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# PHOTOINDUCED TWO-ELECTRON REDUCTION OF METHYL VIOLOGEN DIMER BY 2-PROPANOL THROUGH INTRAMOLECULAR PROCESS AND FORMATION OF VIOLOGEN RADICAL CATION DIMER

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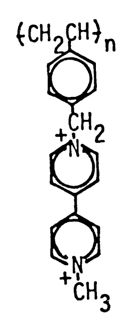
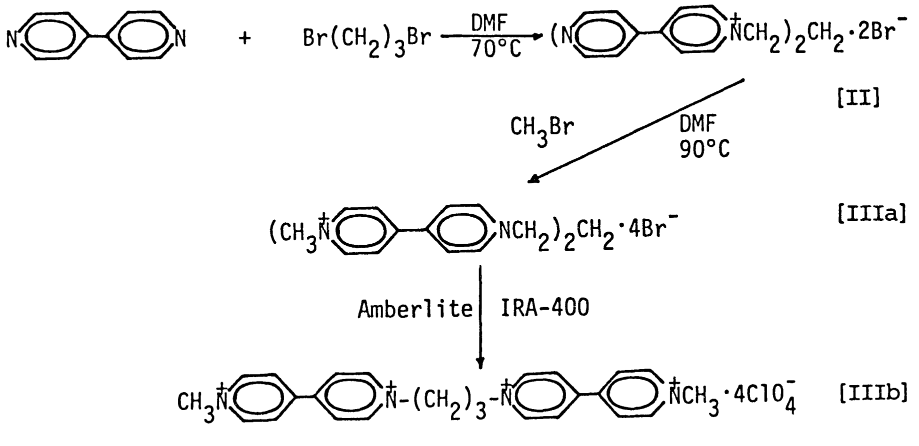
In the photoreduction of the newly synthesized methyl viologen dimer, 1',1"-trimethylene-bis(1-methyl-4,4'-bipyridinium) perchlorate, by 2-propanol, the exclusive formation of the stable radical cation dimer at room temperature was observed, which gave an unequivocal evidence for the intramolecular process.

As a part of our investigation[1)] on the role played by synthetic polymers in the photochemical reaction, the neighboring group participation has been found in the photoreduction of a viologen-containing polymer I by 2-propanol. This finding led us to study a more explicit model for the mechanism. We now report the preparation of a new dimer model of methyl viologen, 1',1"-trimethylene-bis(1-methyl-4,4'-bipyridinium) perchlorate IIIb and the exclusive formation of the radical cation dimer IV. This gives an unequivocal evidence for the intramolecular process in the photoreduction.

1,1'-Trimethylene-bis-4-bipyridinium bromide II was prepared by warming a solution of an excess of 4,4'-bipyridyl in N,N-dimethylformamide (DMF) with 1,3-dibromopropane. A light yellow precipitate separated out and was recrystallized from water (55% yield). Treatment of II with an excess of methyl bromide



[I]



Scheme: Preparation of Methyl Viologen Dimer in DMF in a glass autoclave afforded IIIa in a quantitative yield. IIIa was converted to the corresponding perchlorate IIIb by Amberlite IRA-400 which was previously treated with perchloric acid. (Scheme)

U.V. irradiation ($\lambda > 300$ nm) of an oxygen-free solution of IIIb ($5 \times 10^{-4}$M) and 2-propanol (0.65 M) in water using quartz apparatus and a 300 W medium pressure mercury arc lamp led to photoreduction of IIIb, that is, the formation of radical cation, which showed the absorption maxima at ∿850, 533, and 360 nm. The time profile for photoreduction was shown in Fig. 1, in which a monotonous increase of the radical cation species was observed during the course of photolysis. The same spectral change was also observed by the treatment of IIIb ($6.5 \times 10^{-5}$M) with an excess of sodium hydrosulfite ($1.7 \times 10^{-2}$M) under anaerobic condition, where both methyl viologen groups of IIIb were reduced to form the doubly reduced form IV.

As shown in Fig. 1, the spectrum obtained by photoreduction was different from that of methyl viologen radical cation ($MV^{+\cdot}$) at ambient temperature. $MV^{+\cdot}$ has been known to exist in the equilibrium with a dimer species $(MV^{+\cdot})_2$.[2)3)]

$$(MV^{+\cdot}) \quad + \quad (MV^{+\cdot}) \rightleftharpoons (MV^{+\cdot})_2$$

The observed spectrum in the photolysis corresponds to that of the dimer $(MV^{+\cdot})_2$ which was stable only at the very low temperature.[3)] Therefore, the spectral difference between the photoreduced IIIb and $MV^{+\cdot}$ in Fig. 1 can be best explained by intramolecular association of the $MV^{+\cdot}$ groups in the photoreduced IIIb. In other words, the $MV^{+\cdot}$ groups of IV exists mostly in an associated form.

The mechanism for the photoreduction of $MV^{2+}$ by alcohols has been proposed, in which the primary step was the electron transfer from alcohol to an excited $MV^{2+}$, and the subsequent one was the fast electron transfer reaction between the resultant alkoxy radical and $MV^{2+}$ in the ground state.[4)] As a result one photon

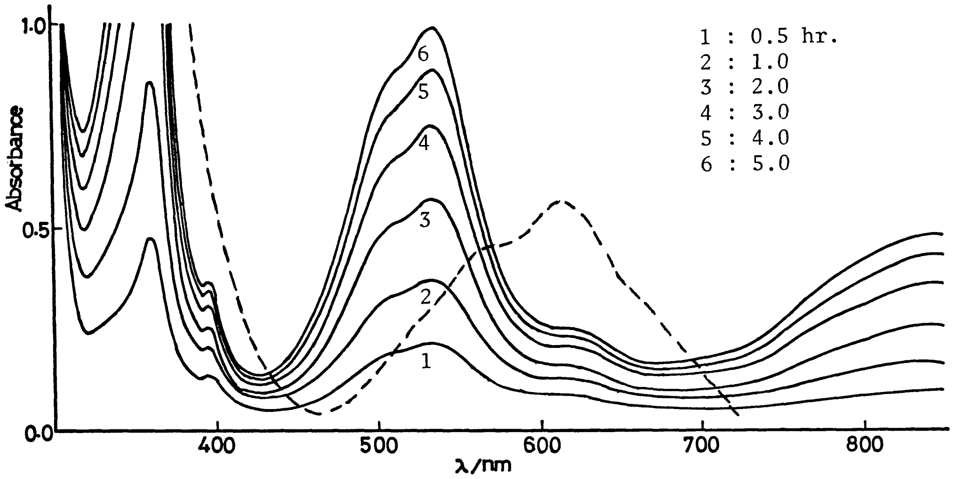
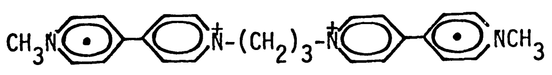


Fig. 1. Photoreduction of IIIb (——). The visible absorption spectrum of $MV^{+\cdot}$ at 25°C (----).

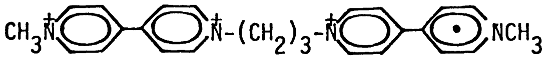
induces the reduction of two moles of $MV^{2+}$ and the oxidation of one mole of alcohol. In the present system the second step was involved as the intramolecular process to form the doubly reduced IIIb, IV. Therefore, the singly reduced IIIb, V, will not show up in the spectra even at the early stage of the photoreduction. The initial rate of the formation of radical cation was compared with that of $MV^{2+}$ using the same concentration of viologen moieties. As shown in Fig. 2, the rate enhancement was observed. This was also confirmed by the glc measurement of produced acetone. Therefore, the suggested process may have contributed to the rate enhancement.

There is one remaining possibility for the assignment of the spectra. Several examples are known in which the association of a cation radical with the parent molecule also exhibits the similar spectral change.5) Such a possibility in the present system can be ruled out by the fact that the spectrum of the singly reduced IIIb, V, corresponds to that of the monomeric $MV^{\dot{+}}$. V was formed by the electron transfer reaction from benzhydrol radicals, which were generated by unimolecular thermolysis of benzopinacol ($2 \times 10^{-3}$M) at 60°C in a methanol solution containing IIIb ($8 \times 10^{-3}$M) under anaerobic condition. The time profile for the thermal reaction showed a monotonous increase of the radical cation V. (Fig. 3) The final solution have not given any significant change in the spectrum (7 in Fig. 3) on standing over two months. Therefore, there was no indication of intermolecular electron transfer process to lead to the formation of IV by the electron exchange between V in spite of the exothermicity of the association.6)7)



[IV]

Doubly reduced IIIb



[V]

Singly reduced IIIb

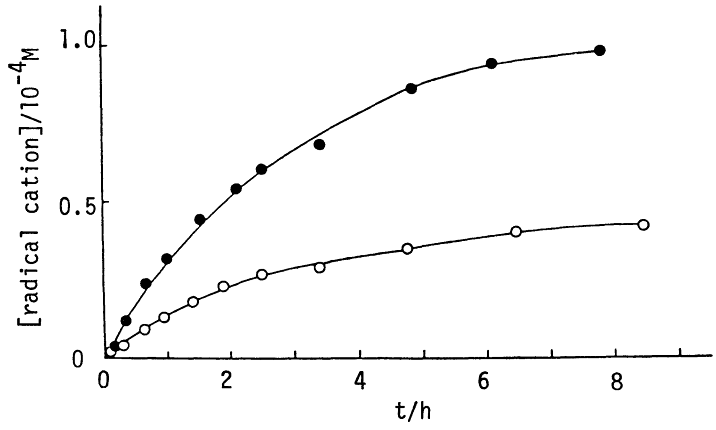


Fig. 2. Plots of [radical cation] vs. irradiation time for IIIb (●) and $MV^{2+}$ (○) systems. $[MV^{2+}] = 10^{-3}$M, $[IIIb] = 5 \times 10^{-4}$M, [2-Propanol] = 0.65 M, 25°C.

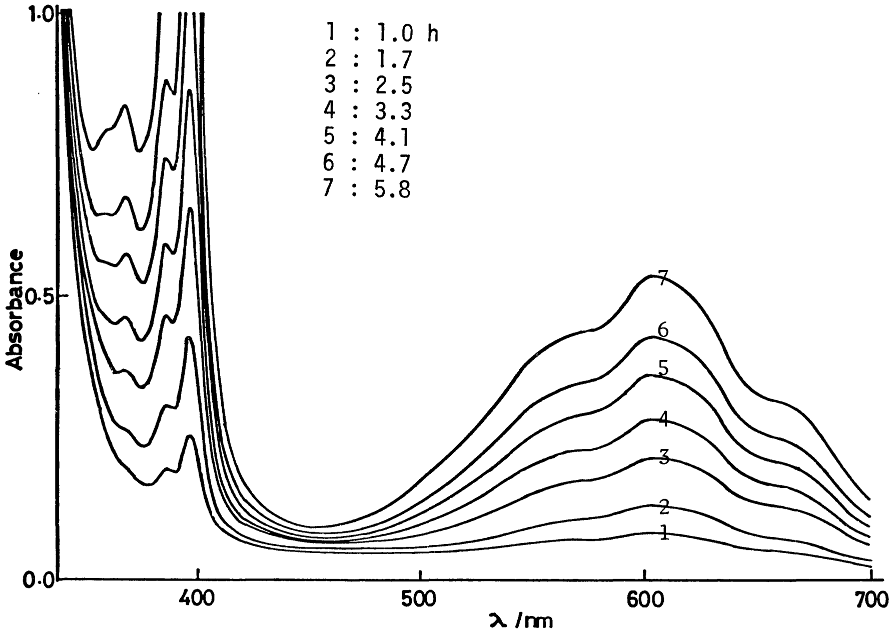


Fig. 3. Reduction of IIb by Benzhydrol radicals at 60°C. [IIb] = 8 x $10^{-3}$M, [Benzopinacol] = 2 x $10^{-3}$M.

It may be concluded that photoinduced two-electron reduction of IIb by 2-propanol takes place through the intramolecular process to give the associated radical cation dimer, IV.

## References

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