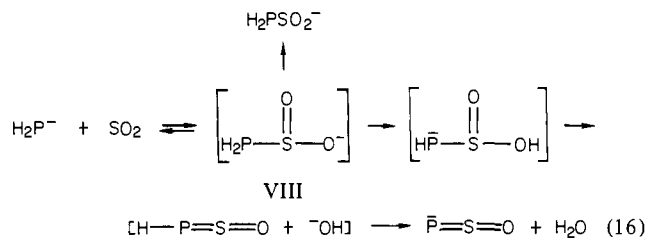


gas-phase examples except for studies of the thermodynamic properties of gaseous EuPO_2^{21} and of gaseous NaPO_2^{22} . Nitrogen dioxide, with its very large electron affinity of 2.4 eV,²³ readily accepts an electron from H_2P^- at about the collision rate, giving solely NO_2^- and H_2P ($\text{EA}(\text{H}_2\text{P}) = 1.25 \text{ eV}$).^{24,25}

Approximately one third of the reaction between phosphide and sulfur dioxide also proceeds by electron transfer. However the remainder of the reaction occurs by pathways similar to those described for OCS and CS_2 . The PSO^- ion is formed by initial nucleophilic attack at sulfur, proton transfer from phosphorus to oxygen, loss of HO^- , and finally proton abstraction (eq 16); al-



ternatively, collisional stabilization of the intermediate VIII gives the adduct H_2PSO_2^- . The PSO^- ion has been observed in the negative ion mass spectra of the organophosphorus pesticides Dursban and Azinphos Methyl,²⁶ but we have found no examples of the adduct H_2PSO_2^- .

We cannot speculate confidently at this time as to whether the ion at m/z 63 is PO_2^- or PS^- (eq 7c), though we favor the former since loss of HS^- from some reactive complex should be more favorable, on a gas-phase acidity basis, than loss of HO_2^- . Either of the possibilities can, however, be tested. The two candidates for this product ion have been generated independently in other reactions, PS^- from phosphide and carbon disulfide and PO_2^- from phosphide and oxygen. Therefore a study of their subsequent ion-molecule reactions, for example, $\text{PS}^- + \text{CS}_2 \rightarrow \text{PS}_2^- + \text{CS}$,

may allow qualitative identification of the unknown species in the reaction of H_2P^- and SO_2 . We will report on developments in this area in forthcoming publications.

D. Reactions of H_2P^- with CH_3X and $(\text{CH}_3)_3\text{SiCl}$. Phosphide reacts with trimethylsilyl chloride at the collision rate presumably because of the ease with which silicon can accommodate a pentacoordinate intermediate. However, the reaction efficiency diminishes rapidly through the series $\text{CH}_3\text{I} > \text{CH}_3\text{Br} > \text{CH}_3\text{Cl}$ (Table II). Since amide reacts rapidly with all the methyl halides and with trimethylsilyl chloride,²⁷ it is clear that phosphide is considerably less nucleophilic than amide. This supports the observation that phosphide reacts much less efficiently than amide with the molecules listed in Table II, whenever a nucleophilic mechanism is involved.

Conclusion

With this study we have accomplished several objectives. We have shown that phosphide reacts readily with a variety of molecules via familiar reaction mechanisms, including proton transfer, electron transfer, nucleophilic addition, and nucleophilic substitution. Many similarities exist between the reactions of phosphide and those of amide. However, we have elucidated some distinct differences in both the reactivity and mechanism and have attributed these differences to properties such as basicity, nucleophilicity, bond strengths, and electron affinities. The reactions allow the gas-phase synthesis of many previously unknown phosphorus-containing anions. We plan to explore further the ion-molecule chemistry of these species including their reactivity, basicity, and nucleophilicity.

Acknowledgment. We gratefully acknowledge support of this work by the U.S. Army Research Office.

Registry No. H_2P^- , 13937-34-3; N_2O , 10024-97-2; CO_2 , 124-38-9; OCS, 463-58-1; CS_2 , 75-15-0; O_2 , 7782-44-7; NO_2 , 10102-44-0; SO_2 , 7446-09-5; $(\text{CH}_3)_3\text{SiCl}$, 75-77-4; CH_3Cl , 74-87-3; CH_3Br , 74-83-9; CH_3I , 74-88-4.

- (21) Balducci, G.; Gigli, G.; Guido, M. *J. Chem. Phys.* **1979**, *70*, 3146.
 (22) Gingerich, K. A.; Miller, F. *J. Chem. Phys.* **1975**, *63*, 1211.
 (23) Dunkin, D. B.; Fehsenfeld, F. C.; Ferguson, E. E. *Chem. Phys. Lett.* **1972**, *15*, 257.
 (24) Smyth, K. C.; Brauman, J. I. *J. Chem. Phys.* **1972**, *56*, 1132.
 (25) Smyth, K. C.; McIver, R. T.; Brauman, J. I.; Wallace, R. W. *J. Chem. Phys.* **1971**, *54*, 2758.
 (26) Harvan, D. J.; Hass, J. R.; Busch, K. L.; Bursey, M. M.; Ramirez, F.; Meyerson, S. *J. Am. Chem. Soc.* **1979**, *101*, 7409.

- (27) Unpublished results from this laboratory.
 (28) Su, T.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 347.
 (29) DePuy, C. H., unpublished results.
 (30) Ferguson, E. E.; Fehsenfeld, F. C.; Schmeltekopf, A. L. *Adv. Chem. Ser.* **1969**, *No. 80*, 83.
 (31) Tanaka, K.; Mackay, G. I.; Payzant, J. D.; Bohme, D. K. *Can. J. Chem.* **1976**, *54*, 1643.
 (32) Damrauer, R.; DePuy, C. H.; Bierbaum, V. M. *Organometallics* **1982**, *1*, 1553.

Association of Methyl Viologen and Its Cation Radical with Dihexadecyl Phosphate Vesicles

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Abstract: A strong association of methyl viologen with negatively charged DHP vesicles is demonstrated. This adsorption is probed with ESR spectroscopy which monitors the formation of the methyl viologen cation radical produced by UV irradiation. This interaction is shown to be electrostatic in nature since no association was observed with the positively charged dioctadecyldimethylammonium bromide vesicles. The interaction is of sufficient strength with DHP that the methyl viologen is not removed when the dispersion undergoes gel filtration on a Sephadex column. These results have important implications to vesicular studies which utilize methyl viologen as an electron acceptor.

Methyl viologen, MV^{2+} , is an electron acceptor frequently used in both homogeneous¹ and heterogeneous² solar-energy-converting

systems. The radical cation of methyl viologen, $\text{MV}^{\cdot+}$, usually formed via a photosensitized electron-transfer process can generate

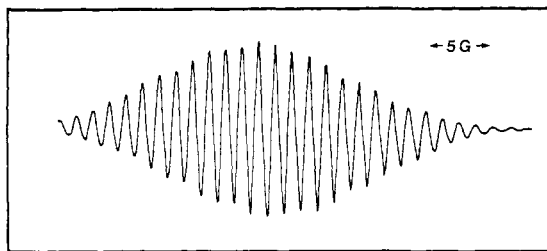


Figure 1. ESR spectrum obtained upon UV photolysis of a 2.5×10^{-4} M MV^{2+} aqueous solution which had been thoroughly purged with argon. Instrument settings: microwave power, 7 MW; modulation amplitude, 2.5 G scan time, 4 min; time constant, 0.128 s.

hydrogen from water provided a proper catalyst is present. Such a process is strongly dependent on the properties of the system employed. One such heterogeneous system uses surfactant vesicles which differ from other surfactant aggregates (micelles, microemulsions) by having a closed bilayer structure.³ These structures are considered promising due to their potential to separate the oxidizing and reducing products of photosensitized redox reactions.^{2c,d,4}

The effects of hydrophobic and hydrophilic character of the electron donor and acceptor as well as the surface properties of vesicles on the efficiency of the electron-transfer process leading to the formation of MV^{+} have been recognized.^{4b,5} However, the nature of the interaction of MV^{2+} (and its reduced form, MV^{+}) with the charged vesicle interface and the influence of this interaction on MV^{+} formation have not yet been reported. In the present paper, we address these issues by determining the effect of both positively and negatively charged surfactant vesicles on the direct photochemical formation of MV^{+} in the presence and absence of the sacrificial electron donor, ethylenediaminetetraacetic acid (EDTA).

Experimental Section

Dihexadecyl phosphate (DHP) and dioctadecyldimethylammonium bromide (DODAB) were purchased from Fisher and ICN Pharmaceutical, respectively. Both surfactants were recrystallized from acetone and methanol, respectively. Dioctadecyldimethylammonium chloride (DODAC) was prepared by passing a methanol/water solution of DODAB twice through a freshly prepared chloride ion exchange resin, followed by recrystallization from methanol. EDTA (Aldrich) and MV^{2+} (BDH) were used without further purification.

Vesicle dispersions containing 5 mg of surfactant per mL of water were prepared by sonification at elevated temperatures. Following 10 min of centrifugation, the vesicles were passed through a Sephadex column (18 cm \times 1.5 cm). The final concentration of the surfactants in a typical sample containing 25×10^{-4} M MV^{2+} and/or 2.5×10^{-3} M EDTA was about 3×10^{-3} M and 3.5×10^{-3} M of DODAB and DHP, respectively.

ESR spectra were obtained on a Varian E109E spectrometer with the TM_{110} cavity. The solutions were purged for 15 min with argon prior to each run.

Results and Discussion

Viologens readily undergo photochemical reduction to their radical cations in both aqueous and alcoholic deaerated solution.^{6,7} When a solution of MV^{2+} is irradiated with UV light of about 260 nm (abs max),⁸ the formation of MV^{+} is manifested by the appearance of a blue color ($\epsilon_{609} = 1.4 \times 10^4$ M⁻¹ cm⁻¹).⁸ In

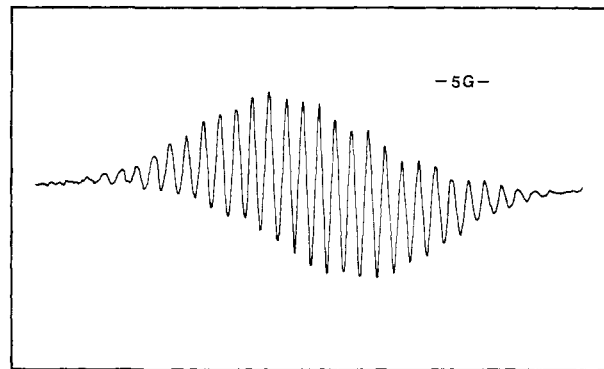
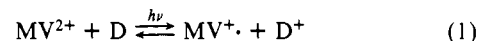


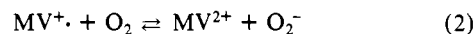
Figure 2. ESR spectrum obtained upon UV photolysis of a 2.5×10^{-4} M MV^{2+} aqueous solution containing 2.5×10^{-3} M EDTA and DHP vesicles (0.2 wt %). Instrument settings are as in Figure 1.

addition to the optical detection of MV^{+} , a more sensitive monitoring of MV^{+} is provided by the ESR technique. Therefore, in the present study, we chose to generate MV^{+} by UV excitation of MV^{2+} while monitoring the reduced species "in situ" with ESR spectroscopy. Although the exact mechanism for MV^{+} formation is unknown, the process can be represented by eq 1, where D represents an electron donor. In the absence of an added donor, D most likely is the chloride counterion which is complexed with MV^{2+} .⁹



Hence, addition of an electron donor such as EDTA should enhance the formation of MV^{+} . Figure 1 presents the expected ESR signal of MV^{+} ,^{6,7} produced upon illumination of 2.5×10^{-4} M MV^{2+} in water. When EDTA was added (2.5×10^{-3} M), the ESR signal intensity was increased approximately four times. These intensities were determined at the maximum in a plot of MV^{+} production vs. time of illumination. For a longer time of illumination, a reduction in intensity was observed, presumably the result of the photochemical destruction of MV^{+} itself. These ESR signal intensities of the MV^{+} in water (control) were used as reference values for the experiments in vesicular systems.

It is interesting to note that in the control experiments as well as in the experiments with vesicles described below, residual O_2 can significantly alter the results. When O_2 was not completely removed (due to insufficient purging), we observed an induction period before the MV^{+} could be detected. This is accounted for by eq 2, where superoxide, O_2^{-} , is generated.^{2b} O_2^{-} can dispro-



portionate or react with other species present to eventually rid the solution of O_2 . In order to circumvent this induction period, we rigorously purged the solution with argon directly in the ESR cell. These results point out the critical dependence of experimental results on residual O_2 in systems where MV^{+} is produced.

In the DHP vesicle system¹⁰ the photochemical formation of MV^{+} was significantly reduced over that of the control. In addition, the ESR spectrum (Figure 2) is broadened as evidence by the more pronounced derivative shape. This broadening prevents a direct comparison of intensities; nevertheless, it is estimated that formation of MV^{+} is reduced by approximately one order of magnitude over the control. The presence of DHP vesicles has therefore altered both the production efficiency and the environment of MV^{+} .

The ESR broadening suggests that the MV^{+} is adsorbed on the surface of the DHP vesicles. Since the vesicles are negatively charged,¹¹ it is expected that both MV^{2+} and MV^{+} should be electrostatically attracted to the vesicle surface. An immobilization (on the ESR time scale) of MV^{+} as a result of this electrostatic

(1) Whitten, D. G. *Acc. Chem. Res.* **1980**, *13*, 82. Meyer, T. J. *Ibid.* **1978**, *11*, 94.

(2) (a) Harbour, J. R.; Hair, M. L. *J. Phys. Chem.* **1977**, *81*, 1791. (b) Henglein, A. *Ibid.* **1982**, *86*, 2291 and references therein. (c) Brugger, P.-A.; Grätzel, M. *J. Am. Chem. Soc.* **1980**, *102*, 2461 and references therein. (d) Ford, W. E.; Otvos, J. W.; Calvin, M. *Nature (London)* **1978**, *274*, 507. (e) Infelta, P. P.; Fendler, J. H.; Grätzel, M. *J. Am. Chem. Soc.* **1980**, *102*, 1479.

(3) Fendler, J. H. *Acc. Chem. Res.* **1980**, *15*, 7.

(4) (a) Tunuli, M. S.; Fendler, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 2507. (b) Monserrat, K.; Grätzel, M. *Ibid.* **1981**, *103*, 184. (c) Katagi, T.; Yamamura, T.; Saito, T.; Sasaki, Y. *Chem. Lett.* **1981**, 1451.

(5) Tunuli, M. S.; Fendler, J. H. *ACS Adv. Chem. Ser.* **1982**, *177*, 53.

(6) Bruim, F.; Heineken, F. W.; Bruin, M.; Zahlan, A. *J. Chem. Phys.* **1982**, *36*, 2783.

(7) Johnson, C. S., Jr.; Gutowsky, H. S. *J. Chem. Phys.* **1963**, *39*, 58.

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

(9) Ebbesen, T. W.; Levey, G.; Patterson, L. K. *Nature (London)* **1982**, *298*, 547. We thank a referee for bringing this reference to our attention.

(10) Lukac, S.; Harbour, J. P. *J. Chem. Soc., Chem. Commun.* **1982**, 154.

(11) Lukac, S., submitted for publication.

interaction would result in the observed broadening. Alternatively, an electron transfer between MV^+ and adsorbed MV^{2+} could also account for the broadening or even electron exchange between adsorbed MV^+ radicals.¹² In either case, a strong interaction with the surface is suggested.

The reduced production of MV^+ most likely results from the repulsion of the Cl^- by the negatively charged DHP vesicles. In other words, the MV^{2+} , upon adsorption at the vesicular surface, has exchanged the Cl^- for a phosphate group. This loss of the Cl^- greatly reduces the quantum yield of MV^+ production. However, a contribution from surface immobilization of MV^{2+} to a reduced photoproduction of MV^+ cannot be completely disregarded. In such a case, the rate of the back reaction of eq 1 may be increased and/or the efficiency of generation reduced due to the different environment the MV^{2+} experiences on the vesicle interface.

Addition of EDTA to the DHP dispersion results in a less than 2-fold increase in intensity as compared to the control samples in which a 4-fold increase was observed. This result suggests that MV^{2+} in its adsorbed state is partially shielded by the negative charge of the vesicle's interface which tends to repel the negatively charged EDTA (at pH 7; EDTA exists as dianion) thereby reducing the interaction of EDTA with MV^{2+} .

The appearance of such a small ESR signal for MV^+ in these DHP vesicle systems, coupled with the observed line broadening, suggests that essentially all of the MV^{2+} is strongly adsorbed to the vesicle surface. This is feasible since a calculation assuming an "average" vesicle diameter¹³ of 1000 Å and a loading of 0.2% wt% DHP results in a surface area that is more than sufficient to accommodate all of the 2.5×10^{-4} M MV^{2+} . Lysing of the DHP vesicles (containing adsorbed MV^{2+}) by freezing and subsequent centrifugation resulted in an ESR spectrum as shown in Figure 1. This also demonstrates the direct involvement of the vesicles in producing the observed changes.

If the interaction between MV^{2+} and DHP is strong, it becomes of practical interest to determine whether or not the MV^{2+} can be removed from the surface of vesicles by passage through a Sephadex column. This is a conventional method for the preparation of asymmetric vesicles free from solutes which are external to the vesicles. When such an experiment was performed, it was determined that at least 50%¹⁴ of the MV^{2+} was retained by the surface of the vesicles. This evidence demonstrates the strong interaction of MV^{2+} with the DHP vesicle surface.

(12) Takuma, K.; Sakamoto, T.; Nagamura, T.; Matsuo, T. *J. Phys. Chem.* **1981**, *85*, 619.

(13) The average diameter of DHP vesicles of 1000 Å was obtained by the comparison of electron microscopy data with those from light-scattering experiments: Lukac, S.; Perovic, A.; Desgreniers, S.; Landheer, D., unpublished results.

(14) Since an undetermined dilution occurs when vesicles are passed through the column, this value represents a minimum in comparison to the control.

The addition of DODAB vesicles into MV^{2+} solution also significantly reduced the MV^+ signal (by about factor 10) upon irradiation. Nevertheless, the signal remained well resolved (as in Figure 1). Interestingly, when EDTA was added, a rise of the signal to a level comparable with that of the control was observed. Such behavior was paralleled in an independent experiment which showed that KBr in homogeneous solution significantly reduces MV^+ formation and that addition of EDTA brings back the normal level of production. This can be explained by eq 1 where Br^- replaces Cl^- as the donor and the back reaction of Br^- and MV^+ becomes very fast. Addition of EDTA provides a more suitable donor and gives rise to the normal production rate. Hence in the DODAB experiments, Br^- is partially exchanged with the Cl^- (counterion of MV^{2+}) and the production is significantly reduced. This explanation of the effect of DODAB vesicles was confirmed in an experiment with DODAC (chlorine derivate of DODAB) vesicles where no significant decrease in MV^+ production was observed. Hence, these experimental results support the contention that Cl^- acts as a donor in the system not containing EDTA.

The results with DODAB demonstrate that the MV^{2+} is not affected by the positively charged DODAB vesicle surfaces and reacts as if in solution. This is corroborated by an experiment in which passage of a DODAB/ MV^{2+} system through the Sephadex column resulted in a vesicle system free of MV^{2+} .

Our experimental results reveal the complexities associated with the utilization of MV^{2+} as an electron acceptor in heterogeneous systems. The induction period can be essentially reduced to zero provided sufficient purging of oxygen is achieved. In the presence of negatively charged DHP vesicles, very strong association with MV^{2+} occurs which results in the complete adsorption of MV^{2+} onto the DHP vesicles. (This of course will depend on the ratio of MV^{2+} to vesicle surface area.) This phenomenon is consistent with the fact that a significant percentage of the MV^{2+} is retained by the DHP vesicles during passage through the Sephadex column. The photogenerated MV^+ is also strongly adsorbed to the vesicle surface as evidenced by the broadening in the ESR spectrum.

Such a strong interaction of both MV^{2+} and MV^+ with DHP vesicles is of considerable significance and it should be taken into account in all studies where negatively charged vesicles (or other surfaces) are employed in conjunction with MV^{2+} .^{4a,15} Positively charged DODAB (or DODAC) vesicles, on the other hand, do not affect the distribution or photochemical efficiency of MV^{2+} production. This "in situ" monitoring of the MV^+ formation by ESR spectroscopy provides a very sensitive means of probing the associative nature of MV^+ with vesicular surfaces.

Registry No. Methyl viologen, 1910-42-5; dihexadecyl phosphate, 2197-63-9; ethylenediaminetetraacetic acid, 60-00-4.

(15) Lee, L. Y.-C.; Hurst, J. K., presented at 183rd ACS National Meeting, Las Vegas, March, 1982.