J. Am. Chem. Soc. **1984**, *106*, 7400–7404

Picosecond Photochemistry of Methyl Viologen

Thomas W. Ebbesen,* Lewis E. Manring,† and Kevin S. Peters†

Contribution from the Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556, and the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. *Received April 4, 1984*

Abstract: The photochemistry of the dithiocyanate complex, ($MV^{2+}(SCN^-)_2$), is very similar to ($MV^{2+}(Cl^-)_2$) and yields $MV^{+}\cdot$ and $(SCN^-\cdot)_2$ with a quantum yield of 0.16 as observed by nanosecond flash photolysis. Picosecond flash photolysis reveals that both the monothiocyanate and the dithiocyanate complexes give charge transfer upon excitation (respectively ($MV^+\cdot SCN\cdot$) and ($MV^+\cdot SCN\cdot SCN^-$)) with a quantum yield of ~0.3. The radical pair ($MV^+\cdot SCN\cdot$) undergoes geminate recombination with a rate constant $\gtrsim 6 \times 10^9$ s^{-1} while ($MV^+\cdot SCN\cdot SCN^-$) rearranges to ($MV^+\cdot(SCN^-\cdot)_2$) in less than 30 ps. ($MV^+\cdot(SCN^-\cdot)_2$) forms a bonded radical pair with an association constant $K_{rr} = 120$ M^{-1}. Half of the ($MV^+\cdot(SCN^-\cdot)_2$) formed undergoes geminate recombination (5×10^8 s^{-1}) while for the other half the two radicals diffuse apart (5×10^8 s^{-1}). $MV^+\cdot$ and $(SCN^-\cdot)_2$ reencounter by second-order kinetics (6×10^{10} M^{-1} s^{-1}). The picosecond photochemistry of $MV^{2+}(Cl)_2$ is also analyzed and compared with that of $MV^{2+}(SCN^-)_2$. The energetics of these reactions are considered, and the general consequences of these results are discussed.

Viologens have been used as electron acceptors in a great variety of studies in such areas as herbicidal activity and photosynthesis,[1] photochemistry,[2] photoelectrochemistry, and solar energy conversion.[3] Therefore it is most important to fully understand the photochemistry of viologens.

The photochemistry of methyl viologen, $MV^{2+}(X^-)_2$, has been mostly analyzed in alcoholic solutions,[4] but it has also been studied in polymers[5] and on cellulose,[6] and it has been observed in acidic solution[7] although, as we have pointed out elsewhere, the results were inconclusive.[8]

Both in alcoholic and aqueous solutions the photochemistry of $MV^{2+}(Cl^-)_2$ depends on the existence of ground-state charge-transfer halide complexes.[9] From the nanosecond flash photolysis study we showed that the products from exciting the dichloride complex in water were the radicals $MV^+\cdot$ and $(Cl^-\cdot)_2$.[9] To further analyze the events leading to these radicals it is reported here first the results of both nanosecond and picosecond studies on $MV^{2+}(SCN^-)_2$. The behavior of the chloride and thiocyanate salts are identical as observed by nanosecond flash photolysis; however, for picosecond absorption measurements the latter is more convenient since both radicals formed absorb in the visible spectrum. Then by comparison with $MV^{2+}(SCN^-)_2$, the picosecond flash photolysis results of $MV^{2+}(Cl^-)_2$ are analyzed.

Experimental Section

The static spectroscopy was performed with a Cary 219. A SLM photon-counting spectrofluorometer was used to measure emission. For the nanosecond laser flash photolysis a Molectron UV 400 (pulse width 10 ns) was used, exciting the samples at 337 nm in a pseudo-front-face setup, unless otherwise indicated. The quantum yield measurements were done with the 265 nm excitation wavelength of a Quanta Ray Nd-Yag laser system, and naphtalene was used as actinometer.[10] The picosecond laser flash photolysis apparatus has been described elsewhere.[11] The pulse width was 30 ps, and the excitation wavelengths were 355 and 266 nm for $MV^{2+}(SCN^-)_2$ and $MV^{2+}(Cl^-)_2$, respectively, unless otherwise indicated.

The methyl viologen dichloride (1,1′-dimethyl-4,4′-bipyridinium dichloride) was purchased from Sigma Chem. Co. The thiocyanate salt was obtained by passing the chloride salt through an ion-exchange column (Anga 542, J. T. Baker Chem. Co.) loaded with thiocyanate. The solutions were buffered with a 0.1 M phosphate (pH 7). The presence of the phosphate did not interfere with the experiments.

Results

(1) Ground-State Complexation. Upon addition of excess SCN^- to a solution of MV^{2+} a new band appears at the longer wavelengths in the absorption spectrum of MV^{2+} as shown by the differential absorption in Figure 1, parts b, c, and d. As can be seen this absorption band (with a maximum at about 310 nm) increases with increasing [SCN^-] and is indicative of the formation

---

* Address correspondence to this author at the University of Notre Dame.

† Harvard University.

(1) See, for example: Dodge, A. D. *Endeavour* **1971**, *30*, 130. Farrington, J. A.; Ebert, M.; Land, E. J.; Fletcher, K. *Biochim. Biophys. Acta* **1973**, *314*, 372. Levey, G.; Ebbesen, T. W. *J. Phys. Chem.* **1983**, *87*, 829. Schmidt, G. W.; Matlin, K. S.; Chua, H. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 610.

(2) See, for example: Creutz, C.; Keller, A. D.; Sutin, N.; Zipp, A. P. *J. Am. Chem. Soc.* **1982**, *104*, 3618. Westmoreland, T. D.; Le Bozec, H.; Murray, R. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5952. Guarr, T.; McGuire, M.; Strauch, S.; McLendon, G. *J. Am. Chem. Soc.* **1983**, *105*, 616. Maverick, A. W.; Najdzionek, J. S.; MacKenzie, D.; Nocera, D. G.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 1878. Kimura, M.; Doi, S. *J. Chem. Soc., Dalton Trans. 1* **1983**, 37. Smalley, J. F.; Feldberg, S. W.; Brunschwig, B. S. *J. Phys. Chem.* **1983**, *87*, 1757. Cosa, J. J.; Gsponer, H. E.; Previtali, C. M. *J. Photochem.* **1982**, *19*, 271. Penner, T. L.; Moebius, D. *J. Am. Chem. Soc.* **1982**, *104*, 7407. Ford, W. E.; Tollin, G. *Photochem. Photobiol.* **1982**, *36*, 647. Lee, L. Y.-C.; Hurst, J. K.; Politi, M.; Kurihara, K.; Fendler, J. H. *J. Am. Chem. Soc.* **1983**, *105*, 370. Rieger, A. L.; Edwards, J. O.; Levey, G. *Photochem. Photobiol.* **1983**, *38*, 123. Otruba, J. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1983**, *105*, 6503. Almgren, M. *J. Phys. Chem.* **1981**, *85*, 3599. Miyashita, T.; Muakata, T.; Matsuda, M. *J. Phys. Chem.* **1983**, *87*, 4529. Kitamura, N.; Kawanishi, Y.; Tazuke, S. *Chem. Lett.* **1983**, 1185. Umrikhina, A. V.; Bublichenko, N. V.; Krasnovskii, A. A. *Biofizika* **1983**, *28*, 197. Oishi, S.; Tajime, K.; Shiojima, I. *J. Mol. Catal.* **1982**, *14*, 383. Martens, F. M.; Verhoeven, J. W.; Varma, C. A. G. O.; Bergwerf, P. *J. Photochem.* **1983**, *22*, 99.

(3) See, for example: Hawecker, J.; Lehn, J.-M.; Ziessel, R. *Nouv. J. Chim.* **1983**, *7*, 271. Magliozzo, R. S.; Krasna, A. I. *Photochem. Photobiol.* **1983**, *38*, 15. Misawa, H.; Sakuragi, H.; Usui, Y.; Tokumaru, K. *Chem. Lett.* **1983**, 1021. Launikonis, A.; Loder, J. W.; Mau, A. W.-H.; Sasse, W. H. F.; Summers, L. A.; Wells, D. *Aust. J. Chem.* **1982**, *35*, 1341. Mercer-Smith, J. A.; Mauzerall, D. *Photochem. Photobiol.* **1981**, *34*, 407. Willner, I.; Otvos, J. W.; Calvin, M. *J. Am. Chem. Soc.* **1981**, *103*, 3203. Nagamara, T.; Kurihara, T.; Matsuo, T.; Sumitani, M.; Yoshihara, K. *J. Phys. Chem.* **1982**, *86*, 4368. Harriman, A.; Porter, G.; Richoux, M.-C. *J. Chem. Soc., Faraday Trans. 2* **1972**, *78*, 1955. Amouyal, E.; Grand, D.; Moradpour, A.; Keller, P. *Nouv. J. Chim.* **1982**, *6*, 241. Kurimura, Y.; Katsumata, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2560. Sassoon, R.; Rabani, J. *Isr. J. Chem.* **1982**, *22*, 138. Katagi, T.; Yamamura, T.; Saito, T.; Sasaki, Y. *Chem. Lett.* **1982**, 1451. Okura, I.; Aono, S.; Takeuchi, M.; Kusunoki, S. *Nouv. J. Chim.* **1982**, *6*, 221. Moser, J.; Graetzel, M. *J. Am. Chem. Soc.* **1983**, *105*, 6547. Kuczynaki, J.; Thomas, J. K. *J. Phys. Chem.* **1983**, *87*, 5498. Kajiwara, T.; Hasimoto, K.; Kawai, T.; Sakata, T. *J. Phys. Chem.* **1982**, *86*, 4516. Ward, M. D.; White, J. R.; Bard, A. J. *J. Am. Chem. Soc.* **1983**, *105*, 27. Kiwi, J. *J. Phys. Chem.* **1983**, *87*, 2274. Graetzel, M.; Frank, A. J. *J. Phys. Chem.* **1982**, *86*, 2964. Willman, K. W.; Murray, R. W. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *133*, 211. Neumann-Spallart, M.; Kalyanasundaram, K. *J. Phys. Chem.* **1982**, *86*, 2681. Harrison, D. J.; Calabrese, G. S.; Ricco, A. J.; Dresner, J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 4212. Duerr, H.; Doerr, G.; Zengerle, K.; Curchod, J.-M.; Braun, A. M. *Helv. Chim. Acta* **1983**, *66*, 2652.

(4) Furue, M.; Nozakura, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 513. Ledwith, A.; Russell, P. J.; Sutcliffe, L. H. *Proc. R. Soc. London, Ser. A* **1973**, *332*, 151. Brown, N. M. D.; Cowley, D. J.; Murphy, W. J. *Chem. Commun.* **1973**, 592. Rodgers, J. J. *Photochem. Photobiol.* **1979**, 1031.

(5) Kamogawa, H.; Masui, T.; Nanasawa, M. *Chem. Lett.* **1980**, 1145.

(6) Kaneko, M.; Motoyoshi, T.; Yamada, A. *Nature (London)* **1980**, *285*, 468.

(7) McKellar, J. F.; Turner, P. H. *Photochem. Photobiol.* **1971**, *13*, 437.

0002-7863/84/1506-7400$01.50/0

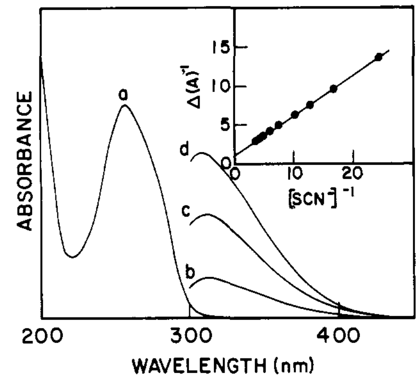

Figure 1. (a) Absorbance spectrum of $MV^{2+}(SCN^-)_2$; (b, c, and d) the growth of the charge-transfer band of the ground-state dithiocyanate methyl viologen complex as a function of $[SCN^-]$ ($[MV^{2+}] = 10^{-3}$ M) as seen by differential absorption. Inserted is the Benesi–Hildebrand plot for the charge-transfer complex (see text).

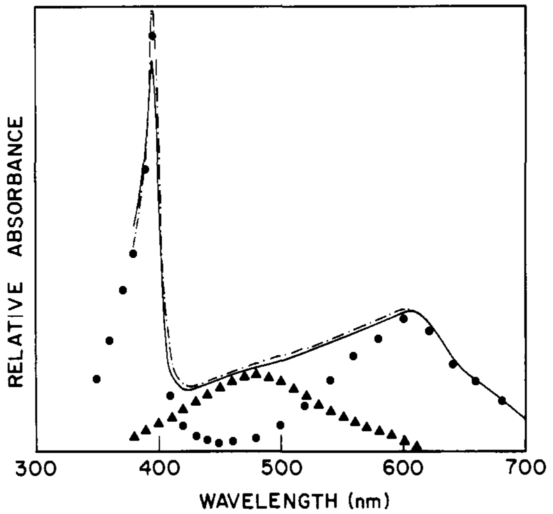

Figure 2. Comparison between the initial transient spectrum (after nanosecond pulse) (—) and the theoretical spectrum (–·–) calculated by assuming it to be the sum of the spectra of $MV^{+}\cdot$ (ϵ_{606} = 13 700 M^{-1} cm^{-1})[12] (●) and $(SCN^-\cdot)_2$ (ϵ_{480} = 7800 M^{-1} cm^{-1})[13] (▲) at equimolar concentrations.

of a ground-state charge-transfer complex. Inserted in Figure 1 is the Benesi–Hildebrand plot giving a value of 2.0 M^{-1} for the association constant K_{2SCN} of the complex. This is assumed to be the constant for the association of the second SCN^- to the monothiocyanate complex

$$(MV^{2+}SCN^-) + SCN^- \rightleftharpoons (MV^{2+}(SCN^-)_2) \quad K_{2SCN} \quad (a)$$

as is indicated by the photochemistry results discussed in the next section. The formation of the monothiocyanate complex will not interfere with the Benesi–Hildebrand plot for the binding of the second SCN^- as long as its constant, K_{1SCN}, is much larger than K_{2SCN}. Unfortunately, K_{1SCN} could not be determined by the Benesi–Hildebrand method (probably because of the low extinction coefficient of $(MV^{2+}SCN^-)$) nor by the activity of SCN^- in $MV^{2+}(SCN^-)_2$ solutions because of the interference of halides (already at 1 ppm) at the specific SCN^- electrode.

(2) Photochemistry. Nanosecond Flash Photolysis. $MV^{2+}(SCN^-)_2$ may undergo intracomplex charge transfer and rearrangement upon excitation at 337 nm

$$MV^{2+}(SCN^-)_2 + h\nu \rightarrow MV^{+}\cdot + (SCN^-\cdot)_2 \quad <10 \text{ ns} \quad (b)$$

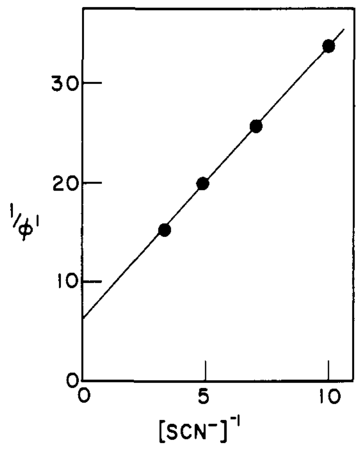

Figure 3. The inverse of the observed initial quantum yields of reaction b (in nanosecond flash photolysis experiments) is plotted against the inverse of the $[SCN^-]$ (see text).

as shown in Figure 2. The observed spectrum is the sum of equimolar quantities of $MV^{+}\cdot$ and $(SCN^-\cdot)_2$. (In a previous paper[9] the pair of radicals of the type formed in reaction b was labeled as a radical pair which was obviously a misnomer.) Reaction b occurs faster than the time resolution of our nanosecond apparatus (10^{-8} s). And since the quantum yield of reaction b is dependent on the $[SCN^-]$, we wished to determine, by an indirect method, whether it was due to competition kinetics after excitation of methyl viologen or to the fact that only one of the species in the ground state equilibria led to the products.

If only the dithiocyanate complex undergoes reaction b, then using an excitation wavelength where the dithiocyanate complex has approximately the same extinction coefficient as the other species present, the observed quantum yield of reaction b, ϕ', is the product of the true quantum yield ϕ of reaction b for the complexed species and the fraction of complexed species present in the solution:

$$\phi' = \phi \frac{K_{2X}[X^-]}{1 + K_{2X}[X^-]} \quad \text{where X = SCN} \quad (c)$$

The second term in eq c is valid only if $[SCN^-] \gg [MV^{2+}]$ which was the case in these experiments. Thus by plotting $1/\phi'$ vs. $1/[SCN^-]$ (Figure 3) $1/\phi$ is the intercept and $1/\phi K_{2SCN}$ is the slope and we find $\phi = 0.16\ (\pm\ 0.04)$ and $K_{2SCN} = 2.3\ (\pm\ 0.4)\ M^{-1}$ by using 265 nm excitation light. This value of K_{2SCN} is in good agreement with the one determined by the Benesi–Hildebrand plot given above. Therefore just as for the chloride species,[9] reaction b occurs only for the ground-state charge-transfer complex.

The radicals formed in the pulse disappear by essentially diffusion-controlled second-order kinetics

$$MV^{+}\cdot + (SCN^-\cdot)_2 \rightarrow MV^{2+}(SCN^-)_2 \quad k'_r \quad (d)$$

where k'_r ($3 \times 10^{10}\ M^{-1}\ s^{-1}$) is independent of pH (1–8), as expected. The disproportionation reaction of $(SCN^-\cdot)_2$ does not interfere with reaction d to any significant degree, because its rate constant is much smaller ($2k = 3 \times 10^9\ M^{-1}\ s^{-1}$).[14]

A picosecond study was then undertaken to try to understand some of the earlier events leading to the radical products of reaction b and to verify directly that reaction b only occurs for the dithiocyanate charge-transfer complex.

Picosecond Flash Photolysis. Immediately after the excitation pulse at 355 nm, the characteristic spectrum of $MV^{+}\cdot$ is observed with a peak around 600 nm. However, Figure 4, parts a and b, shows that at the shorter wavelengths the absorption is too strong to be that of $MV^{+}\cdot$ alone and indicates that $(SCN^-\cdot)_2$ is already present. The two dots in Figure 4a indicate the relative absor-

---

(8) Ebbesen, T. W.; Levey, G.; Patterson, L. K. *Nature (London)* **1982**, *298*, 545.

(9) Ebbesen, T. W.; Ferraudi, G. *J. Phys. Chem.* **1983**, *87*, 3717.

(10) Bensasson, R.; Goldschmidt, C. R.; Land, E. J.; Truscott, T. G. *Photochem. Photobiol.* **1978**, *28*, 277.

(11) Simon, J.; Peters, K. S. *J. Am. Chem. Soc.* **1983**, *105*, 4875.

(12) Watanabe, T.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 2617.

(13) Hug, G. L. *Natl. Stand. Ref. Data Ser. (Natl. Bur. Stand.)* **1981**, 69.

(14) Ross, A. B.; Neta, P. *Natl. Stand. Ref. Data Ser. (Natl. Bur. Stand.)* **1979**, 65.

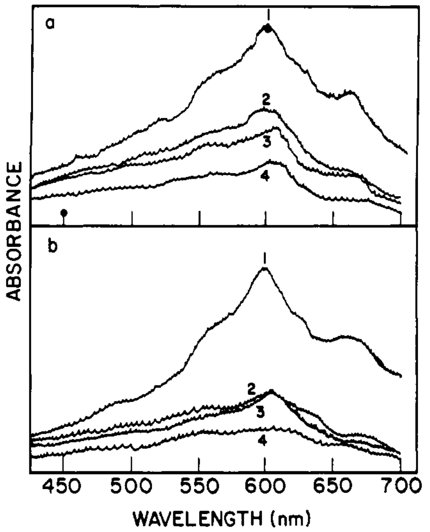

Figure 4. Observed spectra at two [SCN$^-$], (a) 0.128 M and (b) 0.416 M, at various times after picosecond laser pulse: (1) 77 ps, (2) 163 ps, (3) 334 ps, and (4) 1 to 50 ns. The two dots in part a indicate the expected relative absorbances at 600 and 450 nm if $MV^{+}\cdot$ was initially present alone.

bances at 600 and 450 nm if $MV^{+}\cdot$ was present alone. But $MV^{+}\cdot$ and $(SCN^{-}\cdot)_2$ are not present in equimolar concentrations. Another important feature, which helps in the understanding of these spectral results, is that the total initial yield of $MV^{+}\cdot$ is constant and independent of [SCN$^-$] (0.1 to 1 M) and [MV^{2+}] for a given absorbance at the 355 nm excitation wavelength. The initial amounts of $(SCN^{-}\cdot)_2$ do, however, decrease with the [SCN$^-$] (as can be seen by comparing the absorbance at the shorter wavelengths in Figure 4, parts a and b). Since neither the electron-transfer reaction from SCN$^-$ to MV^{2+} nor the subsequent reaction between SCN· and SCN$^-$ to form $(SCN^{-}\cdot)_2$ could occur in 30 ps with [SCN$^-$] $\simeq$ 0.1M if they were due to diffusional encounter between the species, both reactions must be intramolecular, or more correctly intracomplex. This indicates that two species absorb at the excitation wavelength and give $MV^{+}\cdot$ with the same quantum yield but only one of the species leads to $(SCN^{-}\cdot)_2$ formation. The obvious candidates that absorb at the excitation wavelength are the mono- and dithiocyanate complexes which both will undergo charge transfer upon excitation:

$$(MV^{2+}SCN^{-}) \xrightarrow{h\nu} (MV^{+}\cdot SCN\cdot) \qquad \phi_{ct1} < 30\ \text{ps} \qquad (e)$$

$$(MV^{2+}(SCN^{-})_2) \xrightarrow{h\nu} (MV^{+}\cdot SCN\cdot SCN^{-}) \qquad \phi_{ct2} < 30\ \text{ps} \qquad (f)$$

In the case of the dithiocyanate complex (reaction f) the counterions rearrange within the same time resolution to give the stable radical pair:

$$(MV^{+}\cdot SCN\cdot SCN^{-}) \rightarrow (MV^{+}\cdot (SCN^{-}\cdot)_2) \qquad \phi_{ra} < 30\ \text{ps} \qquad (g)$$

Thus the initial spectrum obtained on the picosecond time scale is the sum of the spectra of $(MV^{+}\cdot SCN\cdot)$ and $(MV^{+}\cdot(SCN^{-}\cdot)_2)$, and the proportion of the latter varies according to the concentration of [SCN$^-$].

In both parts a and b of Figure 4, a fraction of the $MV^{+}\cdot$ decays within 160 ps, leaving the spectrum of $(MV^{+}\cdot(SCN^{-}\cdot)_2)$. However, as the [SCN$^-$] increases, the fraction of $MV^{+}\cdot$ disappearing decreases while the amount of $(MV^{+}\cdot(SCN^{-}\cdot)_2)$ left increases. Therefore the fraction of $MV^{+}\cdot$ disappearing is interpreted as geminate recombination in the radical pair $(MV^{+}\cdot SCN\cdot)$

$$(MV^{+}\cdot SCN\cdot) \rightarrow (MV^{2+}SCN^{-}) \qquad \phi_{gr} = 1,\ k_{gr} \qquad (h)$$

where $k_{gr} \gtrsim 6 \times 10^{9}\ \text{s}^{-1}$.

Of the $(MV^{+}\cdot(SCN^{-}\cdot)_2)$ present at 160 ps, ~50% disappears within 1 ns, independently of its initial concentration, leaving spectra a(4) and b(4) in Figure 4. Then from 1 to 50 ns the spectra do not change. From the nanosecond flash photolysis results reported above it is known that the product at 50 ns is the separated radicals $MV^{+}\cdot$ and $(SCN^{-}\cdot)_2$. Therefore back-electron transfer and diffusional separation of the radicals must be in competition

$$(MV^{+}\cdot(SCN^{-}\cdot)_2) \rightarrow (MV^{2+}(SCN^{-})_2) \qquad \phi_{bt} = 0.5,\ k_{bt} \qquad (i)$$

and

$$(MV^{+}\cdot(SCN^{-}\cdot)_2) \rightarrow MV^{+}\cdot + (SCN^{-}\cdot)_2 \qquad \phi_{ds} = 0.5,\ k_{ds} \qquad (j)$$

where k_{bt} and k_{ds} both are $\sim 5 \times 10^{8}\ \text{s}^{-1}$.

The nanosecond photochemistry of $MV^{2+}(Cl^{-})_2$ was already reported in a previous paper.[9] The picosecond photochemistry of $MV^{2+}(Cl^{-})_2$ in water was analyzed with the 266 nm excitation wavelength. Because of the lower signal-to-noise ratio at this wavelength and because the $Cl_2^{-}\cdot$ absorption peak (340 nm) is below the limit of the detection system (~400 nm), it was much more difficult to analyze the picosecond flash photolysis results of $MV^{2+}(Cl^{-})_2$. However, from observing only the absorption of $MV^{+}\cdot$ generated in the laser pulse, some of the features are strikingly similar with those of the thiocyanate complexes. Therefore the analysis was carried out by analogy with $MV^{2+}(SCN^{-})_2$ results just described. First, $MV^{+}\cdot$ is formed within the time resolution of the picosecond apparatus and the initial quantum yield of $MV^{+}\cdot$ was constant within experimental error when [Cl$^-$] was varied from 0.1 to 0.4 M. Thus just as for the thiocyanate species, both the mono- and the dichloride complexes lead to $MV^{+}\cdot$ with approximately the same quantum yield. A tentative analysis of the kinetics suggests that $(MV^{+}\cdot Cl\cdot)$ undergoes back-electron transfer in less than 1 ns while $(MV^{+}\cdot Cl_2^{-}\cdot)$ undergoes diffusional separation with a quantum yield of 0.6 within 2 ns. These results with those of $MV^{2+}(SCN^{-})_2$ are summarized in Table I and will be discussed in the next section.

Since no photophysics was observed with the complexed species, attempts were made to detect excited states of the uncomplexed species. With use of the 266 nm excitation wavelength of the picosecond laser, no transients absorbances were observed between 400 and 700 nm for the SCN$^-$, Cl$^-$, and Br$^-$ salts of MV^{2+} with $[MV^{2+}(X^{-})_2] < 10^{-3}$ M. Only the characteristic spectrum of the solvated electron was observed in certain conditions when the laser intensity was too high and the water was ionized, confirming a recent report.[15] Finally with use of a sensitive single-photon-counting spectrofluorometer, no emission was detected from any of these salts either in their complexed or uncomplexed forms that could be attributed to methyl viologen.

Discussion

The quantum yields of reaction b for $MV^{2+}(Cl^{-})_2$ and $MV^{2+}(SCN^{-})_2$ are essentially identical (~0.2), while for the Br$^-$ and I$^-$ salts it is less than 0.01 due to the intracomplex heavy-atom effect.[9] Since the oxidation potential of the anions varies as Cl$^-$ > Br$^-$ > SCN$^-$ > I$^-$, there seems to be no correlation between the energy gaps of the charge-transfer transitions (as estimated from these potentials) and the observed quantum yield. At the same time one would not expect the triplet charge-transfer state, ^{3}CT, to be so much lower in energy than the excited-singlet charge-transfer state, ^{1}CT, that complete electron transfer cannot occur from ^{3}CT. Therefore it seems most likely that Br$^-$ and I$^-$ increase the probability of intersystem crossing to the ground state (^{3}CT to S_0) by spin–orbit coupling as has been observed for other types of donor–acceptor complexes.[16] All the transitions are non-radiative and evidently very fast since the radical pairs are formed within 3×10^{-11} s.

Table I gives the summary of all the observed reactions and their parameters for the thiocyanate and chloride complexes. The quantum yields ϕ_{ct1} and $\phi_{ct2}\phi_{ra}$ were calculated from ϕ_{ds} and ϕ (the quantum yield of reaction b). ϕ_{gr} potentially includes primary recombination in the solvent cage and secondary recombination as defined by Noyes.[17]

---

[15] Miyasaka, H.; Masuhara, H.; Mataga, N. *Chem. Phys. Lett.* **1983**, *98*, 277.

[16] Birks, J. B. In "Photophysics of Aromatic Molecules"; Wiley-Interscience: New York 1970; Chapter 9.

Table I. Summary of Reactions for $MV^{2+}(X^-)_2$

reactions		SCN⁻	Cl⁻
(1) $MV^{2+} + X^- \rightleftharpoons (MV^{2+}X^-)$	K_{1X}		
(2) $(MV^{2+}X^-) + X^- \rightleftharpoons (MV^{2+}(X^-)_2)$	K_{2X}	$2.0\ M^{-1}$	$1.5\ M^{-1}$
(3) $(MV^{2+}X^-) + h\nu \rightarrow (MV^{+}\cdot X\cdot)$	k_{ct1}	$>3 \times 10^{11}\ s^{-1}$	$>3 \times 10^{10}\ s^{-1}$
	ϕ_{ct1}	$\simeq 0.3$	$\simeq 0.3$
(4) $(MV^{+}\cdot X\cdot) \rightarrow (MV^{2+}X^-)$	k_{gr}	$>6 \times 10^{9}\ s^{-1}$	$10^{9}\ s^{-1}$
	ϕ_{gr}	1.0	
(5) $(MV^{2+}(X^-)_2) + h\nu \rightarrow (MV^{+}\cdot X\cdot X^-)$	k_{ct2}	$>3 \times 10^{10}\ s^{-1}$	$>3 \times 10^{10}\ s^{-1}$
	ϕ_{ct2}		
(6) $(MV^{2+}X\cdot X^-) \rightarrow (MV^{+}\cdot(X^-\cdot)_2)$	k_{ra}	$>3 \times 10^{10}\ s^{-1}$	
	$\phi_{ct2}\phi_{ra}$	$\simeq 0.3$	$\simeq 0.3$
(7) $(MV^{+}\cdot(X^-\cdot)_2) \rightarrow MV^{+}\cdot + (X^-\cdot)_2$	k_{ds}	$\simeq 5 \times 10^{8}\ s^{-1}$	$\simeq 6 \times 10^{8}\ s^{-1}$
	ϕ_{ds}	$\simeq 0.5$	$\simeq 0.6$
(8) $MV^{+}\cdot + (X^-\cdot)_2 \rightarrow (MV^{+}\cdot(X^-\cdot)_2)$	k_r	$\simeq 6 \times 10^{10}\ M^{-1}\ s^{-1}$	$>10^{10}\ M^{-1}\ s^{-1}$
(9) $(MV^{+}\cdot\ X^-\cdot)_2) \rightarrow (MV^{2+}(X^-)_2)$	k_{bt}	$\simeq 5 \times 10^{8}\ s^{-1}$	$\simeq 4 \times 10^{8}\ s^{-1}$
	ϕ_{bt}	$\simeq 0.5$	$\simeq 0.4$

The rate constant for the diffusional separation of the radical pair (reaction 7, Table I) can be estimated by using the equation

$$k_{ds} = 4\pi 10^{-3} N(D_{A^-} + D_{D^+}) \frac{a\delta}{a\Delta V(e^{\delta} - 1)} \qquad \text{(k)}$$

with $v = e_0^2/(\epsilon kTa)$ and $\Delta V = (2\pi \times 10^{-3})Na^3$ where N is Avogadros number, D_{A^-} and D_{D^+} are diffusion coefficients of A^- and D^+, a is the separation of A^- and D^+, and e_0, k, and ϵ are respectively the elementary charge, Boltzmann constant, and dielectric constant of the medium. For $a < 7$ Å and $D_{A^-} + D_{D^+} > 10^{-5}$ cm² s⁻¹, we obtain $k_{ds} > 5 \times 10^9\ s^{-1}$ in water at room temperature. This calculated value of k_{ds} is at least an order of magnitude larger than that found experimentally ($5 \times 10^8\ s^{-1}$). This is best explained by the fact that $MV^{+}\cdot$ and $X_2^-\cdot$ interact more strongly than expected from simple Coulombic attraction. Indeed, a nonnegligeable equilibrium constant, K_{rr}, for the radical pair $(MV^{+}\cdot(SCN^-\cdot)_2)$ can be calculated from the ratio k_r/k_{ds}, which gives $\sim 120\ M^{-1}$. Therefore this bonded radical pair might not undergo physical processes such as secondary recombination expected of radical pairs having no constraints to remain near each other.[17] Both the geminate pairs and the pairs formed through recombination by second-order kinetics (reactions 6 and 8) will most likely undergo reaction 9 with quantum yield ϕ_{bt}. In the case of geminate pairs ϕ_{bt} represents the quantum yield of geminate recombination excluding primary recombination which occurs on a much shorter time scale and most likely secondary recombination, as defined by Noyes, for the reasons just discussed. ϕ_{bt} also represents the quantum yield of the second-order recombination (or back transfer) reaction d as observed in the nanosecond experiments. Thus reaction d is kinetically limited by the diffusional separation of the intermediate bonded radical pair.

One question which arises from these results is the following: why is $(MV^{+}\cdot(X^-\cdot)_2)$ so stable if there is such a strong interaction between the two radicals? Unfortunately, with the evidence available we are unable to elucidate this aspect. It is interesting to note though that the potential barrier for back-electron transfer increases significantly on going from $(MV^{+}\cdot X\cdot)$ to $(MV^{+}\cdot(X^-\cdot)_2)$.

The minimum energy necessary for reaction 1

$$(MV^{2+}(X^-)_2) \rightarrow (MV^{+}\cdot X\cdot X^-) \qquad \text{(l)}$$

can be estimated from

$$\Delta G = E(D^+/D) - E(A/A^-) + \textstyle\sum \Delta G_a \qquad \text{(m)}$$

where $E(D^+/D)$ and $E(A/A^-)$ are the oxidation and reduction potential, respectively, of the final separated donor and acceptor and $\sum \Delta G_a$ is the sum of the association and dissociation energies of the various species involved. For example, the redox potentials of $MV^{2+}/MV^{+}\cdot$ and $(SCN^-\cdot)_2/(SCN^-)_2$ are −0.44[20] and 1.5 V,[19] respectively. $\sum \Delta G_a$ is calculated from K_{1SCN}, K_{2SCN}, K_{rr}, and the equilibrium constant for the formation of $(SCN^-\cdot)_2$ from $SCN\cdot$ and SCN^-.[19] $\sum \Delta G_a$ is then larger than 31.3 kJ/mol (0.324 eV) since only a minimum value of K_{1SCN} is known. The minimum energy ΔG required for reaction 1 is then according to eq m ~218.4 kJ/mol (2.26 eV). In other words, photons with a wavelength shorter than 550 nm are necessary for reaction 1 to occur when X^- is SCN^-. This calculation assumed that the ¹CT state is isoenergetic with $(MV^{+}\cdot X\cdot X^-)$ and that the energy of $X_2^-\cdot$ formation from $X\cdot$ and X^- remains unchanged when it occurs intracomplex. Both assumptions are unlikely, and therefore the energy calculated from equation m is only a rough estimate of the required energy.

In listing the reactions in Table I, no details were presented as far as the possible spin states for the radical pairs as discussed by Weller for radical pairs originating from exciplexes[21] since we have no information pertaining to this aspect.

Methyl viologen being electron deficient will form complexes with a wide variety of negatively charged or electron-rich compounds,[22-28] besides the halides.[8,9] In some cases the resulting complexes are inactive[22] and in others they have their own interesting photochemistry.[23-28] Therefore when MV^{2+} is used as an electron acceptor in photochemical studies where there is a large concentration of anions (or compounds such as alcohols), careful verifications must be made to whether or not the methyl viologen is contributing to the observed photochemistry.[29]

A recent report illustrates well how the yield of $MV^{+}\cdot$ (in the absence of a photosensitizer) varies as a function of the type of anions present and their concentration.[28] In the presence of phosphate dihexadecyl vesicles the yield of $MV^{+}\cdot$ decreased because the phosphate concentration was much higher than that of the chloride and efficiently competed for MV^{2+}. Addition of EDTA increased in turn the $MV^{+}\cdot$ yield by replacing a fraction

---

[17] Noyes, R. M. *J. Am. Chem. Soc.* **1955**, *77*, 2042.

[18] Knibble, H.; Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1968**, *72*, 257.

[19] Endicott, J. F. "Concepts of Inorganic Photochemistry"; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley-Interscience: New York, 1975; Chapter 3.

[20] Homer, R. F.; Mees, G. G.; Tomlinson, T. E. J. *J. Sci. Food Agr.* **1960**, *11*, 309.

[21] Weller, A. *Z. Phys. Chem.* (*Weisbaden*) **1982**, *130*, 129.

[22] Rougee, M.; Ebbesen, T.; Ghetti, F.; Bensasson, R. V. *J. Phys. Chem.* **1982**, *86*, 4404.

[23] Hoffman, M. Z.; Prasad, D. R.; Jones, G., II; Malloy, V. *J. Am. Chem. Soc.* **1983**, *105*, 6360.

[24] Barnett, J. R.; Hopkins, A. S.; Ledwith, A. *J. Chem. Soc., Perkin Trans. 2* **1973**, 80.

[25] Deronzier, A.; Esposito, F. *Nouv. J. Chim.* **1983**, *7*, 15.

[26] Poulos, A. T.; Kelley, C. K. *J. Chem. Soc., Faraday. Trans. 1* **1983**, *79*, 55.

[27] Sullivan, E. P.; Dressick, W. J.; Meyer, T. J. *J. Phys. Chem.* **1982**, *86*, 1473.

[28] Lukac, S.; Harbour, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 4248.

[29] Fox, M. A.; Lindig, B.; Chen, C.-C. *J. Am. Chem. Soc.* **1982**, *104*, 5828.

of the phosphate as counterion thereby probably forming the photoactive MV^{2+}–EDTA complex also reported recently.[23] Similar competition between Br$^-$ and EDTA for MV^{2+} was observed[28] where Br$^-$ reduced the MV$^{+}\cdot$ yield as expected from our recent findings.[9]

The toxicity of MV^{2+}(Cl$^-$)$_2$ as a herbicide is believed to occur through its reduction by the photosynthetic system.[1] As discussed in a preliminary account,[8] this is certainly the major toxic pathway. Our results suggest that the photochemistry of methyl viologen charge-transfer complexes is a potential parallel toxic pathway since it results in the additional formation of a strong reactive oxidizing agent such as (X$^-\cdot$)$_2$. However, it must be added that the importance of this pathway will of course depend on the location of the methyl viologen in the plant cell. At a given location the relative concentrations of the various anions will determine which are associated with MV^{2+}, while the type of counteranion will determine the photoactivity and the extent of absorption in the solar spectrum, and therefore the potential phototoxicity.

Conclusion

The photochemistry of methyl viologen, in general, seems to involve only the complexed form of the species most probably because the excited states are very short lived. The photochemistry of the halide complexes presents many interesting and unusual features such as the following: very fast intracomplex rearrangement of the counteranion with its radical form, formation of a bonded radical pair, and generation of both strong reducing and oxidizing radicals, and this with a relatively high quantum yield for the final separated species. Potential applications of the photochemistry of methyl viologen include, for example, generation of H$_2$ and Cl$_2$ from MV$^{+}\cdot$ and (Cl$^-\cdot$)$_2$ with an upper quantum efficiency of 0.2 with use of solar energy. Finally, when used as an herbicide, the photochemistry of methyl viologen complexes may play a role in the phototoxicity.

Acknowledgment. K.S.P. is grateful for the financial support from N.S.F. (N.S.F. CHE-8117519). The authors are grateful for the very useful scientific discussions held with G. Ferraudi and C. Previtali. The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2577 from the Notre Dame Radiation Laboratory.

Registry No. MV$^{+}\cdot$, 25239-55-8; MV^{2+}SCN$^-$, 92525-86-5; MV^{2+}(SCN$^-$)$_2$, 92525-87-6; SCN$^-$, 302-04-5.

A Silicon Phthalocyanine and a Silicon Naphthalocyanine: Synthesis, Electrochemistry, and Electrogenerated Chemiluminescence

Bob L. Wheeler,[†] G. Nagasubramanian,[†] Allen J. Bard,*[†] Lee A. Schechtman,[‡] David R. Dininny,[‡] and Malcolm E. Kenney*[‡]

Contribution from the Department of Chemistry, University of Texas, Austin, Texas 78712, and the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.

Received February 21, 1984

Abstract: The synthesis, spectral characterization, and electrochemical behavior of bis(tri-*n*-hexylsiloxy)(2,3-phthalocyaninato)silicon [SiPc(OR)$_2$], its dimer [RO(SiPcO)$_2$R], and its naphthalocyanine analogue [SiNc(OR)$_2$] are described. All compounds show near-UV absorption corresponding to Soret and N bands and intense absorption in the visible–near-IR region corresponding to Q bands. In CH$_2$Cl$_2$, within the solvent stability limit, there are two reductions and one oxidation for SiPc(OR)$_2$ and two reductions and two oxidations for RO(SiPcO)$_2$R and SiNc(OR)$_2$; all appear as reversible one-electron waves, although $n = 2$ for the dimer. The difference in the peak potentials of the first oxidation and first reduction waves agrees well with the excitation energy and fluorescence (corresponding to Q bands) of SiPc(OR)$_2$ and SiNc(OR)$_2$. Both compounds emit upon electrochemical generation of reduced and oxidized forms (electrogenerated chemiluminescence, ecl). The corrected ecl maxima are near 684 nm for SiPc(OR)$_2$ and 792 nm for SiNc(OR)$_2$; the latter corresponds to the longest wavelength ecl emission reported so far. The phthalocyanine dimer, RO(SiPcO)$_2$R, is easier to reduce and easier to oxidize than the monomer. The voltammetric waves in this case involve two-electron transfers with peak splittings characteristic of 1e waves, suggesting that the two phthalocyanine rings in the dimer do not strongly interact. No fluorescence or ecl was observed from the dimer.

Phthalocyanine compounds often show high thermal and chemical stability and interesting optical and electrical properties.[1-5] We and others have been interested in the conductivities of these materials[6,7] and in their application to the sensitization and stabilization of semiconductor electrodes in photoelectrochemical cells.[8,9] The group 4 metal phthalocyanines are of interest because various groups can be attached to the axial (or trans) positions.[10] Further, some group 4 phthalocyanines are linear stacked polymers.[4,11] We describe here the synthesis and the electrochemical and spectroscopic properties of a (trialkylsiloxy)silicon phthalocyanine, bis(tri-*n*-hexylsiloxy)(phthalocyaninato)silicon [SiPc(OR)$_2$], and its 2,3-naphthalocyanine analogue, [SiNc(OR)$_2$] (Figure 1). We also describe the synthesis and properties of the dimeric analogue of the phthalocyanine [RO(SiPcO)$_2$R]. The presence of the trialkylsiloxy groups on the central Si atom leads to relatively high solubility in these

---

[†] University of Texas.

[‡] Case Western Reserve University.

(1) Lever, A. B. P. *Adv. Inorg. Chem. Radiochem.* **1965**, *7*, 27.

(2) Grammatica, S.; Mort, J. *Appl. Phys. Lett.* **1981**, *38*, 445.

(3) Mizuguchi, J. *Jpn. J. Appl. Phys.* **1981**, *20*, 293.

(4) Kuznesof, P. M.; Nohr, R. S.; Wynne, K. J.; Kenney, M. E. *J. Macromol. Sci., Chem.* **1981**, *A16*, 299.

(5) Lever, A. B. P.; Licoccia, S.; Ramaswamy, B. S.; Kandil, A.; Stynes, D. V. *Inorg. Chim. Acta* **1980**, *51*, 169.

(6) (a) Van Ewyk, R. L.; Chadwick, A. V.; Wright, J. D. *J. Chem. Soc., Faraday Trans.* **1981**, *77*, 73. (b) Diel, B. N.; Inabe, T.; Lyding, J. W.; Schoch, K. F., Jr.; Kannewurf, C. R.; Marks, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 1539.

(7) Nohr, R. S.; Kuznesof, P. M.; Wynne, K. J.; Kenney, M. E.; Siebenman, P. G. *J. Am. Chem. Soc.* **1981**, *103*, 4371.

(8) (a) Leempoel, P.; Castro-Acuna, M.; Fan, F.-R. F.; Bard, A. J. *J. Phys. Chem.* **1982**, *86*, 1396. (b) Jaeger, C. D.; Fan, F.-R. F.; Bard, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 2592.

(9) Shepard, V. R., Jr.; Armstrong, N. R. *J. Phys. Chem.* **1979**, *83*, 1268.

0002-7863/84/1506-7404$01.50/0