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## PHOTOCHEMICALLY INDUCED REDUCTION OF VIOLOGENS IN SOLID POLAR APROTIC POLYMER MATRICES

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Photochemically induced reversible reduction of viologens in solid polar aprotic polymer matrices proceeds much more efficiently than that in protic ones. The effects of the N-substituent and anionic part of viologens were also considerable.

It is well known that viologens such as 1,1'-dimethy1-4,4'-bipyridilium dichloride are reduced reversibly to afford highly colored cation radicals.<sup>1,2</sup>

Photochemically induced generations of viologen cation radicals have been reported for alcoholic solutions of viologens<sup>3,4,5</sup> and for polymeric viologens both in aqueous solutions<sup>6</sup> and in solid state<sup>7,8</sup>

In this report, we wish to present the results of investigation conducted on the photochemical behavior of viologens in solid polymer matrices, especially in polar aprotic ones.

In Tables 1 and 2 are given the viologens prepared by the Menschutkin reaction in conventional manners and the polymers employed as matrix, respectively.

Та	uble l. Viol + R-N	ogens synthesiz	zed and used
Compd	X	R'	х-
la	n-C3H7	n-C <sub>3</sub> H <sub>7</sub>	Br
lb	n-C <sub>3</sub> H <sub>7</sub>	n-C3H7	Cl_
lc	n-C3H7	n-C <sub>3</sub> H <sub>7</sub>	1-
2	PhCH <sub>2</sub>	n-C <sub>3</sub> H <sub>7</sub>	Br <sup>-</sup>
3a	PhCH <sub>2</sub>	PhCH <sub>2</sub>	Br <sup>-</sup>
3b	PhCH <sub>2</sub>	PhCH <sub>2</sub>	Cl_
3c	PhCH <sub>2</sub>	PhCH <sub>2</sub>	BF <sub>4</sub>
4	CH300CCH2	сн <sub>3</sub> 00ссн <sub>2</sub>	Cl_

Generally, a matrix polymer (0.5g) was dissolved in water (5 ml). A viologen was then dissolved in the solution to afford 0.099 mole/1 concentration. The resulting solution was spread over a glass plate of 1.2 cm width so as to afford a 1.2 x 2.0 cm area, followed by drying overnight at room temperature. The plate was then stored in a desiccator of 30% RH (sat.CaCl<sub>2</sub> solution) at least overnight before use. The plate taken out of the desiccator was immediately irradiated at a distance of either 5 or 15 cm from a 75W-mercury lamp (Toshiba SHL-100UV) and the result-

ing color-development was recorded on a Hitachi 200-10 spectrophotometer.

As exemplified in Figure 1 and Table 3, the absorbance at the absorption maximum (610 nm) which appeared as the result of the formation of cation radicals in the

	IGOIC Z.	TOTATION ADOU AD	ma or TY
Polymer	Abbreviatio	on Average MW	Remark
Poly(acrylamide) Poly(N,N-dimethyl acrylamide)	Pa <b>m</b> Pmam	$[\eta] = 1.9 \text{ dl/g}^{a}$ $[\eta] = 0.8 \text{ dl/g}^{a}$	Aqueous polymerization Ethanolic polymerizat ion
Poly(vinyl alcohol)	) PVA	20,000	Iwai Chem. Co.
Poly(N-vinyl pyrrolidone)	PVP	10,000	Tokyo Kasei Co.

Table 2. Polymers used as matrix

a. Intrinsic viscosity in water at 30°C.

Table 3	. Effe	ct of mat	rix on	color d	evelopment	
		Irrad.	Absor	bance <sup>a</sup> at	irrad. time	2
Viologen	Matrix	distance cm	30	60	90 sec	t <sup>1</sup> <sup>b</sup>
la	PVA	5	0.12	0.24	0.34	60
	PAM	5	0.00	0.04	0.04	40
	PMAM	5	0.13	0.38	0.56	10
	PVP	5	0.49	1.18	1.47	10
3b	PVA	15	-	0.13	-	600
	PVP	15	-	0.90	-	70
a. Value	at abs.	max.(610	nm).	b. Half.	-recovery ti	ime(min).

solid polymer films containing viologen by UVirradiation is affected profoundly by the kind of matrix. The effect of matrix on the colordeveloping rate was in the decreasing order: PVP, PMAM, PVA, and PAM. It is also to be noted that PVP and PMAM, polar aprotic matrices, provid-

ed much higher color-fading rates  $(t_2^1)$  than PVA and PAM, protic ones.



WAVE LENGTH (nm)



WAVE LENGTH (nm)

Figure 1. Effect of matrix on the color-Figure 1. Effect of matrix on the color-Figure 1. Effect of the film containing 3a and view exposed to UV-light for 90 sec at the dis-fit tance of 15 cm from the lamp: 1 PVP; 2 properties of 15 cm from

Figure 2. Effect of the anionic part of viologen on the color-development of PVP films containing la, lb, and lc and exposed to UV-light for 60 sec at the distance of 5 cm from the lamp.

In Figure 2 and in Table 4 are exemplified the effect of the anionic part of viologen on the spectral changes caused by the reduction. The kind of anion considerably affects the rate of reduction with the decreasing order of Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup> and  $BF_4^-$  in PVP-matrix.

2.0

Table 5 exemplifies the effect of the N-substituent (R and R' in Table 1) in viologen cation on the color-developing rate in PVP-matrix. The order obtained:

dibenzyl > benzyl-propyl > dipropyl is consistent with that of dark normal redox potentials? As regards viologen 4 with methyl ester groups, a somewhat different tendency is observed: absorption maximum at 605 nm which is different from others (610 nm) and rather lower absorbances developed. The value of  $A_{20}/A_{60}$ , however, is rational.

Viologen		Abs	sorbance <sup>b</sup> at i	rrad. time <sup>C</sup>		
		0		20	60 sec	
	3a	0.00		0.88	1.58	
	3c	0.00		0.35	0.88	
	lc	0.00		0.16	0.58	
a.	Matrix PVP. 1	o. Value at a	abs.max.(610	nm). ć.5 c	m from UV-lamp.	
	Table 5. Effect of N-substituent (R and R') on reduction rate <sup>a</sup>					
	Viologen	Absorba	rbance <sup>o</sup> at irrad. time <sup>c</sup>		$A_{00}/A_{c0} \times 100^{d}$	
_		20	40	60 Sec	20' 60	
	la	0.40	1.18	1.58	25	
	2	0.71	-	1.50	47	
	3a	0.88	1.50	1.58	56	
	4	0.52 <sup>e</sup>	0.63 <sup>e</sup>	1.07 <sup>e</sup>	49	

Table 4. Effect of the anionic part of viologen on the photochemically induced reduction

a. Matrix PVP. b. Value at abs.max. c. 5 cm from UV-lamp. d. A: Absorbance. e. At 605 nm (abs.max.).

The results presented above might suggest that the photochemically induced reduction of viologen cation in a solid polar aprotic matrix to afford a highly colored cation radical proceeds at least partially as indicated in eq. 1 under the present experimental condition.

$$\underbrace{v^{2+}}_{t} \xrightarrow{+} x^{\overline{z}} \xleftarrow{k^{y}} (v^{2+})^{*} \xrightarrow{+} x^{\overline{z}} \xrightarrow{v^{\pm}} (v^{2+})^{*} \xrightarrow{+} x^{\overline{z}} \xrightarrow{v^{\pm}} (1)$$

where V and []\* represent viologen cation and the photoexcited state, respectively. Thus, anion X: may be in the "naked" state in polar aprotic matrices such as PVP and PMAM, especially when the ambient RH and therefore the moisture contents of films are low, since such matrices would hardly solvate anions just like their liquid equivalents.<sup>10</sup> Accordingly, such naked anions will attack  $V^{2+}$  more efficiently than the solvated ones such as those in PVA and PAM, protic matrices, thereby providing much higher rates of reduction (Figure 1 and Table 3). The rate order as for anion in PVP, a typical polar aprotic matrix: Cl > Br > I and  $BF_4$  (Figure 2 and Table 4) is consistent with the usual order of nucleophilicity for these anions in liquid polar aprotic solvents. The abstractions of hydrogen radicals from matrices may also occur, especially for PVA, but a large difference in photoreduction efficiency found between PMAM and PAM in which the structure difference lies only in the N-substituent ( Figure 1 and Table 3) also suggests that the mechanism of color-development indicated in eq. 1 can not be disregarded. The fact that color-fading rates  $(t\frac{1}{2})$  in protic matrices such as PVA are much lower than those in polar aprotic ones such as PVP (Table 3) excludes the presence of air oxygen, which promotes color-fading (back reaction), in larger amounts in the former matrices. The fact that lower ambient RHs down to

30% afford higher photoreduction rates, as exemplified in Table 6, may also suggest that lower contents of water, a typical protic solvent, enhance the activating effect of solid polar aprotic matrices.

Viologen	Irrad. distance cm	Irrad. time sec	RH <sup>a</sup> %	Absorbance(610 nm)	Matrix
3a	5	20	30	0.91	PVP
			58	0.74	
			84	0.72	
3 <b>a</b>	5	40	30	0.43	PMAM
			58	0.33	
			84	0.29	
3 <b>a</b>	5	20	30	0.09	PVA
			58	0.06	
			84	0.06	
3b	15	60	30	0.91	PVP
			58	0.77	
			84	0.69	
lb	5	40	30	1.08	PVP
			58	1.04	
			84	0.96	

Table 6. Effect of relative humidity (RH) on photoreduction rate

a. 58% RH: over sat. NaBr solution; 84% RH: over sat. KBr solution.

## References

- 1) L. Michaelis and E.S. Hill, J. Gen. Physiol., <u>16</u>, 859 (1933).
- 2) R.M. Elofson and R.L. Edsberg, Can. J. Chem., 35, 646 (1957).
- 3) M. Koizumi and H. Obata, Bull. Chem. Soc. Jpn., 31, 823 (1958).
- 4) C.S. Johnson, Jr. and H.S. Gutowsky, J. Chem. Physics, <u>39</u>, 1 (1963).
- 5) A. Ledwith, P.J. Russell, and L.H. Sutcliffe, Chem. Comm., 964 (1971).
- M. Okawara, T. Hirose, and N. Kamiya, J. Polym. Sci., Poly. Chem. Ed., <u>17</u>, 927 (1979).
- 7) M.S. Simon and P.T. Moore, J. Polym. Sci., Poly. Chem. Ed., <u>13</u>, 1 (1975).
- H. Kamogawa, H. Mizuno, Y. Todo, and M. Nanasawa, J. Polym. Sci., Poly. Chem. Ed., <u>17</u>, 3149 (1979).
- 9) The Merck Index, 9th Ed., Merck & Co., 9650 (1976).
- 10) e.g., Roberts-Caserio, "Basic Principles of Organic Chemistry, 2nd Ed.," W.A. Benjamin, Inc., 238 (1977).
- 11) e.g., T.W.G. Solomons, "Organic Chemistry", Wiley, 649 (1976).

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