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Photoreduction of Bisviologen Compounds, Viologen-$(CH_2)_n$-Viologen, by 2-Propanol

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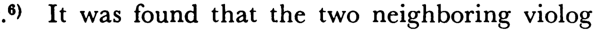
In order to study the polymer effect in the photoreduction of viologen-containing polymers by 2-propanol, bisviologen compounds, V^{2+}–$(CH_2)_n$–V^{2+}, were subjected to photoreduction. The rates of photoreduction occur in the order $n=2>3>4>5>MV^{2+}$. The structure of the photoreduced species was found to be predominantly the doubly reduced species, V^{+}–$(CH_2)_n$–V^{+}, in the cases of $n=2$ and 3, and mixtures of the doubly reduced and singly reduced species, V^{+}–$(CH_2)_n$–V^{2+}, in the cases of $n=4$ and 5. Intramolecular dimeric association of V^+ units was observed for all the compounds except for $n=2$, where the intramolecular association was structurally inhibited. The variation of rate and structure distribution of reduced species was interpreted in terms of the local concentration effect in the photoreduction step.

Methylviologen (MV^{2+}) is known as an efficient electron transfer mediator in the conversion of light energy into chemical energy.[1–5] We are interested in the viologen-containing polymers because we expect the facilitated electron migration along the polymer chain and some possible multi-electron transfer from the reduced polymer. In the previous paper we reported the synthesis of some viologen-containing vinyl polymers and studied the polymer effect in the photoreduction by 2-propanol and in the properties of the reduced polymer.[6] It was found that the two neighboring viologen units on a polymer chain appeared to cooperate in the photoreduction and that this cooperation resulted in the increase of the rate of photoreduction and in the dimeric association of two reduced viologen units. This may be a kind of local concentration effect.

The object of the present paper is to confirm the local concentration effect by the use of model compounds **1** containing two viologen units at various polymethylene intervals. The part of the present work on compound **1b** ($n=3$) has been briefly communicated.[7]



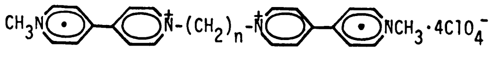
1 (a,b,c,d for n=2,3,4, and 5, respctively)
1′,1″-(Polymethylene)bis(1-methyl-4,4′-bipyridinium)perchlorate.

Results and Discussion

*Structure of Reduced Species (*n*=3).* Figure 1 shows the time profile for the photoreduction of compound **1b** ($n=3$) in an aqueous solution. A monotonous increase of the radical cation species absorbing at 360, 533, and ≈850 nm was observed. The same spectral change was observed by the treatment of **1b** ($n=3$) (6.5×10^{-5} mol dm^{-3}) with an excess of sodium dithionite (1.7×10^{-2} mol dm^{-3}) under anaerobic condition, where both viologen units of **1b** ($n=3$) were reduced to form the doubly reduced form **2**. As shown in Fig. 1, the spectrum obtained on photoreduction was different from that of MV^+ at ambient temperature. MV^+ has been known to exist in an equilibrium with a dimeric associated species $(MV^+)_2$, as in Eq. 1:[8,9]

$$MV^+ + MV^+ \rightleftharpoons (MV^+)_2. \qquad (1)$$

The observed spectrum in the photolysis corresponds to that of the associated form, which was stable only at very low temperatures. Thus, the spectral difference between the photoreduced **1b** ($n=3$) and MV^+ in Fig. 1 can be explained by intramolecular association of the V^+ groups in the photoreduced **1b** ($n=3$). Moreover, we prepared the singly reduced form **3** ($n=3$) and confirmed that its spectrum corresponds to that of monomeric MV^+, as shown in Fig. 2. The singly reduced form **3** ($n=3$) was prepared by the electron transfer reaction from hydroxydiphenylmethyl radicals, which were generated *in situ* by the unimolecular thermolysis of benzpinacol at 60 °C in a methanol solution containing **1b** ($n=3$, Cl$^-$ form) under an anaerobic condition. It has been known that the reduction of MV^{2+} by the hydroxydiphenylmethyl radical was very efficient.[10] The time profile for the



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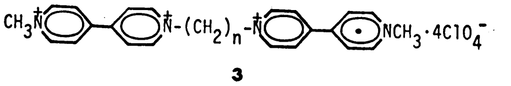

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2: Doubly reduced form, **3**: singly reduced form (a,b,c,d for n=2,3,4, and 5, respectively).

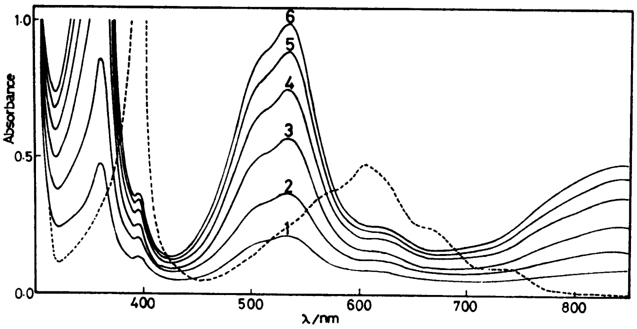


Fig. 1. Absorption spectra of photoreduced species of **1b** ($n=3$) in phosphate buffered aqueous solution (pH 5.9) containing 2-propanol (0.65 mol dm^{-3}). The concentration was [**1b**]=5.0×10^{-4} mol dm^{-3}. Irradiation time, 1: 0.5, 2: 1.0, 3: 2.0, 4: 3.0, 5: 4.0, 6: 5.0 h. Absorption spectrum of MV^+ was shown by a dotted line.

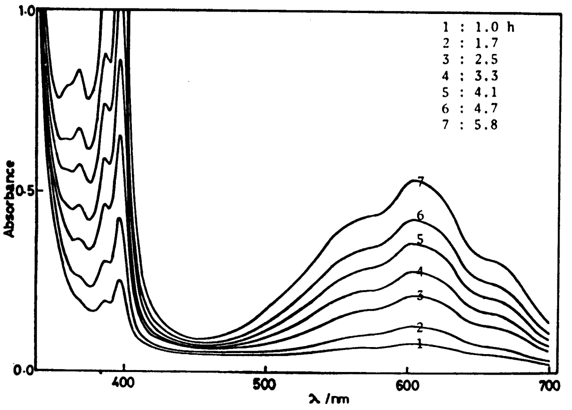


Fig. 2. Reduction of **1b** ($n=3$, Cl^- form) by hydroxyphenylmethyl radical in a methanol solution at 60°C. The concentrations were $[\mathbf{1b}]=8.0\times10^{-3}$ mol dm^{-3} and [benzpinacol]$=2.0\times10^{-3}$ mol dm^{-3}.

thermal reaction (Fig. 2) showed a monotonous increase of the MV^+-type absorption of **3** ($n=3$). Thus, the photoreduced **1b** ($n=3$) has been shown to be **2** in the intramolecular associated form.

It is interesting to note that this assignment excludes the possibility of molecular complexes between the V^+ unit and the V^{2+} unit, although several examples of aromatic compounds are known to exhibit this kind of association.[11] Furthermore, in spite of the exothermicity of the dimeric association, there was no indication of an intermolecular electron transfer process which would lead to the formation of **2** ($n=3$) by the electron exchange between **3**'s ($n=3$).[12,13]

Structure of Photoreduced Species ($n=2$*, 4, and 5).* The absorption spectrum of the partially photoreduced **1a** ($n=2$) shown in Fig. 3A, however, is entirely of the MV^+ type and the completely reduced species obtained with $Na_2S_2O_4$-treatment also showed the same spectrum. It is therefore reasonable to assign the structure **2a** ($n=2$) to the photoreduced **1a** ($n=2$) and to assume that **2a** ($n=2$) does not take an associated structure. Inspection of molecular models shows conformational difficulty in the association.

When **1c** ($n=4$) and **1d** ($n=5$) were completely reduced by $Na_2S_2O_4$, the spectra showed maxima at 536 and 539 nm, respectively, indicating that **2c** ($n=4$) and **2d** ($n=5$) show the intramolecular association like that in **2b** ($n=3$) (Figs. 3C and D). The spectra of the partially photoreduced specimens of **1c** ($n=4$) and **1d** ($n=5$) in Figs. 3 C and D have maxima at 540 and 603 nm in 6 : 4 ratio for $n=4$ and 5 : 5 for $n=5$. These two specimens may be concluded to be mixtures of **2** and **3**.

Rate of Photoreduction by 2-Propanol. Based upon the above interpretation of the absorption spectra, the concentrations of the singly reduced and doubly reduced species are evaluated. The observed absorbance (A) at any given wavelength is given by

$$A = \varepsilon_1 C_1 L + \varepsilon_2 C_2 L, \qquad (2)$$

where ε_1 and ε_2 are the molar extinction coefficients at the wavelength of the singly reduced and doubly reduced species, respectively, C_1 and C_2 are the corresponding concentrations, and L is the light path (1 cm). Table 1 shows λ_{max} and ε_{max} of bisviologen compounds (**1**) and doubly reduced species (**2**) together with the other ε values necessary for the estimation of C_1 and C_2. ε_2 in each case was determined from the absorption spectrum of the doubly reduced species which was produced by the treatment with an excess of $Na_2S_2O_4$. The singly reduced species was assumed to have the same extinction coefficient (ε_1) as that of MV^+. C_1 and C_2 were calculated using equation 2 from absorbance values at two different wavelengths, namely, at 603 nm and 530—540 nm. The latter wavelength is the maximum absorption of the doubly reduced species of **1b** ($n=3$), **1c** ($n=4$), and **1d** ($n=5$). In the case of **1a** ($n=2$), the photoreduced product was found to be only the doubly reduced species, as shown in Fig. 3A. ε_2 in this case is the value of **2a** ($n=2$).

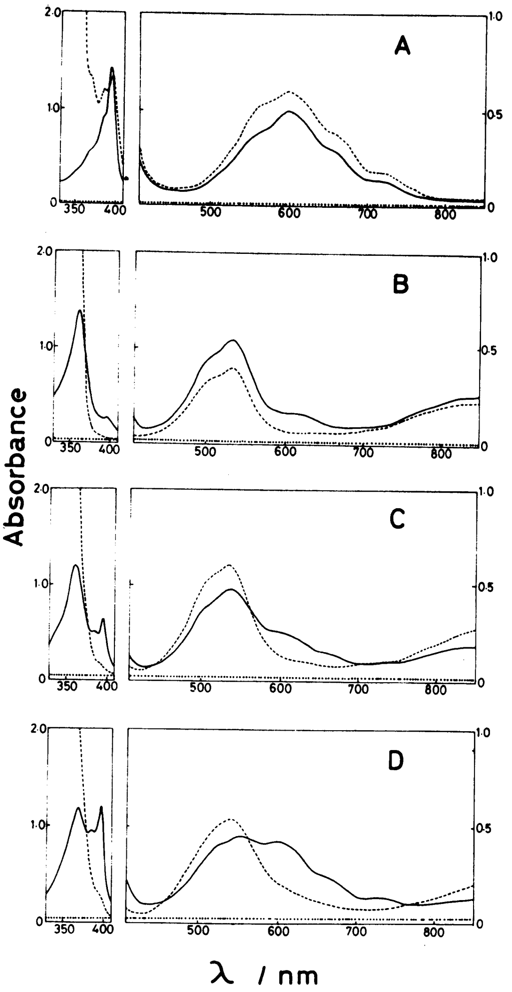


Fig. 3. Absorption spectra of radical cations of **1** partially photoreduced (——) and completely reduced with $Na_2S_2O_4$ (------) and base lines (……) for the latter.
A: [radical ion]$=4.95\times10^{-5}$ unit mol dm^{-3}, [2a ($n=2$)] $=3.01\times10^{-5}$ mol dm^{-3}.
B: [radical ion]$=5.14\times10^{-5}$ unit mol dm^{-3}, [2b ($n=3$)] $=1.67\times10^{-5}$ mol dm^{-3}.
C: [radical ion]$=4.59\times10^{-5}$ unit mol dm^{-3}, [2c ($n=4$)] $=2.54\times10^{-5}$ mol dm^{-3}.
D: [radical ion]$=5.08\times10^{-5}$ unit mol dm^{-3}, [2d($n=5$)] $=2.43\times10^{-5}$ mol dm^{-3}.

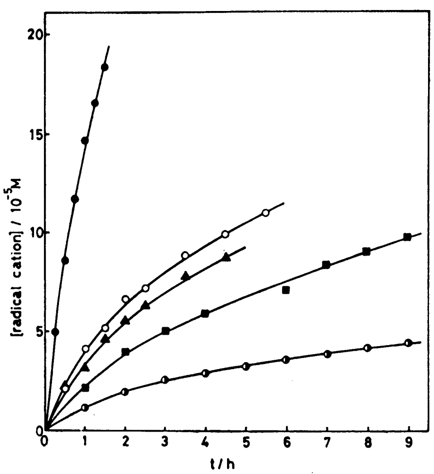


Fig. 4. Photochemical formation of radical cations from bisviologen compounds **1** and MV^{2+} in phosphate buffered aqueous solution (pH 5.9) containing 2-propanol (0.65 mol dm^{-3}). The concentrations were $[\mathbf{1}]=5.0\times10^{-4}$ mol dm^{-3} and $[MV^{2+}]=1.0\times10^{-3}$ mol dm^{-3}.
●: **1a** (n=2), ○: **1b** (n=3), ▲: **1c** (n=4), ■: **1d** (n=5), ◑: MV^{2+}.

The total amount of photoreduced species, C_1+2C_2, is plotted *versus* time in Fig. 4. Bisviologen compounds were found to show no special interunit interaction at the ground state, as shown by similar absorption maxima in Table 1. The rate curves of the photoreduction in Fig. 4, however, show marked differences. The initial rate decreased in the order $n=2>3>4>5>$ MV^{2+}. This fact may be explained in terms of the local concentration effect by the following argument. The photoreduction of MV^{2+} by 2-propanol is known to proceed by the following mechanism:[10)]

$$MV^{2+} \xrightarrow{h\nu} MV^{2+*}, \qquad (3)$$

$$MV^{2+*} + (CH_3)_2CHOH \longrightarrow MV^{+} + (CH_3)_2CHO\cdot + H^{+}, \qquad (4)$$

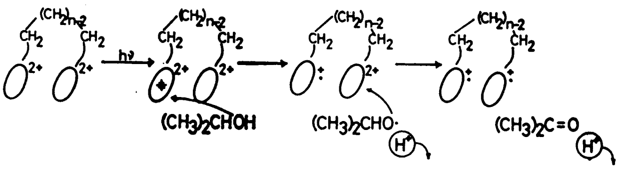
$$MV^{2+} + (CH_3)_2CHO\cdot \longrightarrow MV^{+} + (CH_3)_2C{=}O + H^{+}, \qquad (5)$$

$$\text{Net}\quad 2MV^{2+} + (CH_3)_2CHOH \xrightarrow{h\nu} 2MV^{+} + (CH_3)_2C{=}O + 2H^{+}. \qquad (6)$$

The excited viologen receives an electron from 2-propanol, leaving the alkoxyl radical. The latter in turn gives up another electron to a ground state MV^{2+}. One photon eventually results in the reduction of two MV^{2+} molecules and the oxidation of one alcohol molecule. The alkoxyl radical $(CH_3)_2CHO\cdot$, in addition to reaction 5, has another possibility of reaction 7, which is a backward electron transfer reaction. The competition between reactions 5 and 7

$$MV^{+} + (CH_3)_2CHO\cdot \longrightarrow MV^{2+} + (CH_3)_2CHO^{-} \qquad (7)$$

depends on the relative local concentration of MV^{+} and MV^{2+}. In the case of bisviologen compounds, the alkoxyl radical will find nearby another viologen unit of the bisviologen compound before it diffuses out of the reaction site, and reaction 5 will take place (Scheme 1). Thus the local concentration effect will be exerted favorably on the rate of reaction in bisviologen compound- and viologen polymer-systems, compared with MV^{2+}. It is reasonable that bisviologen compounds with shorter intervening polymethylene chains have higher initial rate because of higher local concentrations of V^{2+} units.



Scheme 1. Mechanism of photoreduction of bisviologen compounds (n=2—5) by 2-propanol.

Figure 4 shows that there was a saturation phenomenon and that the saturation appeared at an earlier stage of conversion in the compounds whose initial rate was slower. The saturation phenomenon is also explained in terms of reaction 7. When the concentration of V^{+} unit increases, the contribution of the backward reaction 7 relative to the forward reaction 5 will increase, leading to saturation in the concentration of V^{+} units. Moreover, if the local concentration effect is small, as in the case of **1d** (n=5) in comparison to **1a** (n=2), the larger contribution of reaction 7 relative to reaction 5 will result in the slower initial rate and at the same time the earlier occurrence of the saturation phenomena. The saturation phenomena in the case of MV^{2+} were explained by Ledwith in terms of the quenching reaction 8 of excited

$$MV^{2+*} + MV^{+} \longrightarrow MV^{2+} + MV^{+} \qquad (8)$$

MV^{2+} with MV^{+}.[10,14)] This reaction alone, however, does not explain the difference in onset of the saturation phenomena among bisviologen compounds.

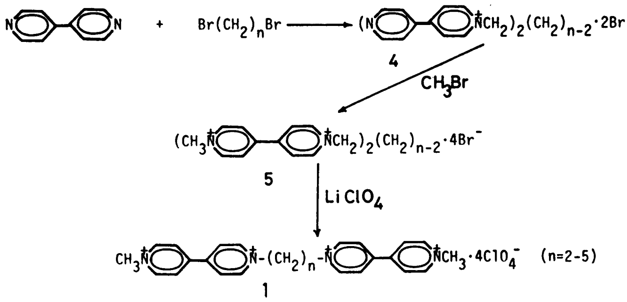
TABLE 1. ABSORPTION SPECTRAL DATA OF METHYLVIOLOGEN AND BISVIOLOGEN COMPOUNDS[a)]

Compound	1 (Bisviologen compounds)		2 (Doubly reduced species)			
	λ_{max}/nm	ε_{max}/mol^{-1} cm^{-1}	λ_{max}/nm	ε_{max}/mol^{-1} cm^{-1}	λ/nm	ε/mol^{-1} cm^{-1}
1a (n=2)	263	4.40×10^4	595	1.99×10^4	603	1.96×10^4
1b (n=3)	260	4.38×10^4	533	2.36×10^4	603	0.18×10^4
1c (n=4)	259	3.88×10^4	536	2.39×10^4	603	0.41×10^4
1d (n=5)	258	4.52×10^4	539	2.20×10^4	603	0.68×10^4
MV^{2+}	256	1.39×10^4	603	1.20×10^4	533[c)]	0.53×10^4

a) Measured at 25 °C. b) Reduced with $Na_2S_2O_4$. c) ε : 0.62×10^4 mol^{-1} cm^{-1} at 539 nm and 0.53×10^4 mol^{-1} cm^{-1} at 536 nm.

Experimental

*Preparation of Bisviologen Compounds, **1a** (n=2), **1b** (n=3), **1c** (n=4), and **1d** (n=5).* 1′,1″-(Polymethylene)bis(1-methyl-4,4′-bipyridnium)perchlorate **1** was prepared according to the following general procedure.



1,1′-(Polymethylene)bis(4-bipyridinium)dibromide **4** was prepared by warming a solution of 4,4′-bipyridine (25 g, 0.16 mol) in *N*,*N*-dimethylformamide (DMF) (200 ml) with α,ω-dibromoalkane (40 mmol) at 70 °C for 24 h. A light yellow precipitate separated out and was recrystallized from water for *n*=2 and 3 and from an acetone–methanol mixture for *n*=4 and 5. Yields of **4** were 25, 55, 50, and 64% for *n*=2, 3, 4, and 5, respectively.

Treatment of **4** (20 mmol) with an excess of methyl bromide (30 ml) in DMF (270 ml) in a glass autoclave (400 ml) at 90 °C for 24 h afforded **5** in nearly quantitative yields. **5** (4 mmol) was converted to the corresponding perchlorate **1** by the treatment with an aqueous solution (100 ml) of $LiClO_4$ (47 mmol) at room temperature. For *n*=5, 94 mmol of $LiClO_4$ was used under the same conditions. Recrystallization from water gave colorless crystals. Yields of **1** were 75, 61, 73, and 47% for **1a** (*n*=2), **1b** (*n*=3), **1c** (*n*=4), and **1d** (*n*=5), respectively.

1a. Found: C, 37.25: H, 3.49; N, 7.30; Cl, 18.43%. Calcd for $C_{24}H_{26}N_4O_{16}Cl_4$: C, 37.52; H, 3.31; N, 7.29; Cl, 18.46%.

1b. Found: C, 37.70; H, 3.71; N, 7.18; Cl, 18.01%. Calcd for $C_{25}H_{28}N_4O_{16}Cl_4$: C, 38.38, H, 3.61; N, 7.16; Cl, 18.13%.

1c. Found: C, 39.16; H, 3.90; N, 7.07; Cl, 17.91%. Calcd for $C_{26}H_{30}N_4O_{16}Cl_4$: C, 39.21; H, 3.80; N, 7.04; Cl, 17.81%.

1d. Found: C, 39.68; H, 4.11; N, 6.98; Cl, 17.41%. Calcd for $C_{27}H_{32}N_4O_{16}Cl_4$: C, 40.02; H, 3.98; N, 6.91; Cl, 17.50%.

A chloride ion type of **1** (*n*=3) was prepared by the replacement of the bromide ion of **5** with a chloride ion; this involved passing an aqueous solution of **5** through a column of anion exchange resin (Amberlite IRA 400).

Photoreaction. Light from a 300 W high pressure mercury lamp was filtered through aqueous 5% potassium hydrogen phthalate to remove light of shorter wavelength than 300 nm. A quartz cell was charged with a viologen sample in an aqueous solution of 2-propanol (0.65 mol dm^{-3}) at pH 5.9 (phosphate buffer, 1/15 mol dm^{-3}), degassed, sealed, and set in a thermostat equipped with a merry-go-round.

Measurements. Electronic absorption spectra were measured by a Hitachi Model 124 spectrophotometer with a thermostatically controlled cell compartment.

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