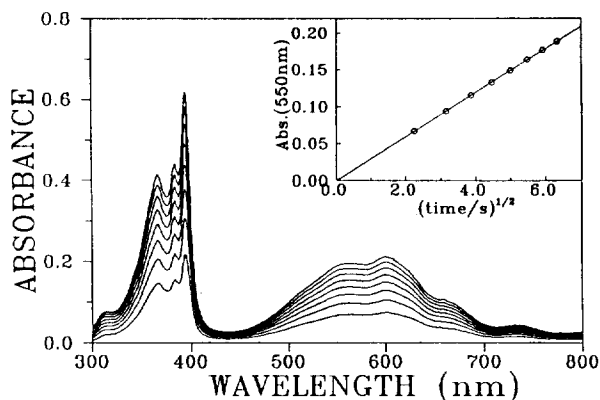
910   *Bull. Korean Chem. Soc.* **1994**, Vol. 15, No. 10

Notes

Figure 1. Absorption spectra of reduced MV^{2+} taken at potential of -0.8 V *vs* Ag/AgCl using an ITO glass electrode: electrolysis time, $0-40$ s (step: 5s, $t=0$ is base line); solution, 1.0 mM $MVCl_2$ and 0.1 M KCl in H_2O. Inset shows absorbances at 550 nm *vs* (electrolysis time/s)$^{1/2}$.
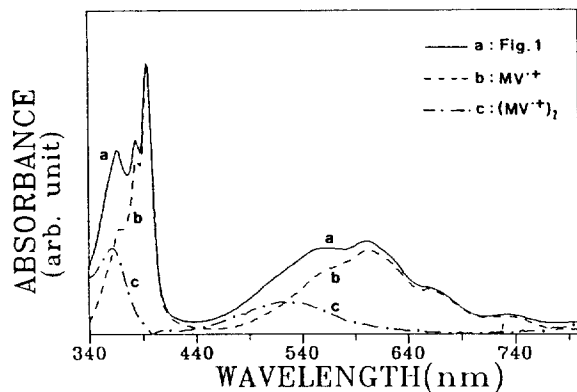

Figure 2. Resolved spectra of Figure 1 taken at $t=40$ s (curve a) into MV^{+} (curve b) and $(MV^{+})_2$ (curve c).

somewhat different from the spectra by others.[10,11]

This study concerns a method to estimate K_D of Eq. (2) from the absorption spectra of the reduced MV^{+} within the propagating diffusion layer using spectroelectrochemical technique. We extracted the absorption spectra of MV^{+} and $(MV^{+})_2$ from a mixture of a monomer-dimer spectrum involving semi-infinite linear diffusion of the electroactive species from the electrode surface.

Figure 1 shows change of absorption spectrum of the reduced viologen obtained in $MVCl_2$/KCl solution as a function of electrolysis time at -0.80 V *vs* Ag/AgCl (3 M NaCl). Indium tin oxide (ITO) coated glass (7×50 mm, Delta Technologies) placed inside the wall of an 1.0 cm (pathlength) absorption cell was used as a working electrode, where the conductive side faced to the solution. The movement of ITO electrode was minimized by inserting a glass spacer at the bottom of the cell. The counter electrode was a Pt wire which was rolled at one end of the glass spacer. The reference electrode was mounted on the top of viologen solution. A Hewlett Packard 8452A diode array spectrophotometer was used to obtain absorption spectra where the potential of the working electrode was controlled with an AFRDE5 bipotentiostat (Pine Instrument). Only the magnitude of absorbance
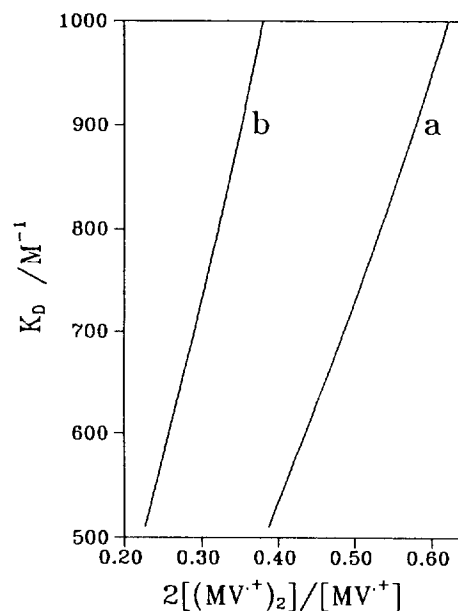

Figure 3. Calculated working curves for K_D *vs* $2[(MV^{+})_2]/[MV^{+}]$ for bulk $[MV^{2+}]=1.0$ (a) and 0.5 mM (b). Note that 2[dimer]/[monomer] corresponds to the absorbance ratio $(A_{dimer}/A_{monomer})$ of the resolved spectra at the isosbestic point, 550 nm.

increased linearly with a square root of electrolysis time without changing shape of spectrum. This indicates that the thickness of diffusion layer increases without change of [monomer]/[dimer] ratio of MV^{+}. From double potential step chronocoulometry experiment, we obtained 8.3×10^{-6} cm^2/s as a diffusion coefficient of MV^{2+} (lit.[5a] 6.56×10^{-6} cm^2/s and lit.[5b] 8.6×10^{-6} cm^2/s). Molar absorption coefficient of the reduced species at 550 nm, the reported isosbestic point of monomer-dimer equilibrium,[10,12] can be calculated from absorbance *vs* (time)$^{1/2}$ plot (inset of Figure 1) using the integrated Cottrell equation as Eq. (3)[13] with measured diffusion coefficient.

$$\text{Absobance}=2\varepsilon_R C_o^* D_o^{1/2} t^{1/2}/\pi^{1/2} \tag{3}$$

We obtained ε_R of 8800 M^{-1}cm^{-1} (at 550 nm), which is in reasonable agreement with the reported value, 8400 M^{-1}cm^{-1}, in Nafion film.[14]

Spectra shown in Figure 1 can be resolved into monomer and dimer components. Figure 2 shows absorption spectra of the MV^{+} and $(MV^{+})_2$ obtained by linear combination of monomer-dimer equilibrium spectra with different ratios of monomer-dimer, *i.e.*, different bulk concentration of MV^{2+}. Successive linear combinations have been carried out until the resolved spectrum of MV^{+} monomer is indistinguishable from the reported spectrum.[15,16] Dimer spectrum is obtained by substraction of monomer component from the original spectrum. Note that the resulting dimer spectrum is similar to spectra under favorable conditions for dimerization, *e.g.*, at low temperature,[10] with high concnetration of viologen,[11] or by the intrisically high hydrophobicity of viologen.[8]

The ratio of absorbances of dimer and monomer at 550 nm is total concentration ratio of the two species, $2[(MV^{+})_2]$ /$[MV^{+}]$, within diffusion-limited region. The growing diff-

Notes

Bull. Korean Chem. Soc. **1994**, Vol. 15, No. 10   911

sion layer was divided into 18 discrete sublayers for calculation. $2[(MV^{\cdot+})_2]/[MV^{\cdot+}]$ value at each sublayer (donoted as j) is related with K_D and total concentration of the reduced species within the sublayer $(C_{R,j})$ by Eqs. (2) and (4);

$$[MV^{\cdot+}]_j + 2[(MV^{\cdot+})_2]_j = C_{R,j} \qquad (4)$$

where j is independent of the overall thickness of propagating diffusion layer. We made working curves of K_D vs $\Sigma_j\{2[(MV^{\cdot+})_2]_j\}/\Sigma_j\{[MV^{\cdot+}]_j\}$ at bulk concentrations of MV^{2+} (Figure 3) using a step-function-like concentration profile[17] reflecting complementary error function for $C_{R,j}$s within the diffusing layer. The fractional concentrations of $C_{R,j}$ were digital-simulated ones using a method of finite differences.[18] K_D value was estimated from the simulated working curves by matching the integrated concentration ratio of $2[(MV^{\cdot+})_2]/[MV^{\cdot+}]$, $i.e.$, $\Sigma_j\{2[(MV^{\cdot+})_2]_j\}/\Sigma_j\{[MV^{\cdot+}]_j\}$ with experimental results as in Figure 2 (0.48 and 0.27 for 1.0 and 0.5 mM of MV^{2+}, respectively). The K_D value was 660 M^{-1} at 21 ℃ (lit[6] 380 M^{-1} and lit[7] 620 M^{-1}).

In conclusion, this work demonstrated that the chemical equilibrium constant of the electrogenerated species can be studied by long pathlength cell under the assumption of semi-infinite linear diffusion. In the course of this work the absorption spectrum of $(MV^{\cdot+})_2$ was confirmed. Some of the dimer spectra reported earlier[1,5-9] are, we believe, the monomer-dimer mixture spectra containing small amount of monomer.

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A New ^{13}C Coupling NMR Parameter for the Stereochemistry of Imine

Eun-Jeong Seo, Kye-Young Kim, and Sueg-Geun Lee*

*Chemical Analysis Div.,
Korea Research Institute of Chemical Technology
P.O. Box 107, Yoo Sung, Daejeon 305-606, Korea*

The information of ^{13}C-^{13}C coupling constants plays an important role in the structural determination of organic compounds.[1] Although its application has been very limited in the area of ^{13}C enriched compounds due to its low natural abundance, recent advances in high field NMR spurred the use of carbon-carbon coupling constants in samples with natural abundance.[2] One of the useful applications of ^{13}C-^{13}C coupling constant was reported by Krivdin and his co-workers about the stereochemistry of oximes in which the difference in coupling constants between anti- and syn-orientation carbon to the nitrogen lone pair electrons and oxime carbon were larger than 7 Hz.[3] In the case of oximes, nuclear Overhauser effect (NOE) can also be applied for the stereochemical analysis.[4] However, when it has non-protonated group in either side of the double bond, which could not be induced to use homonuclear NOE difference experiment, we are faced with new difficulty to solve the configuration of the compound. For N, N'-dicyanoquinone diimines,[5] Neidlein and his co-workers used very insensitive and cumbersome heteronuclear ^{13}C{^{1}H}-NOE difference spectroscopy measurements to elucidate the configuration since homonuclear NOE experiment was not an applicable method. At this stage, we can ask whether the probe of coupling constants for syn-and anti-configuration of oxime is applicable to the other nitrogen derivatives because the different substituents could alter the hybridization to change the coupling constants.[1]

In this note, we report the coupling constants between the imine carbon and substituent α-carbons as a representative of other nitrogen derivatives which have a large difference of electronegativity between substituents on nitrogen nucleus in comparison with oxime.

Imines were prepared by stirring or refluxing the corresponding ketones with amines in the presence of molecular sieves (5A) in benzene according to the literature procedures.[6,7] The products were purified by either vacuum distillation or recrystallization from ethanol prior to NMR experiments. The products were mixture of the syn-and anti-compound and the isomers were not separated. The ratios of syn-and anti-isomer ranged from 3 : 7 to 1 : 9 which were determined