Chem. Mater. **1995,** *7,* 2054–2057

Preparation of a Photochromic Glass Doped with Methylviologen Radical Cation via a Sol–Gel Process

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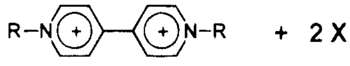
Received February 27, 1995. Revised Manuscript Received June 29, 1995[®]

Methylviologen cation radical is produced by photolysis of methyl viologen dichloride entrapped in a sol–gel glass. The sol–gel glass is shown to be microporous, and it is suggested that the microporosity prevents oxygen diffusion thereby helping to extend the lifetime of the cation radical to a period of months. Initial losses of a substantial fraction of the charge separation are not observed. These results bear directly on efficient photochemical energy storage.

Introduction

Viologens represented in Scheme 1 are important redox reagents that are employed as herbicides and used as mediators of one-electron-transfer processes in solar energy conversion and storage.[2,3] Their cation radicals can be produced by either chemical reduction or photoreduction of the corresponding viologens.[4] The cation radicals thus generated are stable only in the absence of air. They have distinctive colors and associated UV–visible spectra and are popular as redox indicators in photosynthetic research. Various strategies have recently been developed to stabilize photogenerated viologen cation radicals in the presence of air with the goal of efficient photochemical energy storage.[5–9] Specifically, Vermeulen and Thompson reported the successful production of long-lived viologen cation radicals in a layered inorganic matrix.[8,9] Some of the initial charge separation in these layered inorganic matrixes was lost within the first few hours, but some cation radical was retained for periods of up to several months. It was suggested that electron transfer from associated halide ions to the viologen was responsible for the initial charge separation and that reactions which consumed the resulting halogen atoms prevented back electron transfer. In addition, the stability of the system in air was reportedly due to limited diffusion of oxygen within the solid.[8b] In an earlier report, Slama-Schwok et al. showed that methylviologen cation radical ($MV^{\bullet+}$) can be photochemically generated under a nitrogen atmosphere in a base-catalyzed sol–gel glass matrix via electron transfer (ET) from the excited state of pyrene.[7] This ET process is mediated by a third, mobile, charge carrier (*N,N'*-tetramethylene-2,2'-bipyridinium bromide) dissolved in the surrounding solution. The cation radical thus prepared can be stabilized for 4 h, and back electron transfer is reported to be responsible for loss of charge separation.[7]

Scheme 1



We describe an efficient and simple method to photochemically generate *air-insensitive* $MV^{\bullet+}$ in an acid-catalyzed sol–gel matrix. The $M^{\bullet+}$ formed in the acid-catalyzed glass in the presence of air persists for months in some cases with no visually detectable loss of intensity. As in the previous work described by Thompson et al., we attribute the long lifetime of charge separation in the sol–gel glass to limited oxygen diffusion and to reactions that consume the electron source and prevent back electron transfer. The sol–gel process is a technique that can be used to prepare transparent oxide glasses by hydrolysis and condensation of tetraalkylorthosilicates.[7,10–13] Little or no heating is required, and consequently the gel can be doped with molecules whose poor thermal stabilities preclude their incorporation in traditional inorganic hosts. Such molecules become entrapped in the growing covalent gel network rather than being chemically bound to the inorganic matrix.[7] The glasses can also be transparent such that the guest molecule can be electronically excited with visible or UV light. The pore size distribution and available surface area in the glass are functions of the method of glass preparation and curing.[14] It is

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[®] Abstract published in *Advance ACS Abstracts,* August 15, 1995.

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these properties which make the sol–gel technique an attractive one for the preparation of photochromic systems for energy storage.

Experimental Section

Methylviologen dichloride, $MVCl_2$ (Aldrich Chemical Co., >98%) was used as received as were all other reagents. In a typical run 0.03 g of $MVCl_2$ was mixed with 1.5 g of tetramethylorthosilicate (Aldrich Chemical Co., 99%), 0.2 g of water (Burdich and Jackson, HPLC grade), and 0.3 g of methanol (Baker Chemical Co., HPLC grade) followed by the addition of two drops of 1 M HCl solution. The final mixture was cured at ambient temperature over 2 weeks followed by heating at 100 °C for 6 h under a weak vacuum (~100 mmHg). The transparent glass was placed in a 0.02 M methanolic NaOH solution and allowed to stand for 12 h. Direct photolysis of the glass (300 nm, 1.6×10^{16} photons cm^{-2} s^{-1}, Rayonet Photoreactor, Southern New England Ultra Violet Co.) in the base solution gives rapid (less than 30 s) formation of a deep blue color ($MV^{\bullet +}$). Photolysis of the dry glass also produces the blue color. The photoreactor used in this study is also fitted with a small cooling fan to prevent sample heating during photolysis.

Absorption spectra were taken on a Cary 4 (Varian Corporation) UV–visible spectrometer running in the absorption mode. BET surface areas and porosity were measured on an Autosorb 1 (Quantachrom Corp.) gas sorption system. Using nitrogen as the adsorbent, 20-point adsorption isotherms and 20-point desorption isotherms were measured at 77 K after degassing the glasses under vacuum at 80 °C for 4 h.

Results and Discussion

In contrast the previous work by Slama-Schwok et al.,[7] photochemical generation of the radical cation described here does not rely on an ET-mediator solution and is more analogous to Thompson's systems.[8,9] Blue $MV^{\bullet +}$ is generated directly upon photolysis in a transparent sol–gel glass either dry or surrounded by a basic methanol solution. The glass formed in our experiments was prepared by an acid-catalyzed sol–gel process. Masking a portion of the glass to eliminate light exposure prevented formation of the blue $MV^{\bullet +}$, thus demonstrating the role of light in generating the cation radical under the experimental conditions. The lifetime of the cation radical prepared in this manner in glasses that are photolyzed and kept in the aerated basic methanol solution is virtually indefinite as opposed to the 4 h lifetime previously reported.[7] However, removal of the glass from the aerated solution in some instances results in fading of the blue $MV^{\bullet +}$ leaving a yellow species in the glass. In other cases the blue color is retained for months after removing the glass from the basic methanol solution. The property of the glass that allows it to support unquenched $MV^{\bullet +}$ is sensitive to several parameters. Curing the gel under vacuum is critical for long term retention of the blue $MV^{\bullet +}$. Further work is underway to systematically control all parameters affecting the properties of the glass. We believe that very small pores in the final glass are responsible for maintaining $MV^{\bullet +}$ in glasses exposed to air (vide infra).

A photograph of one piece of glass produced in these experiments is shown in Figure 1, and the associated UV–visible spectrum (taken by measuring the transmitted light) for the same piece of glass is shown in Figure 2. The UV–visible spectra of $MV^{\bullet +}$ in the transparent glass becomes increasingly intense with extended irradiation time. The basic spectral features are the same as those of $MV^{\bullet +}$ in a zeolite matrix[6] and in layered inorganic matrixes.[8] This demonstrates that $MV^{\bullet +}$ exists in the glass matrix as a discrete monomeric species. The identity of this species is further supported by the ESR spectrum of the colored glass showing a single transition ($g = 2.0029$), in excellent agreement with previous observations.[6] The source of reduction equivalent in our glasses is not known; however, evidence has been presented for layered inorganic systems which suggests that chloride ion is the electron source in those systems.[8b]

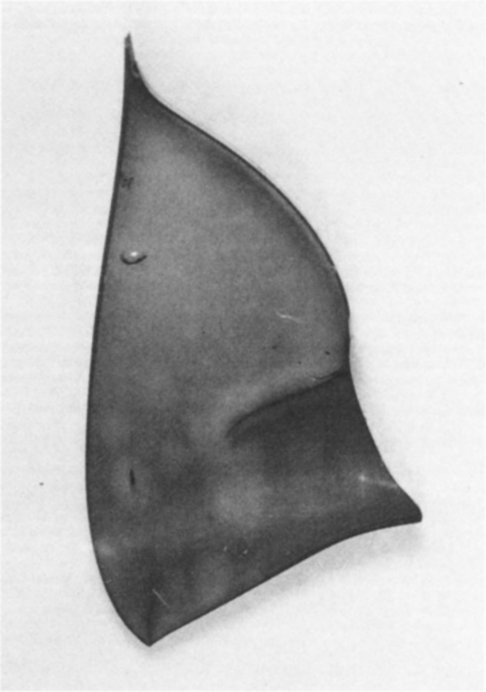

Figure 1. Sol–gel glass containing $MV^{\bullet +}$ produced by photolysis of the glass containing MV^{2+} in a basic methanol solution. The glass was removed from the basic methanol solution subsequent to photolysis and prior to being photographed.

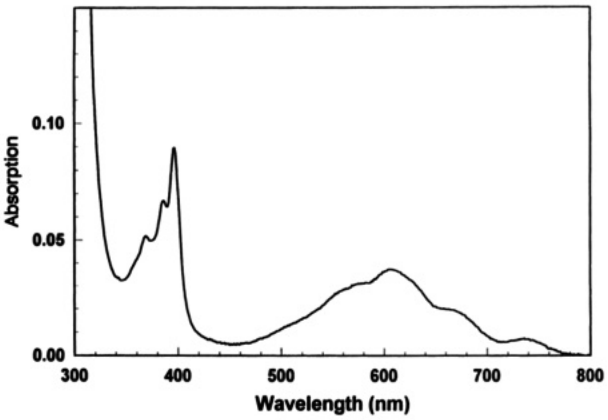

Figure 2. Absorption spectrum of $MV^{\bullet +}$ trapped in the sol–gel glass shown in Figure 1.

The surface areas and pore-size distribution were investigated for two samples produced in this investigation. One sample, referred to as sample A, retained the blue color associated with $MV^{\bullet +}$ in air for months with no visual sign of bleaching. The second sample, referred to as sample B, retained the blue color in air only for 3 h. The adsorption isotherms for both samples (Figure 3) resemble type I curves exhibited by microporous materials; however, at high P/P_0 values they both show a rapid increase in the volume of adsorbed nitrogen, indicative of a material containing macropores.[15] The

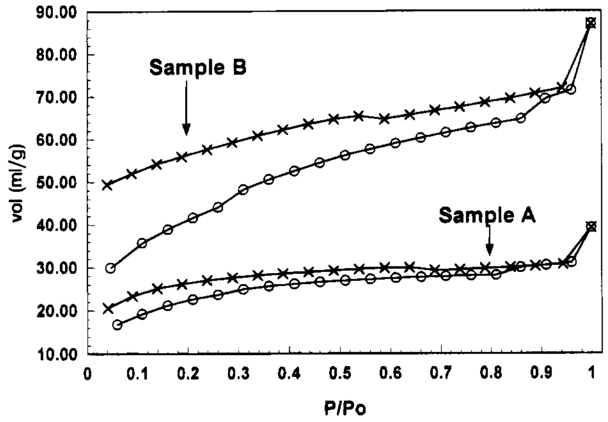

Figure 3. Adsorption isotherms for samples A and B (see text for sample descriptions).

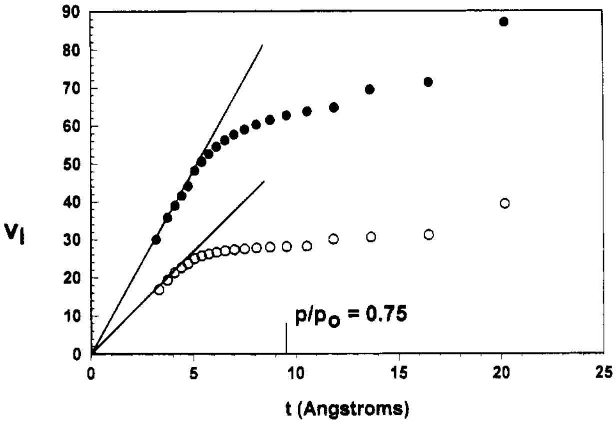

Figure 4. de Boer $v-t$ plot for samples A (open symbols) and B (closed symbols).

total pore volumes, determined at P/P_0 of 0.9994, were 0.0607 mL/g for sample A and 0.1347 mL/g for sample B and represent a significant difference in the two pieces of glass. The hysteresis loops observed in the adsorption–desorption isotherms for both samples did not close even at values of P/P_0 of 0.06, as occasionally observed for microporous materials.[15] The adsorption–desorption curves shown in Figure 3 were measured with a 2-min equilibration time. Extending the equilibration time to 6 min did not lead to closure of the hysteresis at low P/P_0 values, although extending the equilibration time has previously been shown to correct this behavior.[16] Samples A and B had N_2–BET surface areas, S_{BET}, of 81.17 and 148.1 m^2/g, respectively, for multipoint ($n = 4$, $r \geq 0.9999$) BET measurements at P/P_0 values less than 0.211. The observed BET values demonstrate a significant difference in the surface area available to nitrogen adsorption for the two samples. The corresponding BET constants, C, determined for samples A and B were 90.31 and 112.3, respectively. Both of these values are less than the value of 130 for C that was previously determined for a microporous silica gel sample.[15] The similarity of the two C values indicates that while the two samples have considerably different surface areas, they exhibit similar free energies of adsorption for interaction with nitrogen.

The magnitude of C determined for both samples also indicates that it is appropriate to use the t curve of de Boer for performing a micropore, MP, analysis on the glasses. The v_l-t curves for both samples are shown in Figure 4. Samples A (open circles) and B (closed circles) both show downward deviations from the de Boer straight line, indicating the presence of micropores for both samples. Both curves in Figure 4 also show upward trends at large t values, which correspond to high P/P_0 values. This is usually taken to indicate the presence of wide pores in addition to the micropores; however, the upward deviations occur at P/P_0 values greater than 0.75 where the de Boer t curve is thought to be incorrect, and care must be taken in interpreting the upward trend in the data.[15] The surface area calculated from the MP analysis, S_t, for samples A and B were 90.97 and 163.7 m^2/g, respectively.[15] The ratios of S_t/S_{BET} for the two samples are 1.121 (sample A) and 1.105 (sample B). The S_t values determined by the MP analysis cannot be better than S_{BET}, and the discrepancy observed here may be partly due to the presence of larger pores in the glasses. The percent of the total surface area in the micropores, as determined from the MP analysis of the cumulative area in micropores, is indistinguishable from 100%. The cumulative volume in micropores for samples A (0.047 42 mL/g) and B (0.095 25 mL/g), as determined from the MP analysis, correspond to percentages of the total volume available to nitrogen of 78.1% and 70.7%, respectively. Sample A, which retains the blue color associated with $MV^{\bullet-}$, for a longer period of time has a slightly greater percent of the pore volume in micropores. Larger pores present in these samples must contribute relatively small amounts to the total surface area and total pore volume. The percent volume in the micropores for samples A and B are roughly 3 times larger than previously reported for silica samples having both micropores and larger pores.[15]

The pore size distributions calculated using the MP method are shown in Figure 5. From the distributions, the most frequent pore radius for sample A (open circles) is approximately 5.4 Å, with the largest micropores having radi of 9.2 Å. The pore size distribution for sample B (closed circles) shows the most frequent pore radius for this sample to be approximatel 6.4 Å, with the largest pore radius measuring 11.2 Å. Sample B, which retains the blue color associated with $MV^{\bullet-}$ for a shorter period of time, has a larger size for the most frequently encountered pores and also for the largest micropores in the sample. The distributions for samples A and B very closely resemble the distribution previously measured for a microporous silica gel[15] and further demonstrate differences between the physical characteristics of the two samples. These values differ significantly from the 680 M^2 g^{-1} surface area and 20 Å pore size previously reported for the glasses prepared by Slama Schwok et al.[7a] The pore size distributions observed for the glasses described in this report are small enough to prevent leaching of MV out of the glasses. This observation agrees with our failure to detect any leaching of MV from postcure glasses upon soaking in methanol over several hours.

Our results also address the mechanism of $MV^{\bullet-}$ formation in solution and molecular motions in sol–gels. It is known that MV^{2+} can be reduced in the absence of oxygen and without photolysis to form the corresponding $MV^{\bullet+}$ in strongly basic aqueous or methanol solutions. The mechanism of cation radical formation in solution

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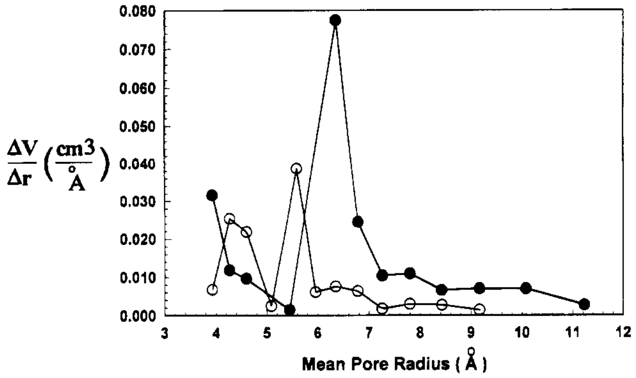
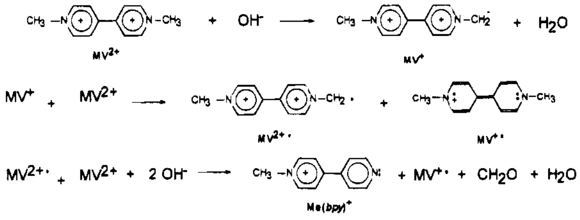


Figure 5. Micropore volume distribution curves determined from the MP analysis for samples A (open symbols) and B (closed symbols).

Scheme 2



has been the focus of several studies.[17] One postulated mechanism involves bimolecular reactions of the type shown in Scheme 2.[17a] According to Scheme 2, formation of $MV^{\bullet +}$ in solution by a nonphotochemical mechanism requires bimolecular reactions involving either MV^+ and MV^{2+} or $MV^{\bullet 2+}$ and MV^{2+}. Restricted diffusion of isolated monomeric species immobilized in the sol–gel glass should eliminate bimolecular reactions. We observe that $MV^{\bullet +}$ is *not* formed when an MV^{2+}-doped sol–gel glass in basic methanol solution is degassed by freeze–pump–thaw cycles (1×10^{-6} Torr). However, when the base-soaked glass is removed from the methanol solution and heated under vacuum the blue $MV^{\bullet +}$ is formed. The blue color appears weakly upon heating at 80 °C and becomes very intense as the temperature is increased to 130 °C. If the formation of $MV^{\bullet +}$ in the glass upon heating is to be attributed to bimolecular reactions, increased motion of species trapped in the glass must become possible as the temperature is raised. To test the bimolecular nature of the reaction in the glass, the experiment was repeated on a sample prepared with 2 orders of magnitude less $MVCl_2$ (0.0003 g instead of the 0.03 g given in the Experimental Section). This sample did not show a blue color upon heating to 130 °C; however, it did turn blue upon photolysis in a basic methanol solution.

For samples prepared with 0.03 g of $MVCl_2$ as described in the Experimental Section, we calculate an average intermolecular separation of ~300 Å in the final glass (assuming equal spacing between molecules). Limited molecular motion of organic species during the curing and postcure stages in sol–gel glasses has previously been demonstrated.[18] We do not believe that our result implies large diffusive movements of sizable organic molecules in glasses that were shown to have very small pores. Alternatively, it is more likely that dimeric or oligomeric aggregates of $MVCl_2$ (MV^{2+}) may be trapped at the start of gelation, as observed for pyrene.[18] Upon further curing, these species become separated by small distances. This behavior was previously revealed by the decrease in pyrene excimer emission during the postgelation cure.[18] The distance of MV^{2+} separation must be great enough so that there are no spectroscopic perturbations on the $MV^{\bullet +}$ formed photochemically (Figure 2). Subsequent heating to higher temperatures may allow for bimolecular reactions between molecules originally separated by short distances. The reaction between MV^+ and MV^{2+} shown in line two of Scheme 2 is an electron-transfer process and can probably be expected to occur over a short distance without direct molecular contact. Additional investigations into the degree of molecular motion in sol–gel glasses are continuing in our laboratory.

Conclusions

A simple method of photochemically generating air-insensitive $MV^{\bullet +}$ in acid-catalyzed sol–gel glasses has been demonstrated. The glass retains the deep blue color associated with $MV^{\bullet +}$ for months in cases where curing has produced pores in the glass that can restrict oxygen diffusion. These findings significantly increase the possible utility of sol–gel glasses doped with various viologens or similar species for solar energy storage. Additionally, the glasses produced in our laboratory have potential applications for optical storage. Further studies of the chemical reactivity of these glasses are underway.

Acknowledgment. Research sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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