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Laser-Induced Photoionization of Two-Electron-Reduced Viologen

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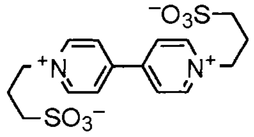
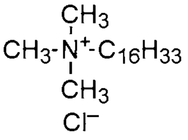
Laser photolysis of two-electron-reduced 1,1'-bis(3-sulfonatepropyl)-4,4'-bipyridinium (PVS^{2-}) produced by the reduction of PVS^0 with $Na_2S_2O_4$ in the cationic micelles of hexadecyltrimethylammonium chloride induced the photoionization of PVS^{2-} to generate comparable amounts of $PVS^{-\bullet}$ and hydrated electrons. Pyrene with a considerably negative reduction potential of -2.09 *vs.* SCE was observed to be reduced in the system.

Although viologens have been widely utilized both as an electron-transfer catalyst for reduction of various organic compounds$^{1)}$ and as an electron mediator in photochemical conversion of light energy to hydrogen,$^{2)}$ the photochemistry of two-electron-reduced viologen has hitherto been a subject of only limited investigation. The present report first describes the novel laser-induced photoionization of a two-electron-reduced viologen derivative (1,1'-bis(3-sulfonatepropyl)-4,4'-bipyridinium) in a cationic micelle in the presence or absence of electron acceptors.

1,1'-Bis(3-sulfonatepropyl)-4,4'-bipyridinium (PVS^0) was synthesized according to the method described by Matsuo *et al.*$^{3)}$ The two-electron reduction of PVS^0 (50 μmol dm^{-3}) was carried out by the addition of more than 20 times excess $Na_2S_2O_4$ in a degassed hexadecyltrimethylammonium chloride (CTAC) solution (10 mmol dm^{-3}) at pH 10.0 (carbonate buffer). The reduced viologens were photolyzed in a quartz cell (1 cm optical path length) by the 3rd harmonic light (355 nm, pulse duration 10 ns, 80 mJ / pulse) of a Nd:YAG laser (Continuum NY-60). The transient absorption

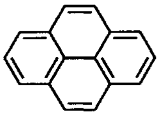


PVS^0



$$CH_3\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N^+}}\text{-}C_{16}H_{33}\quad Cl^-$$

CTAC



Py

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signals were recorded by a digitizing oscilloscope (Phillips PM-3350A) and were analyzed with a microcomputer (NEC PC-9801 DA).

When $Na_2S_2O_4$ was added to the aqueous solution of PVS^0, the solution exhibited a typical absorption spectrum of one-electron-reduced viologen[4)] as shown in Fig. 1a. The addition of $Na_2S_2O_4$ to the CTAC micellar solution of PVS^0, on the other hand, gave a characteristic absorption spectrum assigned to the two-electron-reduced viologen (PVS^{2-})[4)] without the absorption due to the one-electron-reduced PVS^0 ($PVS^{-\bullet}$) (Fig. 1b). The quantitative two-electron reduction of PVS^0 in the presence of excess $Na_2S_2O_4$ was thus possible in the hydrophobic domain of CTAC micelle; in the micellar solution, the PVS^{2-} is formed by the disproportionation reaction of $PVS^{-\bullet}$.[5)] On the other hand, such electron acceptors as pyrene (Py) in the micellar solution was not reduced by $Na_2S_2O_4$ (Fig. 1c).

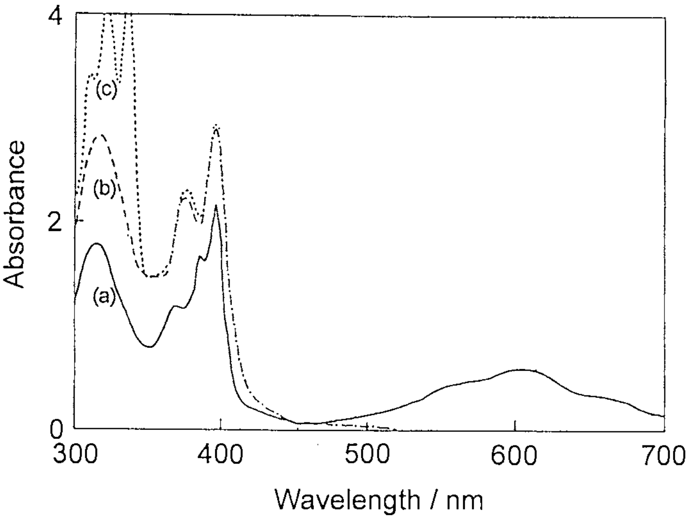

Fig. 1. Absorption spectra obtained by the reduction of PVS^0 (50 μmol dm^{-3}) with $Na_2S_2O_4$: (a) aqueous solution; (b) [CTAC] = 10 mmol dm^{-3}; (c) [CTAC] = 10 mmol dm^{-3}, [Py] = 100 μmol dm^{-3}.

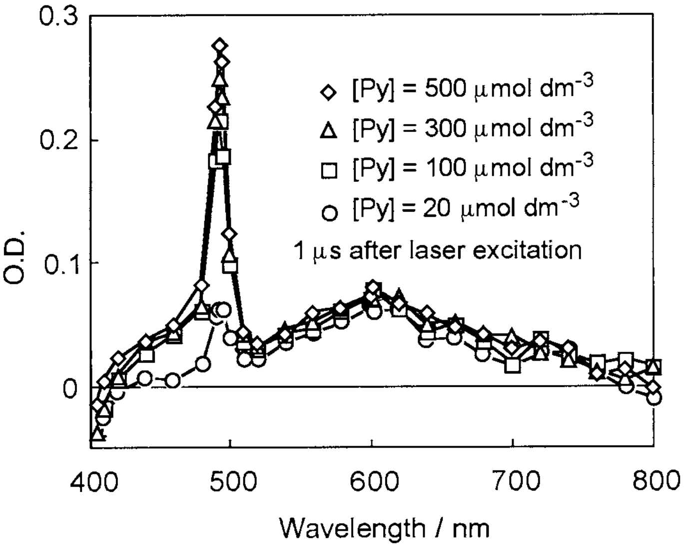

Fig. 2. Transient absorption spectra obtained by the laser photolysis of PVS^{2-} (50 μmol dm^{-3}) in the presence of Py.

In a laser photolysis of a micellar solution containing PVS^{2-} and Py at 355 nm, a transient absorption spectrum with the absorption maxima at 493 and 603 nm was obtained immediately after the laser excitation. The transient absorptions at 493 and 603 nm are reasonably assigned to the absorptions due to pyrene anion radical ($Py^{-\bullet}$)[6)] and $PVS^{-\bullet}$, respectively; the electron transfer from the photoexcited state of PVS^{2-} ($^*PVS^{2-}$) to Py was found to be completed within 0.5 μs after the laser excitation. Since the laser photolysis (at 355 nm) of micellar solution containing Py did not produce the appreciable amount of the photoexcited-state Py (see Fig. 1), the $Py^{-\bullet}$ is not generated by the reaction of $^{*}Py$ and $Na_2S_2O_4$. The concentration of $Py^{-\bullet}$ obtained at 1 μs after the laser photolysis increased with increasing the Py concentration and reached to a maximum value of 5.5 μmol dm^{-3} in the range of [Py] > 100 μmol dm^{-3} (Fig. 2). The amount of $PVS^{-\bullet}$, on the other hand, was little affected by the Py concentration and gave constant value of 5.3 ± 0.6 μmol dm^{-3}. Since the concentration of $Py^{-\bullet}$ did not exceed that of $PVS^{-\bullet}$ even at high Py concentration, an electron transfer from $^{*}PVS^{2-}$ to Py in micelle thus generated the $Py^{-\bullet}$ species. From the comparison with the reduction potentials of Py (-2.09 *vs.* SCE in DMF),[7] PVS^{2-} was found to realize a laser-induced one-electron reduction of organic compound with a considerably negative reduction potential lower than -2.09 V *vs.* SCE.

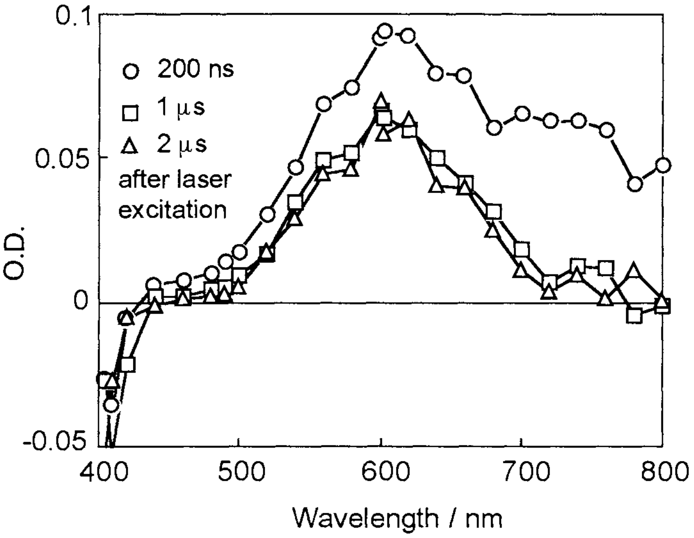

Fig. 3. Transient absorption spectra obtained by the laser photolysis of PVS^{2-} (50 μmol dm^{-3}) in the CTAC micelle (10 mmol dm^{-3}) without Py.

It is of interest and significant here to investigate the photochemical behavior of $^{*}PVS^{2-}$ produced by the laser photolysis of PVS^{2-} in the CTAC micelle in the absence of electron acceptors such as Py. Notably, laser flash photolysis of PVS^{2-} in the CTAC micelle without Py exhibited the absorption maxima of $PVS^{-\bullet}$ at 603 nm and the bleaching at 400 nm due to the disappearance of PVS^{2-} (Fig. 3).

Since the photochemical system in Fig. 3 excludes the electron transfer reaction from $^{*}PVS^{2-}$ to PVS^{0} which is quantitatively reduced to be PVS^{2-} by $Na_2S_2O_4$ in CTAC, the possibility of photoionization is worthy to notice. In the case of the photoionization of PVS^{2-}, the photo-ejected electron should be observed as a hydrated electron ($e^{-}_{aq.}$) since there is no electron acceptor in the present system. In fact, the transient absorption spectrum of $e^{-}_{aq.}$ around 720 nm[8] was observed at 200 ns after the laser excitation. The $e^{-}_{aq.}$ concentration of 2.6 μmol dm^{-3} at the delay time of 200 ns was found to be comparable to that of $PVS^{-\bullet}$ (4.3 μmol dm^{-3});[9] the less $e^{-}_{aq.}$ concentration than that of $PVS^{-\bullet}$ is probably due to the disappearance of $e^{-}_{aq.}$ by a reaction with water,[10] which is exhibited by the rapid decay of the transient absorption at 720 nm in the time domain of 1 μs.

In conclusion, the present laser photolysis of the two-electron-reduced viologen resulted in the novel photoionization of reduced viologen, which was confirmed by the spectroscopic observation of the hydrated electrons.

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9) The concentrations of $e^-_{aq.}$ and $PVS^{-\bullet}$ were calculated by using $\varepsilon_{603\ nm}$ =13000 and $\varepsilon_{720\ nm}$ = 20300 $mol^{-1}\ dm^3\ cm^{-1}$ for the formor[8)] and $\varepsilon_{603\ nm}$ = 13800 and $\varepsilon_{720\ nm}$ = 2200 $mol^{-1}\ dm^3\ cm^{-1}$ for the latter.[4)]

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