J. Phys. Chem. **1983**, *87*, 3717-3721

TABLE VI: Comparison of Sulfate Decomposition[a] and Catalysis Onset Temperatures

metal sulfate	$T(P_d = 1 \times 10^{-6}$ atm), K	catalyst	T(onset), K
$CuSO_4$	710	CuO	760
$CuO \cdot CuSO_4$	730		
$Fe_2(SO_4)_3$	640	Fe_2O_3	800
$NiSO_4$	790	NiO	830
$CoSO_4$	825	CuO	860

[a] Calculated from data in ref 7.

the copper, nickel, and cobalt systems, SO_3 reduction becomes possible close to the temperature at which the sulfate becomes thermodynamically unstable. In the Fe-S-O system, however, there are no known sulfate phases above 640 K under these conditions, but catalytic activity is observed only above 800 K. The decomposition temperature of the corresponding sulfate then sets a lower limit on the temperature at which a metal oxide can become an effective catalyst in SO_3 reduction, but other factors such as the ability of the oxide to chemisorb oxygen also may play an important role in determining catalytic effectiveness.

Close correspondence between sulfate decomposition and catalysis threshold temperatures has significance in studies of sulfate decomposition processes, because the establishment of a solid product phase which catalytically reduces SO_3 from the sulfate lattice will then affect the gas composition and possibly the rate of decomposition of the sulfate. Mass spectrometric and vapor molecular weight information from our study[3] of copper sulfate and basic copper sulfate decomposition processes clearly demonstrates that SO_3 is the dominant (>90%) gaseous decomposition product when less than 1% of the sample has decomposed. In later stages of the experiments, however, the vapor composition changes to mostly SO_2 and O_2; the nucleation of a CuO product phase in the decomposing sulfate samples provides catalytically active surfaces on which SO_3 may decompose, consistent with our observations here of CuO catalytic activity above 750 K. However, the observed pressures are relatively independent of the degree of decomposition of the sample, so that reduction of SO_3 is not so closely coupled with the lattice decomposition step that sulfate decomposition catalysis occurs. In contrast to the results for the copper system, SO_3 is the dominant gas-phase product of the decomposition of both zinc sulfate and basic zinc sulfate even after significant decomposition, as would be expected considering the relatively low degree of catalytic activity observed with ZnO. We intend to investigate the decomposition of iron, nickel, and cobalt sulfates in order to test the validity of this model in other systems where the reaction product phase may act as a "built-in" catlayst.

Acknowledgment. This work was supported by the Office of Basic Energy Sciences, U.S. Department of Energy.

Registry No. SO_3, 7446-11-9; Ru, 7440-18-8; Pt, 7440-06-4; VO_2, 12036-21-4; CuO, 1317-38-0; Cr_2O_3, 1308-38-9; Fe_2O_3, 1309-37-1; NiO, 1313-99-1; Mn_3O_4, 1317-35-7; CoO, 1307-96-6; ZnO, 1314-13-2.

Photochemistry of Methyl Viologen in Aqueous and Methanolic Solutions

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The photochemistry of $MV^{2+}(Cl^-)_2$ (methyl viologen; paraquat; 1,1′-dimethyl-4,4′-bipyridinium dichloride) has been investigated in both H_2O and CH_3OH. It is shown that the observed photochemistry occurs via the ground-state charge-transfer complexation with the halide counterion(s). In H_2O, the radical pair $MV^{+}\cdot Cl_2^{-}\cdot$ is formed with a quantum yield of 0.2 from the dichloride complex ($K_{2Cl} = 1.4$ M^{-1}) with a rate $>10^8$ s^{-1}. The $MV^{+}\cdot Cl_2^{-}\cdot$ formation and decay is pH independent (1.5 to 9), the kinetics of the disappearance being second order. When the Cl^- counterions are replaced by Br^- ($K_{2Br} = 1.8$ M^{-1}) or by I^- ($K_{2I} = 3.2$ M^{-1}) the quantum yield drops dramatically (<0.01). By comparison with Cs^+ it is concluded that an intracomplex heavy-atom effect is observed. In methanol, where the end product is $MV^{+}\cdot Cl^-$, it is shown that the radical pair $MV^{+}\cdot Cl\cdot$ must be an intermediate in the formation of the initial methoxy radical and $MV^{+}\cdot$, the observed quantum yield of the latter being strongly dependent on the chloride concentration. Furthermore, in agreement with previous suggestions in the literature, the results indicate that a weak methyl viologen chloride-methanol complex is involved in the $MV^{2+}(Cl^-)_2$ photochemistry in methanol.

Introduction

In view of the wide interest in and usage of methyl viologen (paraquat; 1,1′-dimethyl-4,4′-bipyridinium dichloride; $MV^{2+}(Cl^-)_2$) as an intermediate in systems designed for solar energy conversion,[1] as an herbicide,[2] and as an electron acceptor in charge-transfer complexes,[3] it is most important to understand its *own* photochemistry. The main photochemical studies of $MV^{2+}(Cl^-)_2$ have been

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(1) See, for example: Johansen, O.; Launikonis, A.; Loder, J. W.; Mau, A. W. H.; Sasse, W. H. F.; Swift, J. D.; Wells, D. *Aust. J. Chem.* **1981**, *34*, 981–91. Chan, S. F.; Chou, M.; Creutz, C.; Matsubara, T.; Sutin, N. *J. Am. Chem. Soc.* **1981**, *103*, 369–79. Kirch, M.; Lehn, J. M.; Sauvage, J. P. *Helv. Chem. Acta* **1979**, *62*, 1345–84. Kalyanasundaram, K.; Gratzel, L. *Ibid.* **1980**, *63*, 478–85. Harriman, A.; Porter, G.; Richoux, M. C.; *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 833–44. Rougee, M.; Ebbesen, T. W.; Ghetti, F.; Bensasson, R. *J. Phys. Chem.* **1982**, *86*, 4404–12.

(2) See, for example: Dodge, A. D. *Endeavour* **1971**, *30*, 130–5. Farrington, J. A.; Ebert, M.; Land, E. J.; Fletcher, K. *Biochim. Biophys. Acta* **1973**, *314*, 372–81. Nanni, E. J.; Angelis, C. T.; Dickson, J.; Sawyer, D. T. *J. Am. Chem. Soc.* **1981**, *103*, 4268–70. Levey, G.; Rieger, A. L.; Edwards, J. O. *J. Org. Chem.* **1981**, *46*, 1255–60. Levey, G.; Ebbesen, T. W. *J. Phys. Chem.* **1983**, *87*, 829–32.

(3) See, for example: Poulos, A. T.; Kelley, C. K.; Simone, R. *J. Phys. Chem.* **1981**, *85*, 823–8. Deronzier, A. *J. Chem. Soc., Chem. Commun.* **1982**, *329*–31. Sullivan, E. P.; Dressick, W. J.; Meyer, T. J. *J. Phys. Chem.* **1982**, *86*, 1473–8. Andrade de Oliviera, L. A.; Haim, A. *J. Am. Chem. Soc.* **1982**, *104*, 3363–6.

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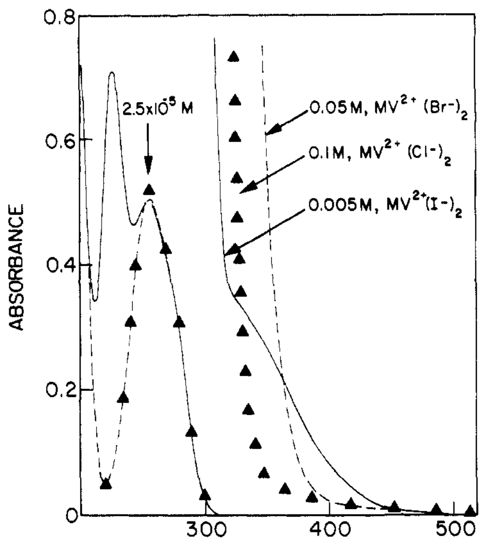

Figure 1. Absorption spectra of $MV^{2+}(X^-)_2$, where X^- = Cl^-, Br^-, or I^- as indicated, in 0.1 M phosphate buffer, pH 7.

done in alcoholic solutions where the reduced species, the radical $MV^{+}\cdot Cl^-$ is the end product.[4-9] However the mechanism involved has never been completely elucidated. In aqueous solutions, the photochemistry of $MV^{2+}(Cl^-)_2$ leads to the formation of the radical pair $MV^{+}\cdot Cl_2^{-}\cdot$ as we recently reported in a preliminary account.[10]

We report and discuss here the results of a complete flash photolysis study of $MV^{2+}(Cl^-)_2$ giving new insight into the photochemistry of methyl viologen both in aqueous and alcoholic solutions. We first investigate the factors influencing the formation of $MV^{+}\cdot Cl_2^{-}\cdot$ in aqueous solutions and its decay kinetics, and then apply the results to probe and clarify the phenomena occurring in methanol solutions. Together with the observations in mixed H_2O-CH_3OH solutions we draw general mechanisms for the photochemistry of $MV^{2+}(Cl^-)_2$ in H_2O and in CH_3OH. The behavior of $MV^{2+}(Br^-)_2$ and $MV^{2+}(I^-)_2$ in H_2O is also discussed.

Experimental Section

The laser flash photolysis studies were done either with a Molectron UV 400 (pulse width 10 ns) at 337.1 nm or with a Tac-II 150 XR excimer laser (pulse width 20–25 ns) at 248.8 nm. The geometry of the excitation–analysis setup was pseudo front face and the analyzed volume was completely covered by the excitation beam.[11] The laser spots can be considered to be of uniform intensity for the precision of the results.[12] The conventional flash photolysis apparatus, which has been described elsewhere,[13] has a 30-μs pulse width. All the flash photolysis systems are controlled, and the results analyzed, by computer.

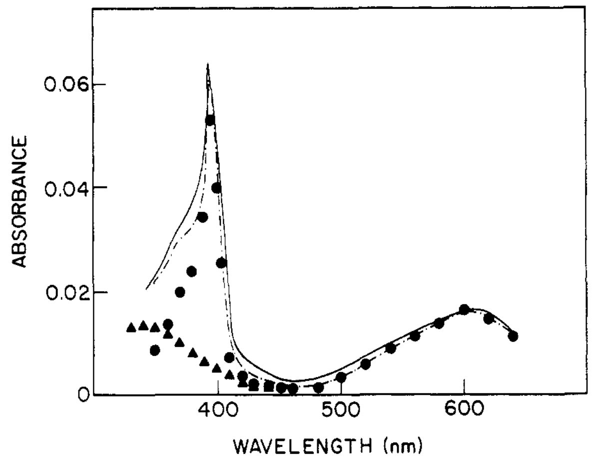

Figure 2. Comparison between the experimental transient spectrum (—) and the theoretical spectrum (-·-·). The latter was calculated by assuming it to be the sum of the spectra of $MV^{+}\cdot$ (ϵ_{605} = 11 000 M^{-1} cm^{-1}) (●) and of $Cl_2^{-}\cdot$ (ϵ_{340} = 8800 M^{-1} cm^{-1}) (▲) at an equimolar concentration of 1.5×10^{-6} M (see text and ref 10).

The methyl viologen dichloride was purchased from Sigma Chemical Co. and recrystallized at least once in ethanol (5 g/200 mL) and subsequently dried for 24 h at 70 °C. Methyl viologen diiodide and dibromide were prepared through an ion-exchange column (Anga 542, J. T. Baker Chemical Co.) from the dichloride salt. Deionized water and methanol (Aldrich Chemical Co., spectrophotometric grade) were used as solvents. When necessary the solution was buffered with 0.1 M phosphate buffer. Anthracene and naphthalene were used as actinometers for the 337.1- and 248.8-nm excitation wavelengths, respectively. The analyzed pathlength was 2 mm in all the laser flash photolysis experiments.

Results and Discussion

1. Aqueous Solutions. The ground-state absorption spectra of the methyl viologen halides are given in Figure 1. As can be seen, there is an increase in the absorbance at longer wavelengths (above 300 nm) on going from Cl^- to Br^- to I^- indicating the charge transfer interaction between the halide and the methyl viologen aromatic structure. On addition of excess quantities of the respective sodium salts, NaX, these features are enhanced. The change in absorbances on addition of the salts was used to determine the association constants, K_{2X}, for the three ground-state complexes by the Benesi–Hildebrand method: 1.4, 1.8, and 3.2 M^{-1} for Cl^-, Br^-, and I^-, respectively, in 0.1 M phosphate buffer (pH 7) (the value for K_{2Cl} was redetermined with more precision than the one given previously[10]). These are the association constants for the complexation of the second halide ion on the methyl viologen as reported previously elsewhere[14] in the case of chloride. On absorption of a photon by the methyl viologen halide the following reaction may occur

$$MV^{2+}(X^-)_2 + h\nu \rightarrow MV^{+}\cdot X_2^{-}\cdot \qquad \text{(a)}$$

as can be seen in the differential spectrum obtained after a 337-nm laser pulse excitation of the chloride complex (Figure 2) and reported previously.[10] The species $MV^{+}\cdot X_2^{-}\cdot$ is observed as having a spectrum which is approximately the sum of the spectra of the individual species $MV^{+}\cdot$ and $X_2^{-}\cdot$ in equimolar concentrations, which is not unexpected for the excitation of such ground-state charge-transfer complexes.[15] The yield of the product $MV^{+}\cdot X_2^{-}\cdot$ is

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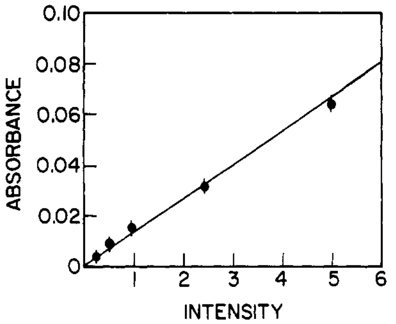

Figure 3. The yield of $MV^{+}\cdot Cl_2^{-}\cdot$ as measured through the absorbance at 395 nm is linear with excitation intensity of the laser, indicating a monophotonic process.

strongly dependent on the halide ion: $Cl^- >> Br^- > I^-$. For this reason the main part of this study was done with the chloride complex. This aspect will be discussed again in more detail later.

Reaction a is monophotonic (Figure 3) and it is faster than the resolution of our apparatus ($\sim 10^8$ s^{-1}). We found that reaction a occurs only for the complexed species, ($MV^{2+}(Cl^-)_2$), whose assocation constant was given above. For example, in the approximation that $[Cl^-] >> [(MV^{2+}(Cl^-)_2)]$ in the solution to be studied (which was the case here), the fraction of complexed molecules in the solution is equal to $K_{2Cl}[Cl^-]/(1 + K_{2Cl}[Cl^-])$. Thus the observed quantum yield ϕ' of $MV^{+}\cdot Cl_2^{-}\cdot$ formation is equal to the product

$$\phi' = \phi \frac{K_{2Cl}[Cl^-]}{1 + K_{2Cl}[Cl^-]}$$

where ϕ is the true quantum yield for the formation of $MV^{+}\cdot Cl_2^{-}\cdot$ from the complexed form ($MV^{2+}(Cl^-)_2$). Thus by plotting $1/\phi'$ vs. $1/[Cl^-]$ we should obtain a linear relationship with a slope $1/(\phi K_{2Cl})$ and an intercept $1/\phi$. Indeed this is observed experimentally, as can be seen in Figure 4. We find $\phi = 0.22$ (±0.04) (at 248.8-nm excitation wavelength) and $K_{2Cl} = 1.5$ M^{-1}, in excellent agreement with the K_{2Cl} determined earlier by the Benesi–Hildebrand method. The quantum yield was also measured with a 337.1-nm excitation source and anthracene as reference[16] and found to be 0.19 (±0.04), in good agreement with the above result.

In the case of the Br^- and I^- complexes the quantum yields are very small (<0.01). The experimental study of these complexes was additionally hampered by the fact that those counterions have absorption spectra that overlap significantly with MV^{2+}, making it impossible to use convenient excitation wavelengths in the UV for low species concentrations. For the above reasons we were unable to do a precise study of the Br^- and I^- complexes. The strong lowering of the quantum yields most probably indicate a heavy-atom effect. However, it must be an intracomplex heavy-atom effect since we found that adding a noncomplexing heavy atom to the solution, CsCl, in high concentrations (up to 10 M) did not decrease the quantum yield. It also suggests that the intersystem crossing affected by the internal heavy-atom effect must be very fast, most probably less than 10^{-10} s. Reduced $MV^{+}\cdot$ yields in the presence of Br^- and I^- has been observed previously when methyl viologen was irradiated in propanol.[4]

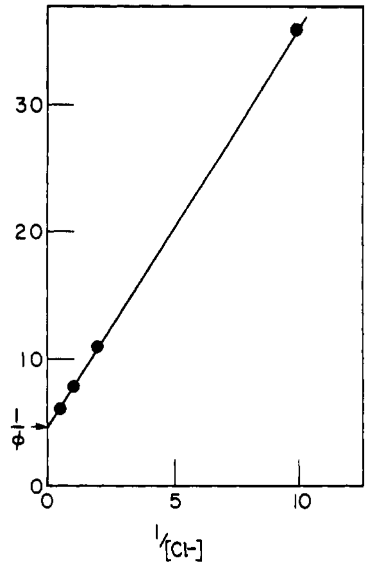

Figure 4. The inverse of the observed quantum yield ϕ' of $MV^{+}\cdot Cl_2^{-}\cdot$ formation is plotted vs. the inverse of the Cl^- concentration present in a 0.1 M phosphate buffer (pH 7) solution ($[MV^{2+}(Cl^-)_2] = 4 \times 10^{-5}$ M; 248.8-nm excitation wavelength).

pH Effect and Decay Kinetics. The initial yield of $MV^{+}\cdot Cl_2^{-}\cdot$ formation was found to be independent of pH in a range from 1.5 to 9. Using conventional flash photolysis with a cutoff filter at 290 nm and 10^{-3} M $MV^{2+}(Cl^-)_2$ with 1 M NaCl, we found that the kinetic order of the $MV^{+}Cl_2^{-}\cdot$ disappearance was also pH independent.[17] The disappearance was second order ($\zeta_{1/2} = 6 \times 10^{-4}$ s for an initial $[MV^{+}Cl_2^{-}\cdot] \simeq 5 \times 10^{-7}$ M) and wavelength dependent. The wavelength dependence is expected since there are at least two parallel reactions: $Cl_2^{-}\cdot + Cl_2^{-}\cdot$ ($2k = 1.4 \times 10^{10}$ M^{-1} s^{-1})[18] and $MV^{+}\cdot + Cl_2^{-}\cdot$. The above behavior indicates fast dissociation of the initial $MV^{+}\cdot Cl_2^{-}\cdot$ complex. The half-lives of $MV^{+}\cdot Br_2^{-}\cdot$ and $MV^{+}\cdot I_2^{-}\cdot$ were longer than 10^{-4} s at pH 7.

2. Methanol Solutions. It has been shown that two $MV^{2+}(Cl^-)_2$ molecules are reduced to $MV^{+}\cdot Cl^-$ for every alcohol molecule consumed under continuous irradiation:[4]

$$2MV^{2+}(Cl^-)_2 + ROH \xrightarrow{h\nu} 2\,MV^{+}\cdot Cl^- + R'O + 2H^+ + 2Cl^- \quad (b)$$

Later a nanosecond laser flash photolysis study[7] in methanol revealed that two distinct steps were involved in the process: first one molecule of $MV^{2+}(Cl^-)_2$ was reduced faster than the resolution of the apparatus ($\sim 10^{-8}$ s) and a methoxy radical is produced which, through a second step, reduced another $MV^{2+}(Cl^-)_2$ (5.1×10^8 M^{-1} s^{-1}).[7] The existence of the methoxy radical in the photolysis of $MV^{2+}(Cl^-)_2$ in methanol had been proven by Ledwith et al.[5] using spin trapping techniques. However, there has been discussion in the literature on whether a methanol–methyl viologen complex was involved in the reduction process as shown in the mechanism

$$MV^{2+}(Cl^-)_2\text{–}CH_3OH \xrightarrow{h\nu} MV^{+}\cdot Cl^-\text{–}CH_3O\cdot + H^+ + Cl^- \quad (c)$$

followed by

$$MV^{+}\cdot Cl^-\text{–}CH_3O\cdot + MV^{2+}(Cl^-)_2 \rightarrow CH_2{=}O + 2MV^{+}\cdot Cl^- + H^+ + Cl^- \quad (d)$$

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(17) We reported earlier[10] a first-order intracomplex back-electron-transfer rate at pH 7, but as was indicated there was a large error margin due to experimental limitations; there might also have been traces of O_2 which can seriously affect such slow kinetics.

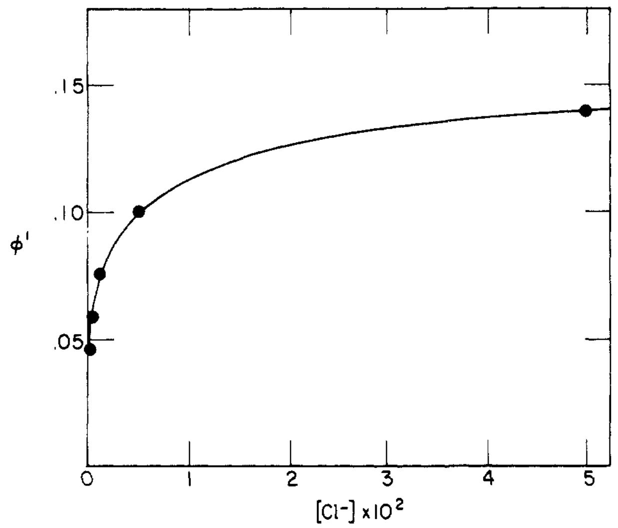

Figure 5. The observed initial quantum yield ϕ' for the formation of $MV^+{\cdot}Cl^-$ in CH_3OH vs. the Cl^- concentration ($[MV^{2+}(Cl^-)_2] = 4 \times 10^{-5}$M; 248.8-nm excitation wavelength).

instead of a diffusion-limited quenching of a hypothetical $MV^{2+}(Cl^-)_2$ excited state

$$CH_3OH + MV^{2+}(Cl^-)_2 \xrightarrow{h\nu} CH_3O{\cdot} + MV^+{\cdot}Cl^- + H^+ + Cl^- \quad (c')$$

$$CH_3O{\cdot} + MV^{2+}(Cl^-)_2 \rightarrow CH_2{=}O + MV^+{\cdot}Cl^- + H^+ + Cl^- \quad (d')$$

The methanol-methyl viologen complex was first suggested by Brown et al.[6] Subsequently it was supported by an argument advanced by Rodgers[7] based on the lifetime of the methoxy radical produced through flash photolysis of $MV^{2+}(Cl^-)_2$ in methanol which was an order of magnitude longer lived than that observed in the pulse radiolysis of methanol.[19]

To try to distinguish between the two mechanisms above and to analyze the first step (c or c′) for which little is known, we carried out a number of experiments in both pure CH_3OH and in mixed H_2O–CH_3OH solutions.

a. Pure Methanol. Role of Cl⁻. In pure CH_3OH no $Cl_2^-{\cdot}$ was observed upon irradiation, only the radical $MV^+{\cdot}Cl^-$ is spectrally detected on a nanosecond time scale. However, the yield of $MV^+{\cdot}Cl^-$ in the first step is dependent on the Cl^- concentration (Figure 5), indicating that a chloride species is involved in the formation of $MV^+{\cdot}Cl^-$. It cannot be $Cl_2^-{\cdot}$ as it reacts too slowly with CH_3OH (3.5×10^3 M^{-1} s^{-1})[20] to have disappeared on our time scale. This leaves only $Cl{\cdot}$, a reactive precursor of $Cl_2^-{\cdot}$, as a possible candidate for the above observations. The formation of $MV^+{\cdot}Cl{\cdot}$ must be intracomplex since the lowest Cl^- concentration ($<10^{-4}$ M) still gave $MV^+{\cdot}Cl^-$ at 10^{-8} s and with no apparent growth kinetics, thereby excluding the possibility of a collisional quenching of a MV^{2+} excited state by Cl^-. It should be remarked, however, that we were not able to plot $1/\phi'$ vs. $1/[Cl^-]$ and obtain a linear plot, as in aqueous solutions for the dichloride complex, most probably because we were not able to adequately maintain a constant ionic strength in methanol. However, an approximate lower limit value on the monochloride association constant in methanol can be estimated from the plateau region in Figure 5: $>2 \times 10^2$ M^{-1}. Thus step c or c′ involves the intermediate $MV^+Cl{\cdot}$ formed intramolecularly from the monochloride complex, $(MV^{2+}Cl^-)Cl^-$.

Figure 5 also shows that at the higher chloride concentrations the observed quantum yield approaches the plateau which is very close to the quantum yield of $MV^+{\cdot}Cl_2^-{\cdot}$ formation in H_2O (0.2) within experimental error. This suggests that the quantum yield of $MV^+{\cdot}Cl{\cdot}$ formation is the limiting factor in the overall quantum yield of photoinduced charge transfer in methyl viologen.

Methanol-Methyl Viologen Complexation. In an effort to distinguish between the two mechanisms: (c and d) and (c′ and d′), we first monitored the change in $MV^{2+}(Cl^-)_2$ absorbance induced by CH_3OH to detect any complexation. Using the Benesi-Hildebrand method, we obtained a linear curve with a correlation coefficient of 0.9998. However, the intercept was so near zero that the MV^{2+}–CH_3OH association constant K_{OH}, could not be determined with any precision. It is possible that the determination was further complicated by solvent effects. However, our results suggest, in agreement with previous analysis,[6,7] that $MV^{2+}(Cl^-)_2$ and CH_3OH form a complex although with a very weak interaction, i.e., small K_{OH}. To try to confirm this point we studied the competition between Cl^- and CH_3OH for MV^{2+} Cl^- in mixed H_2O–CH_3OH solutions as observed through photolysis.

b. Mixed H_2O-CH_3OH Solutions. We have seen now that in water $MV^+{\cdot}Cl_2^-{\cdot}$ is generated while in CH_3OH, $MV^+{\cdot}Cl^-$ is formed under photolysis. In mixed H_2O–CH_3OH solutions there is competition between the two processes. $Cl_2^-{\cdot}$ and $MV^+{\cdot}$ are generally both formed but not in equimolar concentrations as in pure H_2O. The yield of $Cl_2^-{\cdot}$ is dependent on the ratio of $[Cl^-]/[CH_3OH]$. This would be the case if there were two competing reactions of the same type: either first-order reactions competing through complexation or second-order reactions. Since we know that $MV^+{\cdot}Cl_2^-{\cdot}$ formation is intracomplex and that as we have just seen there is strong evidence for MV^{2+}-Cl^-CH_3OH complexation, it seems most reasonable that we are faced with two first-order reactions competing through complexation:

$$(MV^{2+}Cl^-) + Cl^- \underset{}{\overset{K_{2Cl}}{\rightleftharpoons}} (MV^{2+}(Cl^-)_2) \quad (e)$$

$$(MV^{2+}Cl^-) + CH_3OH \overset{K_{OH}}{\rightleftharpoons} (MV^{2+}Cl^-{-}CH_3OH) \quad (f)$$

Then upon irradiation

$$(MV^{2+}(Cl^-)_2) \xrightarrow{h\nu} (MV^+{\cdot}Cl{\cdot}Cl^-) \rightarrow MV^+{\cdot}Cl_2^-{\cdot} \quad (g)$$

and

$$(MV^{2+}Cl^-{-}CH_3OH) \xrightarrow{h\nu} (MV^+{\cdot}Cl{\cdot}{-}CH_3OH) \rightarrow MV^+{\cdot}Cl^-{-}CH_3O{\cdot} + H^+ \quad (h)$$

To check our results with the above scheme we assumed that in a first approximation we have

$$K_{2Cl} = \frac{[(MV^{2+}(Cl^-)_2)]}{[(MV^{2+}Cl^-)][Cl^-]} \quad (i)$$

$$K_{OH} = \frac{[(MV^{2+}Cl^-{-}CH_3OH)]}{[(MV^{2+}Cl^-)][CH_3OH]} \quad (j)$$

and that the constants are independent of the variation in solute and solvent composition. Then

$$\frac{[(MV^{2+}Cl^-{-}CH_3OH)]}{[(MV^{2+}(Cl^-)_2)]} = \frac{K_{OH}[CH_3OH]}{K_{2Cl}[Cl^-]} \quad (k)$$

The ratio of the yields of reactions g and h will be equal to the ratio of the species complexed one way or the other as given by the above equality k. In our laser flash pho-

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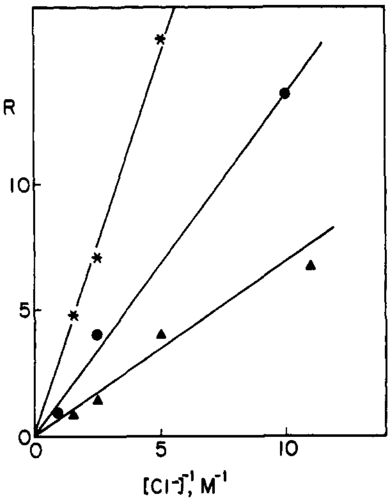

Figure 6. R, the ratio of the yields of the two competing reactions h and g in mixed CH_3OH–H_2O solutions (see text): (*) 40% CH_3OH, $K_{OH}/K_{2Cl} = 0.33$; (●) 25% CH_3OH, $K_{OH}/K_{2Cl} = 0.20$; (▲) 20% CH_3OH, $K_{OH}/K_{2Cl} = 0.15$ ($[MV^{2+}(Cl^-)_2] = 8 \times 10^{-5}$ M, 248.8-nm excitation wavelength).

tolysis experiment we observe the total yield of $MV^{+}\cdot$ formed through reactions g and h, but $Cl_2^{-}\cdot$ gives only the yield of reaction g. Thus

$$\frac{[MV^{+}\cdot] - [Cl_2^{-}\cdot]}{[Cl_2^{-}\cdot]} = \frac{K_{OH}[CH_3OH]}{K_{2Cl}[Cl^-]} = R \qquad (1)$$

R can be calculated from our experimental values of $[MV^{+}\cdot]$ and $[Cl_2^{-}\cdot]$ and plotted against $1/[Cl^-]$ for a given $[CH_3OH]$. As can be seen in Figure 6 we obtained linear plots, giving an average value for $K_{OH}/K_{2Cl} = 0.25$ (±0.1) for a large number of experimental runs in a CH_3OH range of 20–50%. The sample of curves given in Figure 6 show not only the linearity but also the rather large error margin inherent to the experiment. The latter is due to several factors: maintaining the CH_3OH concentration constant while degassing, variation in the ionic strength, and most importantly the increasing uncertainty in R as R increases, i.e., measuring correctly small values of $[Cl_2^{-}\cdot]$ as compared with $[MV^{+}\cdot]$.

We conclude that the photochemistry of $MV^{2+}(Cl^-)_2$ in methanol involves a weak complex between methyl viologen and methanol, i.e., reactions c and d are the most appropriate with the overall results above. In the next section we will recapitulate our results by giving the mechanisms of the photochemistry of $MV^{2+}(Cl^-)_2$ in both H_2O and CH_3OH, and then conclude. But before, in view of our observations, it is worth mentioning the report by Kaneko et al.[21] on the photoreduction of $MV^{2+}(Cl^-)_2$ on solid-phase cellulose. The ground-state $MV^{2+}(Cl^-)_2$ absorption spectrum apparently had a red shift (indicating either interaction with the cellulose or/and complete complexation by the Cl^- counterion in the solid state). An alcohol group of the cellulose was transformed to a ketone and the radical $MV^{+}\cdot$ formed was reported to have specific absorption on the cellulose. This is strikingly similar to the situation in methanol. Thus we might speculate that, just as in CH_3OH, the radical $Cl\cdot$ is also an intermediate in the solid-phase process.

Summary and Conclusion

The photochemistry of $MV^{2+}(Cl^-)_2$ is characterized by the following mechanism in water based on our results:

$$MV^{2+} + Cl^- \rightleftharpoons (MV^{2+}Cl^-) \qquad K_{1Cl} \qquad (1)$$

$$(MV^{2+}Cl^-) + Cl^- \rightleftharpoons (MV^{2+}(Cl^-)_2) \qquad K_{2Cl} = 1.5\ M^{-1} \qquad (2)$$

$$(MV^{2+}(Cl^-)_2) \xrightarrow{h\nu} (MV^{+}\cdot Cl\cdot Cl^-) \qquad \phi_3;\ k_3 > 10^8\ s^{-1} \qquad (3)$$

$$(MV^{+}\cdot Cl\cdot Cl^-) \rightarrow MV^{2+}(Cl^-)_2 \qquad k_4 \qquad (4)$$

$$(MV^{+}\cdot Cl\cdot Cl^-) \rightarrow MV^{+}Cl_2^{-}\cdot \qquad \phi_5 = 0.2;\ k_5 > 10^8\ s^{-1} \qquad (5)$$

$$MV^{+}Cl_2\cdot^{-} \rightarrow MV^{2+}(Cl^-)_2 \qquad k_6 \qquad (6)$$

where reaction 6 is second order.

In methanol where $MV^{+}\cdot Cl^-$ is the end product, the mechanism is different

$$MV^{2+} + Cl^- \rightleftharpoons (MV^{2+}Cl^-) \qquad K'_{1Cl} > 2\ 10^2\ M^{-1} \qquad (7)$$

$$(MV^{2+}Cl^-) + CH_3OH \rightleftharpoons (MV^{2+}Cl^-–CH_3OH) \qquad K_{OH} \qquad (8)$$

$$(MV^{2+}Cl^-–CH_3OH) \xrightarrow{h\nu} (MV^{+}\cdot Cl\cdot–CH_3OH) \qquad \phi_9;\ k_9 > 10^8\ s^{-1} \qquad (9)$$

$$(MV^{+}\cdot Cl\cdot–CH_3OH) \rightarrow (MV^{2+}Cl^-–CH_3OH) \qquad k_{10} \qquad (10)$$

$$(MV^{+}\cdot Cl\cdot–CH_3OH) \rightarrow (MV^{+}\cdot Cl^-–CH_3O\cdot) + H^+ \qquad \phi_{11} \geq 0.16;\ k_{11} > 10^8\ s^{-1} \qquad (11)$$

$$(MV^{+}\cdot Cl^-–CH_3O\cdot) + MV^{2+}(Cl^-)_2 \rightarrow CH_2O + 2MV^{+}\cdot Cl^- + H^+ + Cl^- \qquad k_{12} = 5.1 \times 10^8\ M^{-1}\ s^{-1}\,{}^{7} \qquad (12)$$

We have shown, for the first time, that the $MV^{2+}(Cl^-)_2$ photochemistry is tied directly to the existence of ground-state charge-transfer complexation with the halide counterion(s) both in H_2O and in CH_3OH. In methanol the formation of the methoxy radical involves the radical pair $MV^{+}\cdot Cl\cdot$ as intermediate. Our results are in agreement with previous speculations that a weak complex between methanol and methyl viologen is involved. In H_2O, the ground-state dichloride complex is necessary for the formation of $MV^{+}\cdot Cl_2^{-}\cdot$. The precursor $MV^{+}\cdot Cl\cdot$ is strongly stabilized by the $Cl_2^{-}\cdot$ formation.

While changing the counterion to the halides Br^- and I^- increased the charge-transfer absorption band toward the visible part of the spectrum, the internal heavy-atom effect reduced the quantum yield of the photochemistry so effectively that it more than offset the gain in ground-state absorption. However, the stability of the radical pairs of the type $MV^{+}\cdot X_2^{-}\cdot$ has encouraged us to study such salts as $MV^{2+}(SCN^-)_2$. The latter seems to combine the relatively high quantum yield feature of $MV^{2+}(Cl^-)_2$ with the much stronger absorption characteristics of the other halides. This will be reported in a following paper.

So far we have not discussed the photophysics of methyl viologen since all that has been observed here, on the nano-second time scale, is that some intersystem crossing is enhanced by Br^- and I^-, thereby reducing the final quantum yield of $MV^{+}\cdot X_2^{-}\cdot$ formation. We are presently undertaking a picosecond study which should clarify the early processes leading to the observed photochemistry and give some of the rate constants that elude the nanosecond time scale.

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Registry No. $MV^{2+}(Cl^-)_2$, 1910-42-5; $MV^{2+}(Br^-)_2$, 3240-78-6; $MV^{2+}(I^-)_2$, 1983-60-4; $MV^{+}Cl^-$, 53086-17-2; $MV^{+}Cl_2^-$, 86633-03-6; H_2O, 7732-18-5; CH_3OH, 67-56-1.

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