CHEMISTRY LETTERS, pp. 2075-2078, 1994.

Photosensitized Two-electron Reduction of Viologen and the Reactivity of the Neutral Viologen

Joon Woo PARK,* Jung Ha KIM, Book Kee HWANG, and Kwanghee Koh PARK+
Department of Chemistry, Ewha Womans University, Seoul 120-750, Korea
+Department of Chemistry, Chungnam National University, Taejon, Korea

The initially formed viologen radical cation ($V^{\cdot +}$) is further reduced to yield neutral viologen (V^{o}) by $Ru(bpy)_3{}^{2+}$ sensitized photochemical reduction. By the reactions with water, 75-80% of V^{o} is reoxidized to $V^{\cdot +}$ and the remainder is destroyed. The decreasing order of the reactivity is V^{o} in the absence of β-cyclodextrin (β-CD) > V^{o} in the presence of β-CD > V^{o} covalently bound to β-CD.

Viologens (1,1'-dialkyl-4,4'-bipyridinium, V^{2+}) have received much attention as electron mediators in various types of photochemical and chemical applications.[1] Recently, utilization of viologens as electron mediators for reductive transformation of organic compounds has been reported.[2,3] The efficacy of viologens has been mostly related with the facile one-electron reduction of V^{2+} to cation radical $V^{\cdot +}$. However, the redox potential of $V^{2+}/V^{\cdot +}$, *ca.* -0.7 V (*vs* SCE),[4] limits their broad synthetic applicability. The two-electron reduction products of viologens, neutral viologens (V^{o}), are more potent reducing agents having reduction potential of *ca.* -1.0 V *vs* SCE,[4] which is comparable with that of coenzyme NADH.[5] V^{o} is generated by chemical,[1,6] electrochemical,[7] and radiolytically-induced[8] reductions of the corresponding V^{2+}. Also, it was reported that the induced disproportionation reaction of $V^{\cdot +}$, formed by photosensitized or chemical reductions of V^{2+}, yields V^{o} in water-organic two-phase system.[2] In this communication, we report the photosensitized two-electron reduction of V^{2+} to V^{o} in water or water-DMF media and the reactivity of V^{o} with water. Effects of added β-CD or covalent attachment of viologen to β-CD on the formation and reactivity of V^{o} are also described.

Irradiation of deaerated solutions of dimethyl viologen (MV^{2+}) or methyl viologen-appended β-CD (β-CD-MV^{2+})[9] in the presence of $Ru(bpy)_3{}^{2+}$ photosensitizer and EDTA or triethanolamine at pH 10 reduces the viologen dication.[2,11] The spectrum obtained at early stage of irradiation (spectrum A in Fig. 1) is that of one-electron reduction product $V^{\cdot +}$ (we denote $V^{\cdot +}$ for both $MV^{\cdot +}$ and β-CD-$MV^{\cdot +}$), of which spectral characteristics in various media have been reported.[1,7,8] Judging from ε_{604} = 13500 $M^{-1}cm^{-1}$, the reduction of V^{2+} to $V^{\cdot +}$ is quantitative (spectrum B of Fig. 1). The behavior after quantitative reduction to $V^{\cdot +}$ depends on the solvent media. In DMF/water (volume fraction of DMF was 0.7-0.9) media, further irradiation decreases the absorption near 604 nm and increases that at 374 nm. Clear isosbestic points are shown at 321, 396, 404, and 462 nm. By subtracting the contribution of $V^{\cdot +}$ from the composite spectrum, a typical spectrum of V^{o} is obtained. Prolonged irradiation gives pure V^{o} spectrum (spectrum C in Fig. 1), of which λ_{max} are 374 nm (ε = 37000 $M^{-1}cm^{-1}$) and 394 nm (ε = 41500 $M^{-1}cm^{-1}$). The molar absorptivity values are in fair agreements with reported ones.[12] This indicates clearly that the reduction of $V^{\cdot +}$ to V^{o} is also quantitative in the media. The concentrations of $V^{\cdot +}$ and V^{o} at various irradiation times were calculated from the separated spectra using the aforementioned molar absorptivity values and the results are shown in Fig. 2. In water, only small amount of V^{o} was produced and much of the viologens were destroyed: the concentrations of $V^{\cdot +}$ and V^{o} in the medium were also calculated at various irradiation times and the results are included in Fig. 2.

$V^{\cdot +}$ is in equilibrium with V^{o} by disproportionation reaction (Equation 1).

$$2\,V^{\cdot +} = V^{o} + V^{2+} \qquad (1)$$

The upper limit of the equilibrium constant (K) for the reaction was evaluated from redox potentials to be ~10^{-7} for $MV^{\cdot +}$, irrespective of solvent polarity.[1] Such small K value predicts that more than 99% conversion of V^{2+} to $V^{\cdot +}$ is required to observe appreciable amount of V^{o}, *i.e.* 1% from total concentration of a viologen, 0.050 mM. This accords with our observation shown in Fig. 2. The photoinduced reduction of $V^{\cdot +}$ to V^{o} is not observed when we filter the light near 450 nm by placing a concentrated $Ru(bpy)_3^{2+}$ solution in front of the sample solution. This indicates that V^{o} is formed via $Ru(bpy)_3^{2+}$ sensitized reaction, not by the direct photochemical reaction of $V^{\cdot +}$. If V^{o} is formed only via disproportionation reaction of $V^{\cdot +}$, which is produced by electron-transfer reaction with $^*Ru(bpy)_3^{2+}$ (Equation 2), the rate of conversion of $V^{\cdot +}$ to V^{o} should be extremely slow, which is quite contrary to our observation. From these findings, we are safe in assuming that both V^{2+} and $V^{\cdot +}$ are reduced by the electron-transfer reactions with $^*Ru(bpy)_3^{2+}$,

$$^*Ru(bpy)_3^{2+} + V^{2+} \longrightarrow Ru(bpy)_3^{3+} + V^{\cdot +} \qquad (2)$$

$$^*Ru(bpy)_3^{2+} + V^{\cdot +} \longrightarrow Ru(bpy)_3^{3+} + V^{o} \qquad (3)$$

The oxidized $Ru(bpy)_3^{3+}$ produced by reactions (2) and (3) is reduced by the reactions with sacrificial electron-donors such as EDTA or triethanolamine.

$V^{\cdot +}$ is stable in alkaline medium in the absence of oxygen.[8] However, standing the solutions of V^{o}

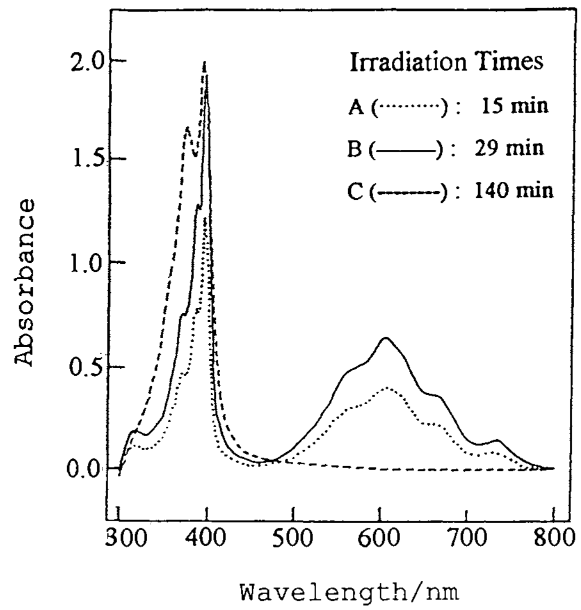

Fig. 1. Absorption spectra of reduction products of viologen obtained by irradition of deaerated 0.05 mM β-CD-MV^{2+}/ 0.050 mM $Ru(bpy)_3^{2+}$/ 0.1 M triethanolamine in 80% DMF-20% water at pH 10.0. The solution prior to irradiation is used as a blank.

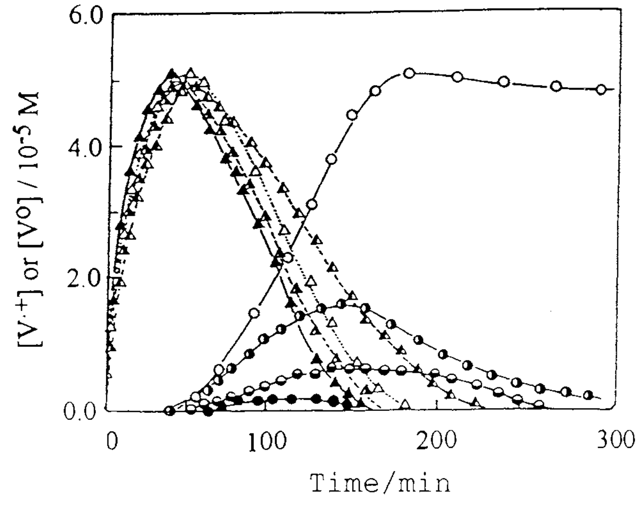

Fig. 2. Dependence of the concentration of the photosensitized reduction products of V^{2+} on irradiation time: (●,▲), MV^{2+} in water in the absence of β-CD; (◒,▲), MV^{2+} in water in the presence of 15 mM β-CD; (◑,Δ), β-CD-MV^{2+} in water; (O,Δ), β-CD-MV^{2+} in 80% DMF-20% water. Circles are for $V^{\cdot +}$ and triangles are for V^{o}. Little difference was observed between MV^{2+} and β-CD-MV^{2+} in 80% DMF-20% water media.

or the mixtures of V^o and $V^{\cdot+}$ results in decrease in $[V^o]$ and increase in $[V^{\cdot+}]$. Also, formation of H_2 gas was detected by gc using Molecular sieves 5A column. The ratio of $-\Delta[V^{\cdot+}]/\Delta[V^o]$ was 0.74 - 0.79 for the entire course of the reactions, regardless of viologens and solvent systems. The disappearance of V^o followed pseudo-first order kinetics with respect to V^o (Fig. 3) and rate constants were approximately proportional to the contents of water in the media. These indicate that V^o molecules react with water in two parallel pathways.

$$V^o + H_2O \xrightarrow{k_1} V^{\cdot+} + OH^- + 1/2\,H_2 \qquad (4)$$

$$V^o \xrightarrow[H_2O]{k_2} P \qquad (5)$$

P does not absorb light appreciably above 300 nm. The characterization of P is beyond the scope of this work: a possible reaction for (5) is addition of water to the hydropyridine rings of V^o.

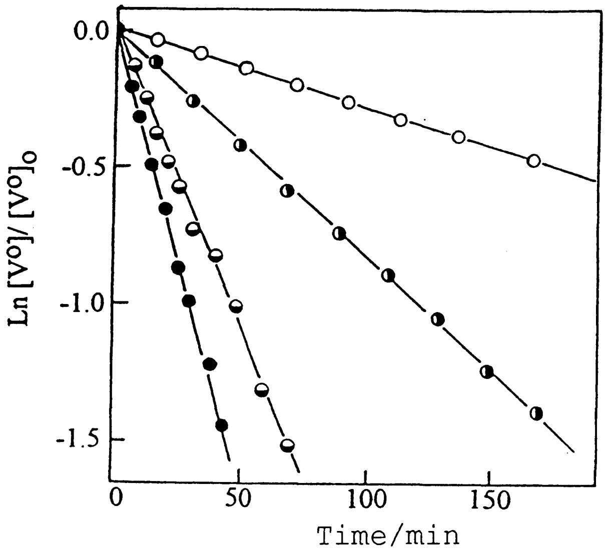

Fig. 3. Pseudo-first order kinetic plots for disappearance of V^o in dark at 25 °C: (●), MV^o in water in the absence of β-CD; (◒), MV^o in water in the presence of 15 mM β-CD; (◑), β-CD-MV^o in water; (O), MV^o in 80% DMF-20% water (V/V). pH of the solutions was 10.0.

The slope of the plots in Fig. 3 corresponds to $(k_1 + k_2)$ value and the $-\Delta[V^{\cdot+}]/\Delta[V^o]$ ratio is $k_1/(k_1+k_2)$. The determined k values are listed in Table 1, which shows that the decreasing order of the reactivity of V^o with water is V^o in the absence of β-CD > V^o in the presence of β-CD > V^o appended to β-CD. This can explain why the yield of V^o in water is highest for β-CD-MV^{2+} and lowest in the absence of β-CD (Fig. 2).

Matsue et al.[13)] reported that binding constant of MV^o with β-CD is 1400 M^{-1}. Thus the fraction of MV^o complexed with β-CD under our experimental condition of [β-CD] = 15 mM is 0.95, which is much larger

Table 1. Rate Constants for Reactions of Neutral Viologen at 25 °C

Viologen	Medium	$(k_1+k_2)\times10^3/\mathrm{min}^{-1}$	$k_1/(k_1+k_2)$	$k_2\times10^3/\mathrm{min}^{-1}$
MV^o	H_2O	31	a)	a)
MV^o	H_2O + 15 mM β-CD	22	a)	a)
β-CD-MV^o	H_2O	8.1	0.74	2.1
MV^o	80 % DMF - 20 % H_2O (V/V)	2.8	0.75	0.70
MV^o	80 % DMF - 20 % H_2O (V/V) and 15 mM β-CD	2.2	0.77	0.51
β-CD-MV^o	80 % DMF - 20 % H_2O (V/V)	1.3	0.77	0.30
β-CD-MV^o	72 % DMF - 28 % H_2O (V/V)	2.2	0.79	0.46
β-CD-MV^o	90 % DMF - 10 % H_2O (V/V)	0.61	0.82	0.11

a) $[MV]^o$ is too small to calculate the ratio.

than the extent of retardation of the reaction rate of MV^o, 30%, by the presence of 15 mM β-CD. This implies that MV^o complexed with β-CD has substantial reactivity with water. This is in quite contrast to the observation of essentially zero reactivity of 1,4-dihydronicotinamides (DHP) complexed with β-CD.[14] A plausible explanation for this is that part of the reduced bipyridine of MV^o protrudes from the cavity of β-CD and can react with water molecules, whereas the dihydronicotinamide moiety of DHP is well protected against hydration reaction upon complexation with β-CD. In this sense, protection of V^o against reaction with water by covalent attachment of the group to β-CD is amazing. The intramolecular interaction of the reduced bipyridine moiety of V^o with the primary hydroxyl side of β-CD, which is shown to be geometrically possible for ethylviologen appended β-CD,[10,15] might be responsible for this.

The viologen-appended β-CDx have a β-CD unit as a chiral binding site, and can bind various guest molecules by hydrophobic and electrostatic interactions exhibiting moderate enantioselectivity of the binding.[10,15,16] It was shown that the reduction rate of ninhydrin by β-CD-dihydronicontinamide is 40-60 times faster than that by free NADH.[17] From these observations and the stabilizing effects of β-CD moiety against reaction of V^o with water, the rate enhancement as well as enantioselectivity is expected for the reduction reactions mediated by viologen-appended β-CD, relative to free viologens or viologens in β-CD solutions. Studies on these aspects are currently underway.

This work was supported by grants from the Korea Science and Engineering Foundation (91-0300-03) and the Center for Biofunctional Molecules (KKP).

References

1) For an extensive list of literatures dealing with the properties and applications of viologens, see: T. M. Bockman and J. K. Kochi, *J. Org. Chem.*, **55**, 4127 (1990).
2) R. Maidan, Z. Goren, J. Y. Becker, and I. Willner, *J. Am. Chem. Soc.*, **106**, 6217 (1984).
3) K. K. Park, C. H. Oh, and W. K. Joung, *Tetrahedron Lett.*, **34**, 7445 (1993) and references cited therein.
4) C. L. Bird and A. T. Kuhn, *Chem. Soc. Rev.*, **10**, 49 (1981).
5) C. O. Schmakel, K. S. V. Santhanam, and P. J. Elving, *J. Am. Chem. Soc.*, **97**, 5083 (1975).
6) M. Mohammad, *J. Org. Chem.*, **52**, 2779 (1987).
7) T. Watanabe and K. Honda, *J. Phys. Chem.*, **86**, 2617 (1982).
8) M. Venturi, Q. G. Mulazzani, and M. F. Hoffman, *Radia. Phys. Chem.*, **23**, 229 (1984)
9) β-CD-MV^{2+} was prepared by the reaction of 6-O-mono-tosylated β-CD with 1-methyl-4,4'-bipyridinium iodide. There were little difference in reaction yield and conditions between this pathway and the reported route[10] which is the reaction of 6-O-monoiodinated β-CD with the 1-alkyl-4,4'-bipyridinium halide.
10) Y. Du, A. Nakamura, and F. Toda, *Bull. Chem. Soc. Jpn.*, **63**, 3351 (1990).
11) The reduction rate of viologens and the yield of V^o in aqueous media are greater as the the concentration of $Ru(bpy)_3^{2+}$ is higher and the intensity of light is stronger.
12) The reported ε_{max} values for MV^o are 36000 (λ_{max} = 388 nm) in water,[8] 27000 (λ_{max} = 396 nm) in acetonitrile,[6] and 42000 $M^{-1}cm^{-1}$ (λ_{max} = 395 nm) in ethanol.[7] The lower ε_{max} values in Refs 6 and 8 could be due to uncertainty of the concentration of V^o, rather than solvent effect.[7]
13) T. Matsue, T. Kano, U. Akiba, and T. Osa, *Chem. Lett.*, **1985**, 1825.
14) J. W. Park, S. Y. Cha, and K. K. Park, *J. Chem. Soc., Perkin Trans. 2*, **1991**, 1613.
15) H. Ikeda, Y. Du, A. Nakamura, and F. Toda, *Chem. Lett.*, **1991**, 1495.
16) Y. Du, A. Nakamura, and F. Toda, *J. Inclusion Phenom. Mol. Recog.* **10**, 443 (1991).
17) M. Kojima, F. Toda, and K. Hattori, *J. Chem. Soc., Perkin Trans. 1*, **1981**, 647; *Tetrahedron Lett.*, **21**, 2721 (1980).

(Received June 6, 1994)