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Ionic Liquid-Enhanced Photooxidation of Water Using the Polyoxometalate Anion $[P_2W_{18}O_{62}]^{6-}$ as the Sensitizer

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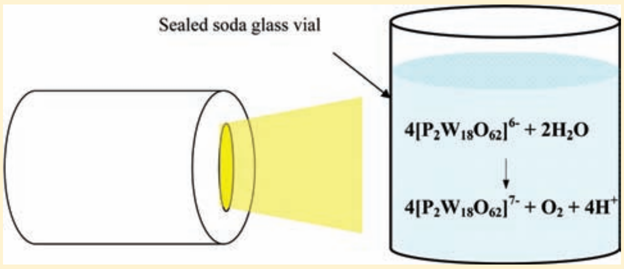
S *Supporting Information*



ABSTRACT: Simple polyoxometalate anions are known to be photoreduced in molecular solvents in the presence of 2-propanol or benzyl alcohol. The use of ionic liquids (ILs) as the solvent is now reported to also allow the photooxidation of water to be achieved. In particular, the photochemistry of the classic Dawson polyoxometalate salt $K_6[P_2W_{18}O_{62}]$ has been studied in detail when water is present in the aprotic IL, 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) and the protic IL, diethanolamine hydrogen sulfate (DEAS). In these and other ILs, irradiation with white light (wavelength 275−750 nm) or UV light (wavelength 275−320 nm) leads to overall reduction of the $[P_2W_{18}O_{62}]^{6-}$ anion to $[P_2W_{18}O_{62}]^{7-}$ and concomitant oxidation of water to dioxygen and protons. The modified structure of bulk water present in ILs appears to facilitate its oxidation. Analogous results were obtained in aqueous solutions containing the protic IL as an electrolyte. The photoproducts (reduced polyoxometalate anion, dioxygen, and protons) were identified by, respectively, voltammetry, a Clark electrode, and monitoring of pH. The formal reversible potentials $E^{0}{}_{\mathrm{F}}$ for $[P_2W_{18}O_{62}]^{6-/7-/8-/9-/10-}$ couples are much more positive than in molecular solvents. The $[P_2W_{18}O_{62}]^{8-}$ and more reduced anions, if formed as intermediates, would efficiently reduce photoproducts H^+ or dioxygen to produce $[P_2W_{18}O_{62}]^{7-}$, rather than reform to $[P_2W_{18}O_{62}]^{6-}$. Thus, under photoirradiation conditions $[P_2W_{18}O_{62}]^{7-}$ acts as a kinetic sink so that in principle indirect splitting of water to produce dioxygen and dihydrogen can be achieved. The equivalent form of photooxidation does not occur in liquid water or in molecular solvents such as MeCN and MeCN/CH_2Cl_2 containing added water, but does occur for solid $K_6[P_2W_{18}O_{62}]$ in contact with water vapor.

■ INTRODUCTION

Photooxidation of water to yield dihydrogen and dioxygen using visible light is relevant to sustainable production of energy:

$$2H_2O_{(l)} + h\nu \rightarrow 2H_{2(g)} + O_{2(g)} \qquad (1)$$

Under electrolysis conditions, water splitting can be represented as the stoichiometric sum of the anode (eq 2) and cathode (eq 3) half-reactions:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (2)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad (3)$$

Dioxygen evolution is significantly more difficult to accomplish than dihydrogen evolution and exploration of photooxidation of water has been pursued intensively.[1]

In biological systems, water oxidation is catalyzed by photosystem II, a protein complex located in the thylakoid membranes of plants, algae, and cyanobacteria.[2] The overall photoreaction leads to reduction of the acceptor plastiquinone PQ:

$$2PQ + 2H_2O + h\nu \rightarrow O_2 + 2PQH_2 \qquad (4)$$

The harvested energy is used to produce the energy carrier ATP and the reductant NADH.

The ruthenium "blue dimer" *cis,cis*-$[(bpy)_2(H_2O)Ru^{III}ORu^{III}(OH_2)(bpy)_2]^{4-}$ and structurally related derivatives have been widely explored as synthetic catalysts.[3] Other systems that present a variety of available redox states have been reported recently and provide attractive possibilities as potential water oxidation catalysts.[4,5] They include ruthenium and iridium complexes containing polyoxometalate anions as ligands.[4]

Photosensitivity of polyoxometalate anions was first reported in 1916,[6] and Hill[7] has summarized the literature. For catalytic operation, effective oxidation of the reduced anions is crucial. Molybdates are more easily reduced than their tungstate analogues, but their reduced forms often cannot be oxidized by dioxygen or the rate of oxidation is slow. In contrast, oxidation of reduced polyoxotungstate anions by dioxygen can be fast. Consequently, irradiation of tungstates may provide access to photoexcited states that are effective oxidants for a large variety of organic compounds but are also effective

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photocatalysts because of fast regeneration of their oxidized forms by dioxygen.[8]

Papaconstantinou reported the photocatalytic oxidation of alcohols by employing aqueous polyoxometalate anions, including aqueous $[P_2W_{18}O_{62}]^{6-}$, as the sensitizer.[9,10] Both protons and dioxygen were able to oxidize the reduced anions. The proposed catalytic cycles were presented in one electron (1e) and/or 2e electron steps. Equations 5−8 provide examples of the simple one electron step formalism with respect to the polyoxometalate redox chemistry:

$$[P_2W_{18}O_{62}]^{6-} + h\nu \rightarrow [P_2W_{18}O_{62}]^{6-*} \quad (5)$$

$$2[P_2W_{18}O_{62}]^{6-*} + (CH_3)_2CHOH \rightarrow 2[P_2W_{18}O_{62}]^{7-} + (CH_3)_2CO + 2H^+ \quad (6)$$

$$2[P_2W_{18}O_{62}]^{7-} + \frac{1}{2}O_2 + 2H^+ \rightarrow 2[P_2W_{18}O_{62}]^{6-} + H_2O \quad (7)$$

$$[P_2W_{18}O_{62}]^{7-} + H^+ \rightarrow [P_2W_{18}O_{62}]^{6-} + \frac{1}{2}H_2 \quad (8)$$

Analogous reaction schemes can be written with generation of $[P_2W_{18}O_{62}]^{8-}$ and more reduced forms.

In a recent study,[11] generation of $[P_2W_{18}O_{62}]^{7-,8-,9-,10-}$ in acidic aqueous media by controlled potential electrolysis indicated that $[P_2W_{18}O_{62}]^{7-}$ reacts extremely slowly with O_2 but not H^+, and that rapid and useful photocatalytic cycles require photochemical generation of $[P_2W_{18}O_{62}]^{8-}$ or more reduced forms, and an intense light source. Presumably, such conditions apply in the studies of Papaconstantinou and colleagues.

Solvent parameters such as polarity and viscosity are known to play significant roles in photochemical processes.[12] Ionic liquids (ILs) have been used to promote photoinduced electron transfer processes involving radical formation.[13] Their use as solvents for photoreactions has demonstrated a number of advantages over molecular solvents, although problems with impurities have been encountered.[14] Reversible potentials of POMs in ILs are more positive than in molecular solvents,[15] a fact that could have significant implications both for the photochemistry and for the catalyst regeneration.

Recently, Zhao et al. discovered that photoinduced oxidation of water occurred upon irradiation of the electron acceptor 7,7,8,8-tetracyanoquinodimethane (TCNQ) dissolved in a "wet" IL, 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]).[16] The overall reactions are as given in eqs 9 and 10, again in a one electron format with respect to the TCNQ redox chemistry:

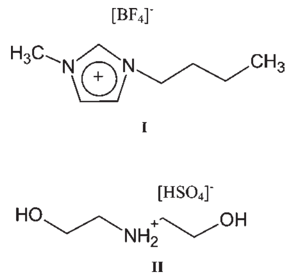
$$4TCNQ^* + h\nu \rightarrow 4TCNQ^* \quad (9)$$

$$4TCNQ^* + 2H_2O \rightarrow 4TCNQ^- + O_2 + 4H^+ \quad (10)$$

The observation was consistent with a diminished activation energy accompanying the modification of the molecular structure of water that occurs when dissolved in the IL.[17] For photooxidation of water, ILs bring the opportunity of modulating both the properties of H_2O and the thermodynamics of a polyoxometalate photosensitizer.

In this study, $[P_2W_{18}O_{62}]^{6-}$ was used as the photosensitizer for oxidation of water in both aprotic and protic IL media. The ILs employed here are aprotic [Bmim][BF_4] (Scheme 1, Structure I) and [Bmim][PF_6] ($Bmim^+$ = butylmethylimidazolium) and protic[18,19] diethanolamine hydrogen sulfate (DEAS) (Scheme 1, structures II, DEA = diethanolamine, S^- = HSO_4^-) and DEAP (P^- = $H_2PO_4^-$). $[P_2W_{18}O_{62}]^{6-}$ can readily accept up to six electrons,[8] so that single or multiple electron processes are in principle available for photoinduced oxidation of water.

Scheme 1. Structures of [Bmim][BF_4] and DEAS



EXPERIMENTAL SECTION

Reagents. $K_6[P_2W_{18}O_{62}]\cdot 14H_2O$ (α isomer) was synthesized according to a literature procedure.[20] KCl (Merck; analytical reagent), trifluoromethanesulfonic acid (triflic acid; Aldrich; ReagentPlus grade), 2-propanol (Merck, HPLC grade), dichloromethane (Merck, HPLC grade), ferrocene (Fc; Aldrich; 99%), [Bmim][BF_4] and [Bmim][PF_6] (Merck, high purity grade, ≥ 99.0%) were used as received. The protic ILs DEAS and DEAP were synthesized and purified according to published procedures.[19] The ILs were stored in a sealed vial in a nitrogen-filled glovebox to minimize water contamination. MeCN (BDH, analytical grade) was dried over basic alumina before use. Bu_4NPF_6 was purchased from GFS and recrystallized twice from hot EtOH.[21] Aqueous 0.1 M phosphate buffer was prepared by adding 9.05 mL of a 0.1 M phosphoric acid (Sigma-Aldrich, Puriss. grade) to 0.95 mL of a 0.1 M potassium dihydrogen phosphate (Merck, Optipur grade) solution. The pH was then adjusted to the required value by addition of dilute HCl (Merck).

Electrochemistry. Voltammetric experiments in aqueous media and in molecular solvents were conducted at 20 ± 1 °C in a conventional 10 mL volume three electrode cell using a BAS (Bioanalytical Systems, West Lafayette, IN) model 100A electrochemical workstation. Cyclic voltammetric studies in ILs were undertaken in electrochemical cells adapted for use with small volumes (0.2−0.5 mL). The glassy carbon (GC) working electrodes used in cyclic voltammetry in molecular solvents and ILs had a diameter d = 0.10 cm (area $A = 7.9 \times 10^{-3}$ cm^2) or d = 0.30 cm ($A = 7.07 \times 10^{-2}$ cm^2). A gold electrode (d = 0.1 cm) also was used in some IL studies.

A BAS RDE-2 accessory interconnected with the BAS model 100 instrument was employed for the rotating disk electrode voltammetry (RDEV). However, a new form of electrochemical cell (Figure 1a) had to be developed for these experiments in the viscous ILs. The viscosities for [Bmim][BF_4] and DEAS are highly dependent on water content; in dry conditions, the values are, respectively, 132[22]and ≥3600[19] mPa s. This cell was designed for use with small IL volumes at fast rotation rates to achieve steady state conditions needed to identify $[P_2W_{18}O_{62}]^{6-}$ redox levels upon exposure to light and to avoid trapping bubbles of air at high rotational speed.[19] The cell is constructed from Poly(methyl methacrylate) (transparent to UV−vis light) and is supported on a cylindrical base that maintains perpendicular alignment with respect to the RDE and at the same time prevents spinning of the cell. The RDE must be immersed at a sufficient depth to preclude trapping of air bubbles at high rotation speeds.[19] To avoid turbulent motion, rotation is slow initially and is increased gradually to a rate necessary to achieve

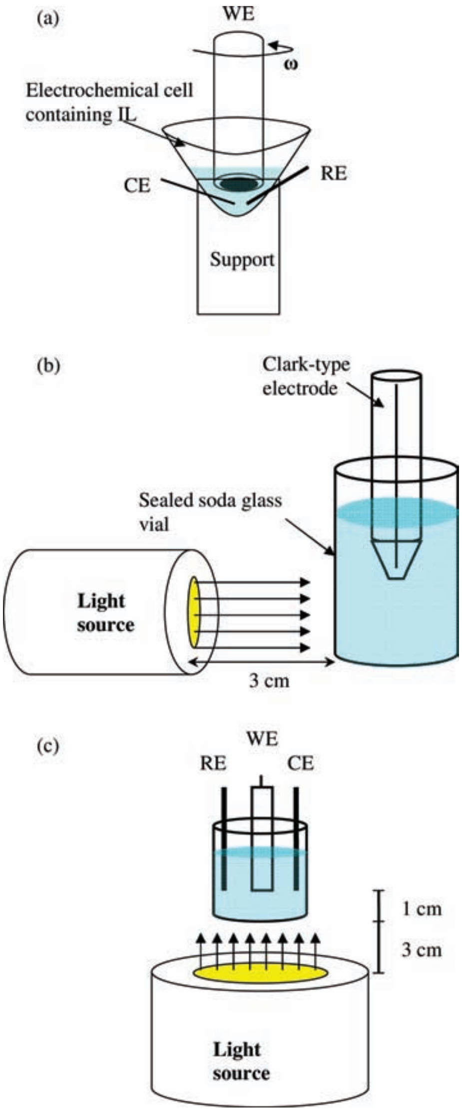


Figure 1. New cell designs that allow: (a) RDE voltammetry at high rotation rates in viscous ILs. The conical cell is 3 cm in height and the diameter at base is 2 cm. (b) Monitoring of dioxygen concentration with a Clark electrode during irradiation with light. pH was monitored with the same configuration by replacing the Clark electrode with a pH electrode. (c) Irradiation of an electrochemical cell with a light source positioned 3 cm below the cell bottom to minimize heating. The working electrode is positioned 1 cm above the bottom of the cell. The light beam irradiates the whole cell during photochemical experiments.

steady state conditions. If the electrode is too deeply immersed, rotation will raise the level to an unacceptably high level. The reference and counter electrodes are positioned below the RDE. The GC working electrode used in this configuration had a diameter of 0.30 cm ($A = 7.07 \times 10^{-2}$ cm^2).

A platinum wire was used as the counter electrode in all voltammetric experiments. In aqueous solutions and aqueous solutions containing IL as electrolyte, the reference electrode was Ag/AgCl (3 M KCl). In IL studies, a silver wire was used as a quasi-reference electrode. Prior to each voltammetric experiment, the working electrode was polished with alumina (0.3 μm) on a clean polishing cloth (Buehler, U.S.A.), rinsed with water and dried under dinitrogen gas. When required, solutions used in voltammetric studies were degassed for at least 10 min with dinitrogen to remove dioxygen and then maintained under a dinitrogen atmosphere for the duration of the measurements. Most of these experiments were conducted under normal benchtop laboratory conditions. However, designated electrochemical measurements were performed with the electrochemical cell contained inside a glovebox. Bulk electrolysis experiments were undertaken at a GC working electrode as described in reference.[11]

Reversible potentials E^0_F are reported against the ferrocene/ferricenium ($Fc^{0/+}$) couple (E^0_F = 0.400 V versus SHE at 25 °C).[23,24] In the case of molecular solvents and ILs, calibration was performed via observation of the voltammogram of ferrocene added after each set of experiments had been completed. In the electrochemistry of $[P_2W_{18}O_{62}]^{6-}$ in aqueous media, a saturated ferrocene solution was prepared by sonication of a suspension of the sparingly soluble solid in aqueous KCl (0.1 M) solution for 30 min. A cyclic voltammogram of this solution is shown in Supporting Information, Figure S1. Solid $K_6[P_2W_{18}O_{62}]$ was added, and cyclic voltammetric data for the $[P_2W_{18}O_{62}]^{6-}$ process were used to establish the potential difference between the oxidation of ferrocene and the reduction of the anion (Supporting Information, Figure S1). Addition of MeCN to this solution containing solid ferrocene followed by sonication showed an increase in current for ferrocene oxidation because of its increased solubility in this mixed H_2O/MeCN solution. No shift in potential was observed upon addition of up to 5% (v/v) MeCN. The potential for reduction of $[P_2W_{18}O_{62}]^{6-}$ was then converted to the $Fc^{0/+}$ scale, and data obtained in aqueous solutions were compared with those obtained in molecular solvents and ILs.

Analytical Techniques. A digital pH meter (Metrohm Model 744 pH electrode, Herisau, Switzerland) with a combination glass electrode and built-in Ag/AgCl (3 M KCl) reference electrode was used to determine the pH after calibration against standard buffers. A Clark-type electrode (model OX10, Unisense Denmark) was employed to monitor dioxygen concentrations (Figure 1b). To avoid direct exposure to UV light, the light beam was located below the Clark electrode and placed 3 cm from the wall of the soda glass vial. This configuration also minimized heating effects, and no change in temperature was detected (±1 °C) upon irradiation with the 7 W light source used in these studies (see below). In experiments where electrochemical monitoring of photochemical experiments was required, the light source was located below the soda glass vial.

Photochemistry. Samples contained in airtight soda glass vials sealed with Blu Tac (Supporting Information, Figure S2) were exposed to a Xe lamp (275–750 nm) light source using a Polilight PL6 lamp (Rofin). A band-pass filter (320 nm cut off) was used when only irradiation with UV light (275–320 nm) was employed. The power output of the lamp at the end of the light guide was 7 W. Full details on the light source are available in ref 25. No significant difference was observed upon irradiation with white or UV light. $[P_2W_{18}O_{62}]^{6-}$ absorbs almost exclusively in the UV region. Although $[P_2W_{18}O_{62}]^{7-,8-,9-}$ also absorb light in the visible region[9-11] (Supporting Information, Figure S3), with the 7 W light source, photoreduction is dominated by UV irradiation. The light source was positioned at the side of (Figure 1b) or below (Figure 1c) the cell of interest at distances indicated in the diagrams. The solution was not stirred during the course of photocurrent experiments. In view of all these features, and relative location of light sources and sensors, the solution exposed to light will not give rise to homogeneous outcomes as the light intensity will be a function of distance from the cell wall. It therefore follows that mass transport by diffusion will be complex, and the location of the sensor will determine the concentration of O_2, H^+, or H_2 detected. It is for these reasons that we have not attempted to quantify yields of products in terms of light input.

Gas Concentration Measurements. The dioxygen concentration was monitored with a microelectrode[26] gas sensor (Clark type). The sensor and the instrumentation were purchased from Unisense A/S, Aarhus, Denmark. The current was measured by an Unisense

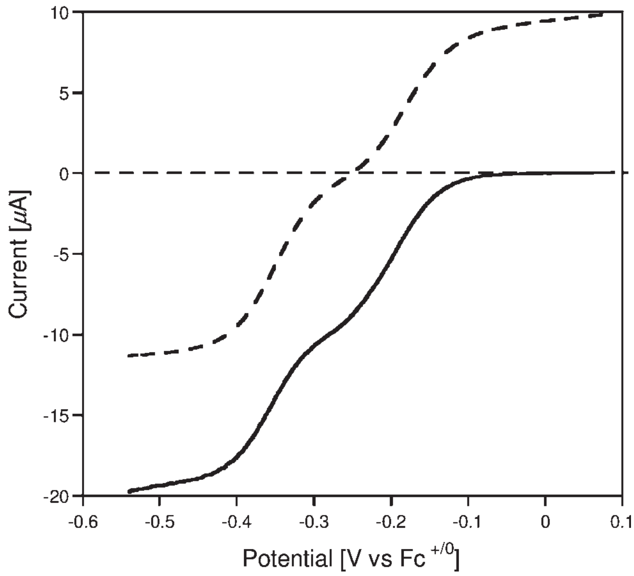


Figure 2. RDE voltammograms at a GC electrode for $K_6[P_2W_{18}O_{62}]$ (0.3 mM) in aqueous potassium phosphate buffer (0.1 M KCl; pH 3.0) containing 2-propanol (9% v/v) before (solid line) and after (dashed line) exposure to white light (275−750 nm) for 2 h. The photoreduced solution (dashed line) contains $[P_2W_{18}O_{62}]^{7-}$; ω = 1592 rpm, ν = 0.01 V s^{-1}.

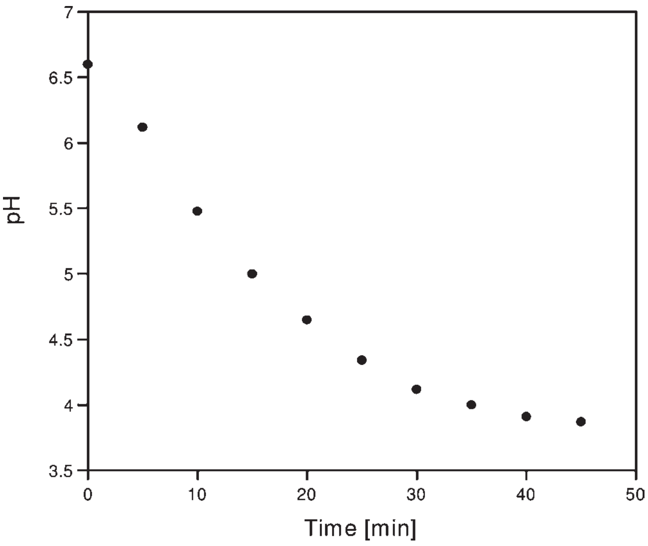


Figure 3. Decrease of pH that occurred in a degassed solution of $K_6[P_2W_{18}O_{62}]$ (0.3 mM) in water (0.1 M KCl) containing 2-propanol (9% v/v) during irradiation with white light (275−750 nm). The data were obtained using the configuration given in Figure 1b (Supporting Information, Figure S2) with a pH electrode.

picoammeter PA2000. A two-point calibration of the Clark-type electrode was performed daily, according to the procedure recommended by the manufacturer.

Gas Chromatography. The product of photooxidation of 2-propanol was verified to be acetone by gas chromatography. A Varian 3700 gas chromatographic instrument was used with a 61 × 1/4 glass column containing a packed column of 10% Carbowax 20 M on 80/100 AW DMCS Chromosorb to separate the unreacted 2-propanol and photochemically generated acetone. The formation of acetone was confirmed by comparison of the retention time determined from an authentic sample, and the concentration quantified by the method of standard additions.

Karl Fischer Titration. Measurements of water content in the ILs was performed with a Metrohm 831 KF Coulometer. To add water, the dry IL solution containing $[P_2W_{18}O_{62}]^{6-}$ was transferred from the drybox into a 2 mL soda glass vial. In some experiments, the vial was left under open benchtop condition for up to 4 h to increase the water content to the required level. Alternatively, water was deliberated added to the vial, which was then sealed with a silica cap, and then the solution was sonicated for 30 min.

UV−vis Spectroscopy. UV−vis absorption spectra of reduced polyoxometalates formed by controlled potential electrolysis of $[P_2W_{18}O_{62}]^{6-}$ were recorded on a Cary 5000 UV/vis/NIR spectrophotometer. The solutions were transferred into the instrument after bulk electrolysis experiments at the appropriate potentials were completed.

RESULTS AND DISCUSSION

Photoelectrochemistry of $[P_2W_{18}O_{62}]^{6-}$ in Aqueous Media. Irradiation of solutions of $[P_2W_{18}O_{62}]^{6-}$ in buffered aqueous acidic media (pH = 3) undertaken for prolonged periods with white light (275−750 nm, total intensity 7 W) did not affect the oxidation level of the anion, as monitored by RDEV (Supporting Information, Figure S4). Solutions remained colorless (Supporting Information, Figure S2b), consistent with the absence of $[P_2W_{18}O_{62}]^{7-}$ or more reduced species. It was apparent that, under these conditions, water did not promote photoreduction of $[P_2W_{18}O_{62}]^{6-}$. However, the presence of an electron donor such as 2-propanol in the aqueous buffer did induce photoreduction to the blue $[P_2W_{18}O_{62}]^{7-}$ level (Supporting Information, Figure S2c), confirmed by the position of zero current (Figure 2).[10,27] Furthermore, acetone was detected (Supporting Information, Figure S5). Longer times of exposure to light did not lead to voltammetric detection of more reduced species. The quantity of acetone produced in these experiments was only slightly in excess of the stoichiometric reaction (eq 11) obtained from summation of eqs 5 and 6

$$2[P_2W_{18}O_{62}]^{6-} + (CH_3)_2CHOH \rightarrow 2[P_2W_{18}O_{62}]^{7-} + (CH_3)CO + 2H^+ \qquad (11)$$

implying as predicted on the basis of data presented in ref 11 that little catalytic regeneration of $[P_2W_{18}O_{62}]^{6-}$ by reaction of $[P_2W_{18}O_{62}]^{7-}$ with O_2 (eq 7) or H^+ (eq 8) occurs. However, this does not preclude the transient formation of $[P_2W_{18}O_{62}]^{8-}$ followed by reaction with $[P_2W_{18}O_{62}]^{6-}$ (eq 12) which is predicted to be very fast.

$$[P_2W_{18}O_{62}]^{8-} + [P_2W_{18}O_{62}]^{6-} \rightarrow 2[P_2W_{18}O_{62}]^{7-} \qquad (12)$$

Irradiation of a 9% v/v 2-propanol aqueous (0.1 M KCl) solution also was carried out in unbuffered solution (initial pH, 6.6) rather than in buffered solution at pH 3.0 for 1 h under both ambient conditions (saturated dioxygen concentration of approximately 290 μM) and at low dioxygen concentrations (≤10 μM) under nitrogen degassing. RDEV experiments confirmed that quantitative formation of one-electron reduced $[P_2W_{18}O_{62}]^{7-}$ (cf, Figure 2) occurred even in the presence of dioxygen. The pH decreased to 3.9 (Figure 3), consistent with the production of protons produced from photooxidation of 2-propanol (eqs 11). RDEV voltammetry and pH measurements in the absence of $[P_2W_{18}O_{62}]^{6-}$ and light confirmed that hydrolysis to $[P_2W_{17}O_{61}]^{6-}$ or related species is insignificant.

No evidence of $[P_2W_{18}O_{62}]^{8-}$ or more reduced forms was obtained upon prolonged irradiation of the initial $[P_2W_{18}O_{62}]^{6-}$ or the $[P_2W_{18}O_{62}]^{7-}$ solution. Gas chromatographic (GC) analysis (Supporting Information, Figure S5) confirmed acetone as the principal product of 2-propanol oxidation at all pH values. The concentration of O_2 in solution, monitored during irradiation with a Clark-type electrode, remained almost steady during 1 h of photolysis to form 2-propanol, again implying the absence of a significant level of catalysis. However, storage of this irradiated solution in the dark led to very slow consumption of O_2 (Figure 4) because of oxidation of the reduced $[P_2W_{18}O_{62}]^{7-}$ species back to $[P_2W_{18}O_{62}]^{6-}$ (eq 7).

A series of aerobic and anaerobic photochemical experiments (Supporting Information, Figure S6) was performed under the buffered conditions of Figure 2 with variable times of exposure to white light. The irradiated solutions were allowed to incubate in the dark for 12−16 h. RDE and other data confirm that reaction of $[P_2W_{18}O_{62}]^{7-}$ with H^+ (eq 8) is not favored whereas reduction of O_2 (eq 7) does occur, but is very slow (half-life of hours). The acetone concentration found is slightly in excess of that predicted by overall stoichiometric reaction given in eq 11, implying minimal catalytic turnover even after 3 h of irradiation with UV or white light. Consequently, the one-electron reduced anion $[P_2W_{18}O_{62}]^{7-}$ would appear to be a final product under these conditions, and the reaction cycle, as presented in the potentially available catalytic scheme (eqs 5−8), is too slow to be useful in any practical sense, at least with light intensities and pH values employed in this study.

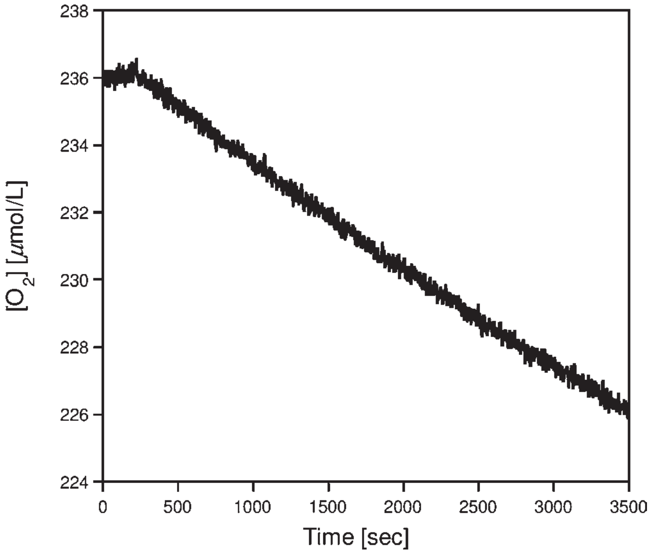


Figure 4. Decrease in the concentration of dioxygen detected during the reoxidation of $[P_2W_{18}O_{62}]^{7-}$ formed photochemically by irradiation of 0.2 mM $[P_2W_{18}O_{62}]^{6-}$, in an aqueous solution of 0.1 M KCl at pH 3.65 containing 9% (v/v) 2-propanol. The data were acquired using the cell setup as in Supporting Information, Figure S2.

A repetitive series of light-dark experiments in aqueous media containing 2-propanol (9% v/v) also was undertaken in phosphate buffer (pH 3.00) containing $[P_2W_{18}O_{62}]^{6-}$ (1 mM), and KCl (0.1 M). After degassing with dinitrogen to remove dioxygen, this solution was irradiated with white light for 2 h. The photoproduction of $[P_2W_{18}O_{62}]^{7-}$ was confirmed by RDEV, and a color change from colorless to blue was observed. The solution was then left overnight in the dark under a nitrogen atmosphere and ambient conditions. On visual inspection on the next day, the solution was colorless, and RDE voltammograms obtained after dinitrogen degassing showed that $[P_2W_{18}O_{62}]^{7-}$ had been fully oxidized back to $[P_2W_{18}O_{62}]^{6-}$. This solution was irradiated further for 2 h and again stored in the dark overnight in the absence of dioxygen with the same result. This procedure was repeated for four consecutive 24 h cycles. All findings are consistent with conclusions on the reactions of $[P_2W_{18}O_{62}]^{7-}$ when generated by bulk electrolysis in aqueous media.[11] In essence $[P_2W_{18}O_{62}]^{7-}$ is unreactive toward O_2 or H^+, and this has significant implications in endeavors to provide catalytic cycles and in photooxidation of water (see later).

Electrochemistry and Photoelectrochemistry of $[P_2W_{18}O_{62}]^{6-}$ in ILs. The reversible formal potentials ($E^0{}_F$) for reduction of anions $[P_2W_{18}O_{62}]^{6-/7-/8-/9-/10-}$ depend strongly on solvent polarity.[28] Higher polarity shifts $E^0{}_F$ to more positive values. Indeed, in aqueous solutions, the processes appear at potentials that are 800−1500 mV more positive than found in molecular solvents such as CH_2Cl_2 and MeCN (Table 1).[29,30] The $E_F{}^0$ value has significant implications in the photochemistry with respect to catalyst regeneration (eqs 7 and 8). Furthermore, if the potentials in the excited state (presence of light) follow the same trends as applies in changing from a molecular solvent to an IL medium in the dark, or they are shifted to even more positive values, then the energetics of reaction of the excited state (eq 6) with 2-propanol or another electron donor may become more favorable than in conventional molecular solvents.

The techniques used to obtain $E^0{}_F$ values for the polyoxometalate redox chemistry in ILs were cyclic and RDE voltammetry. It was found necessary to sonicate suspensions of $K_6[P_2W_{18}O_{62}]$ in

Table 1. $E^0{}_F$ **Values vs** $Fc^{0/+}$ **in Molecular Solvents and ILs Calculated from Cyclic Voltammograms Obtained from Reduction of** $[P_2W_{18}O_{62}]^{6-}$ **at a GC Electrode** (ν = 0.15 V s^{-1})

	$E^0{}_F$ values for designated processes (mV vs $Fc^{0/+}$)			
medium	$[P_2W_{18}O_{62}]^{6-/7-}$	$[P_2W_{18}O_{62}]^{7-/8-}$	$[P_2W_{18}O_{62}]^{8-/9-}$	$[P_2W_{18}O_{62}]^{9-/10-}$
H_2O (pH 5.75)	−165	−335	−715	−880
CH_2Cl_2	−1030	−1415	−2005	−2360
MeCN	−920	−1280	−1850	−2215
[Bmim][PF$_6$]	−455	−705	−1155	−1415
[Bmim][BF$_4$]	−470	−715	−1160	−1435
DEAS	−225	−415	−775[a]	−1045[a]
DEAP	−245	−430	−835[a]	−1115[a]

[a] Reaction involves proton transfer coupled to electron transfer (see eqs 18 and 19).

the ILs to obtain sufficiently high concentrations of $[P_2W_{18}O_{62}]^{6-}$ for voltammetric studies. In terms of favoring the energetics of the excited state reactions (eqs 5 and 6), it is desirable to have E^0_F values as positive as possible. The E^0_F values for of the $[P_2W_{18}O_{62}]^{6-/7-}$ process in aprotic [Bmim][BF$_4$] and [Bmim]-[PF$_6$] are similar and about 250 mV more negative than those found in protic DEAS or DEAP (Table 1). This implies that photooxidation would be more favorable in the protic IL. Larger potential differences (protic ILs more negative) are found for the second, third, and fourth reduction processes (Table 1). This is likely to be significant if multiple electron transfer steps accompany the photoelectrochemistry.

The voltammetry of $[P_2W_{18}O_{62}]^{6-}$ in aprotic ILs parallels that in aqueous media with respect to proton affinity. In the absence of trifluoromethanesulfonic acid, the first four reduction steps in [Bmim][BF$_4$] have relative peak current intensities of 1:1:1:1, but in the presence of a sufficiently high acid concentration, this ratio becomes approximately 1:1:2:2 (Figure 5a). This effect is due to the stronger proton affinities of the more highly reduced ions leading to coalescence of the reduction processes. Thus, with high proton concentrations, two 2e$^-$ processes are present into the scanned potential range. This now mimics the voltammetry in the protic ILs and in acidic aqueous media.

Figure 5b exhibits cyclic voltammograms of a degassed solution of $[P_2W_{18}O_{62}]^{6-}$ in "wet" [Bmim][BF$_4$] (water content ~2000 ppm) before and after irradiation with UV light for 20 min. The initial voltammogram featured the expected four processes with 1:1:1:1 relative peak current intensities. After irradiation, a pattern close to 1:1:2:2 is present (Figure 5b). In addition, the solution turned blue, the characteristic color of the reduced anions. These observations are consistent with photoreduction of $[P_2W_{18}O_{62}]^{6-}$ and generation of H$^+$ as a product, similar to that observed in aqueous solutions containing 2-propanol. Analogous behavior was found in water saturated [Bmim][PF$_6$].

RDE voltammograms were obtained under the same conditions in [Bmim][BF$_4$] containing 2000 ppm water. The rotation rates >5000 rpm required for steady state conditions (Figure 6) were achieved in the purpose-built cell (Figure 1a). It can be concluded that $[P_2W_{18}O_{62}]^{6-}$ has undergone photoreduction to give $[P_2W_{18}O_{62}]^{7-}$. While the net level of conversion was low, further RDE voltammetric experiments revealed that the $[P_2W_{18}O_{62}]^{7-}$ generated by the irradiation process was quantitatively oxidized back to $[P_2W_{18}O_{62}]^{6-}$ on standing in the "wet" [Bmim][BF$_4$] aprotic IL in the dark for 1 h as confirmed by the change of the solution from blue to colorless. Importantly, cyclic voltammograms showed that the peak ratio for the reduction process reverted back to 1:1:1:1 format instead of the 1:1:2:2 one seen after irradiation, indicative of a decrease of proton concentration as expected when $[P_2W_{18}O_{62}]^{7-}$ reacts with dioxygen or H$^+$ as in eqs 7 and 8. This behavior contrasts with that in aqueous solution, where $[P_2W_{18}O_{62}]^{7-}$ generated in the presence of 2-propanol was oxidized back to $[P_2W_{18}O_{62}]^{6-}$ only after several hours of standing in the dark. An analogous slow photocatalytic cycle was also observed in "wet" protic ILs DEAS and DEAP containing about 5000 ppm water. However, the peak ratio in protic IL media was 1:1:2:2 even before irradiation with light, so no change of the relative peak current intensities was observed on standing in these media because of the high concentration of protons always available in these ILs.

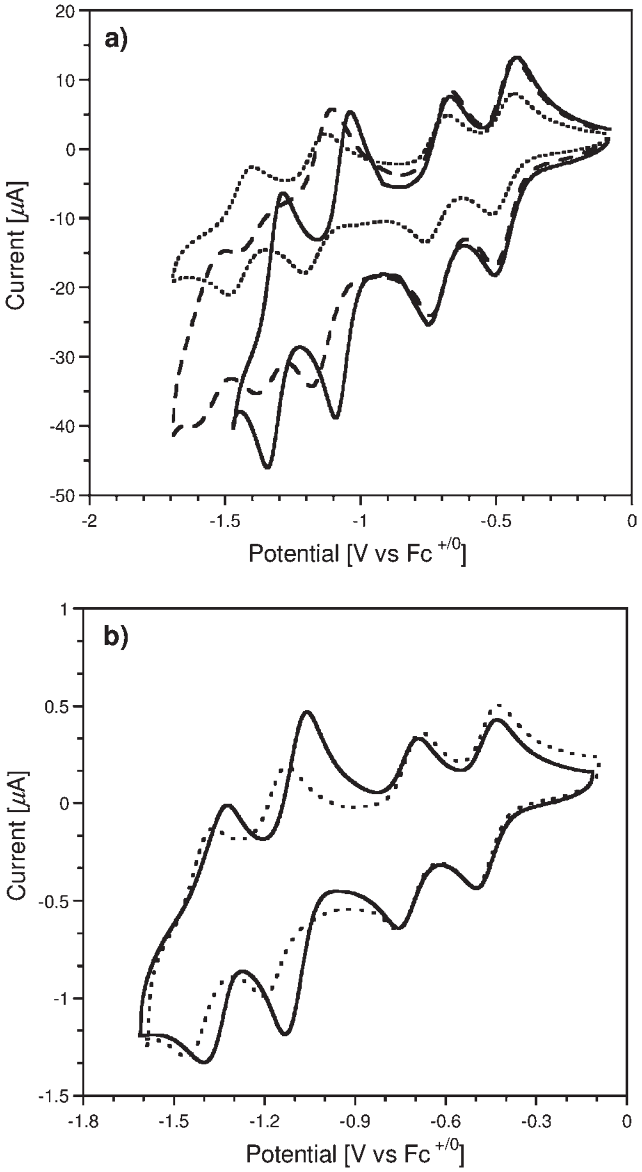


Figure 5. Cyclic voltammetry at a GC electrode for degassed solutions of K$_6$[P$_2$W$_{18}$O$_{62}$] in [Bmim][BF$_4$]. ν = 0.15 V s^{-1}. (a) Concentration, 1.6 mM; Concentration of triflic acid: 0,(dotted line); 50 mM, (dashed line); 250 mM, (solid line). (b) Concentration, 0.3 mM. Before (dotted line) and after (solid line) irradiation with UV light (275−320 nm) for 20 min.

Assuming that the overall reactions in the presence of light were predominantly as in eqs 13 and 14

$$[P_2W_{18}O_{62}]^{6-} + h\nu \rightarrow [P_2W_{18}O_{62}]^{6-*} \qquad (13)$$

$$4[P_2W_{18}O_{62}]^{6-*} + 2H_2O \rightarrow 4[P_2W_{18}O_{62}]^{7-} + O_2 + 4H^+ \qquad (14)$$

then in addition to formation of $[P_2W_{18}O_{62}]^{7-}$ and H$^+$ as detected above, oxygen should be evolved. A 2 mL soda glass vial cell sealed with Blu-Tack was again employed to ascertain that one of the photoreaction products was O$_2$. A gold working

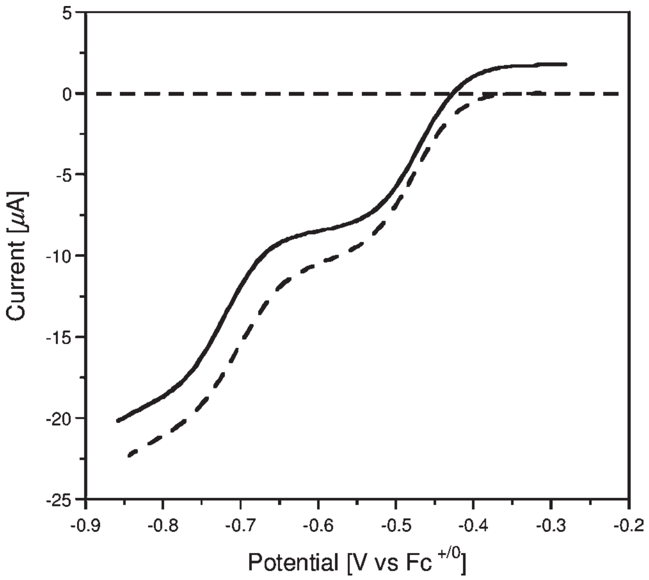


Figure 6. RDE voltammetry at a GC electrode for a solution of $K_6[P_2W_{18}O_{62}]$ (0.4 mM) in [Bmim][BF_4], before (dashed line) and after (solid line) irradiation with UV light (275−320 nm) for 1 h under benchtop conditions; ω = 5420 rpm, ν = 0.01 V s^{-1}.

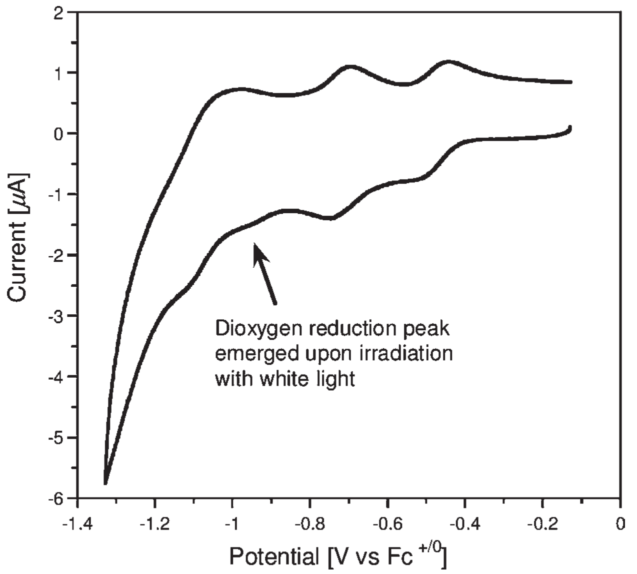


Figure 7. Cyclic voltammetry at a gold electrode for a saturated solution of $K_6[P_2W_{18}O_{62}]$ in [Bmim][BF_4]. Reduction current for O_2 peak appears at ~0.95 V after irradiation with white light (λ = 275−750 nm) for 20 min; ν = 0.15 V s^{-1}.

electrode was used in this particular experiment. Control experiments confirmed the air tightness of the cell. Cyclic voltammograms of a degassed saturated solution of $K_6[P_2W_{18}O_{62}]$ in "wet" [Bmim][BF_4] showed no oxygen reduction current between −0.850 V and −1.015 V (vs Fc$^{0/+}$). However, illumination of the solution for 20 min led to development of reductive current at about −950 mV (Figure 7), indicating oxygen is now present and generated by irradiation with light.

All of the above data are consistent with photooxidation of H_2O to O_2 and H^+ upon irradiation of "wet" [Bmim][BF_4] solution containing $[P_2W_{18}O_{62}]^{6-}$ as the sensitizer with UV or white light, plausibly facilitated by the modified form of the structure of water dissolved in ILs.[16,31] The above experiments employing $K_6[P_2W_{18}O_{62}]$ were also repeated in the "wet" aprotic IL, [Bmim][PF_6] (water content ~1200 ppm) and in "wet" (water content ~800 ppm) protic ILs DEAS and DEAP. Analysis of Karl Fischer titration data established that water loss accompanies its photooxidation in all ILs here studied, and RDEV confirmed that in all cases net photoreduction of $[P_2W_{18}O_{62}]^{6-}$ to $[P_2W_{18}O_{62}]^{7-}$ occurred. However, after prolonged irradiation with white light, the quantity of water oxidized in "wet" [Bmim][BF_4] calculated from Karl Fischer titration data based on the quantity of reduced $[P_2W_{18}O_{62}]^{7-}$ species was smaller than expected as calculated on the basis of the stoichiometric reaction given in eq 15 (smaller by 60 to 80%)

$$4[P_2W_{18}O_{62}]^{6-} + 2H_2O \rightleftarrows 4[P_2W_{18}O_{62}]^{7-} + O_2 + 4H^+ \quad (15)$$

This apparent discrepancy is attributed to regeneration of water during the course of oxidation of the reduced $[P_2W_{18}O_{62}]^{7-}$ back to $[P_2W_{18}O_{62}]^{6-}$ as in eq 7 that occurs between the end of the irradiation period and analysis of water content by the Karl Fisher method (at least 30 min). Apparently, the IL environment not only favors water photooxidation but it also increases the kinetics of reformation of water as noted above. Thus, a very slow catalytic cycle is operative which removes (oxidizes) and then regenerates water during irradiation of $[P_2W_{18}O_{62}]^{6-}$ with UV or white light in "wet" ILs.

Photochemical experiments were repeated for solid $K_6[P_2W_{18}O_{62}]$ salt in contact with water vapor or 2-propanol vapor at room temperature. Sealed soda glass vials containing the reactants were exposed to sunlight for seven days. The pale yellow salt turned blue in both cases, and RDE voltammograms and pH determination after the product was dissolved in aqueous nonbuffered solution confirmed the presence of reduced $[P_2W_{18}O_{62}]^{7-}$ anion and protons, respectively. Reaction with 2-propanol vapor was detected visually after 3 days, whereas experiments involving water vapor required 6 days. An analogous experiment with $[P_2W_{18}O_{62}]^{6-}$ (0.3 mM) dissolved in water and exposed to sunlight showed no evidence of photooxidation on exposure to sunlight. However, when 9% v/v 2-propanol was present, detection of the blue $[P_2W_{18}O_{62}]^{7-}$ occurred very rapidly upon exposure to sunlight. This outcome indicates that photoreduction of $[P_2W_{18}O_{62}]^{6-}$ also may be facilitated by the different structure of water in the vapor phase relative to that in neat water or when water is dissolved in molecular solvents.

Electrochemistry and Photoelectrochemistry in Aqueous Media Using DEAS as an Electrolyte. An increase in the concentration of the conventional electrolyte KCl from 0.1 to 5 M in aqueous media does not significantly alter the E^0_F value associated with the $[P_2W_{18}O_{62}]^{6-/7-}$ couple or even more reduced couples. Thus, ionic strength is not very important in the thermodynamic sense, at least in the dark. Furthermore, photochemical reduction of $[P_2W_{18}O_{62}]^{6-}$ was not detected in aqueous solutions with KCl (0.1 to 5 M) present as the electrolyte.

A solution of $K_6[P_2W_{18}O_{62}]$ (0.2 mM) in water containing DEAS (0.05 M) as the electrolyte exhibited a pH of 3.5 and gave rise to cyclic voltammograms with peak current ratios for the first 4 reduction processes of about 1:1:2:2, as expected under acidic conditions (compare Figures 8 and 5). The four processes may

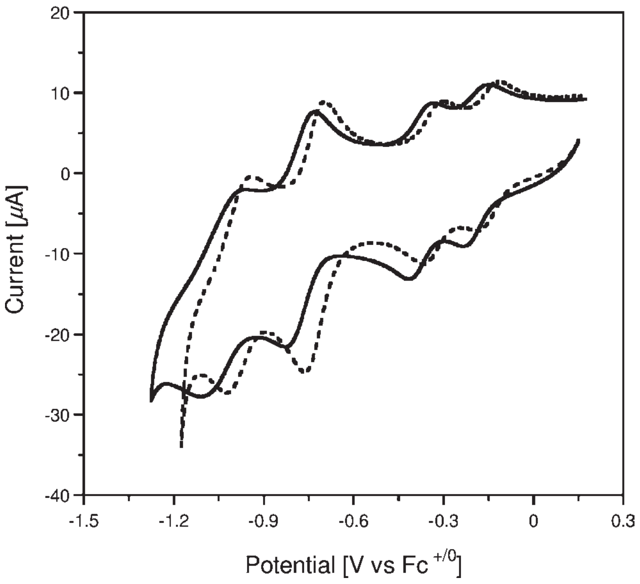


Figure 8. Cyclic voltammograms at a GC electrode for a solution of $K_6[P_2W_{18}O_{62}]$ (0.2 mM) in aqueous solution containing (solid lines) 0.05 M and (dotted lines) 0.83 M of DEAS as supporting electrolyte; ν = 0.15 V s^{-1}.

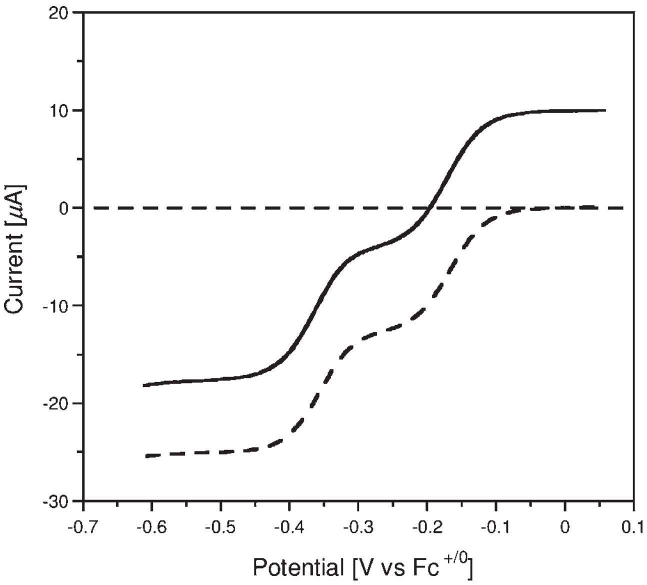


Figure 9. RDE voltammograms at a GC electrode for an aqueous solution of $K_6[P_2W_{18}O_{62}]$ (0.4 mM) and DEAS (0.21 M) before (dashed line) and after (solid line) irradiation with UV light (275−320 nm) for 1 h; ω = 1200 rpm, ν = 0.01 V s^{-1}.

be represented by eqs 16−19:

$$[P_2W_{18}O_{62}]^{6-} + e^- \rightleftarrows [P_2W_{18}O_{62}]^{7-} \qquad (16)$$

$$[P_2W_{18}O_{62}]^{7-} + e^- \rightleftarrows [P_2W_{18}O_{62}]^{8-} \qquad (17)$$

$$[P_2W_{18}O_{62}]^{8-} + 2e^- + 2H^+ \rightleftarrows [P_2W_{18}O_{60}(OH)_2]^{8-} \qquad (18)$$

$$[P_2W_{18}O_{60}(OH)_2]^{8-} + 2e^- + 2H^+ \rightleftarrows [P_2W_{18}O_{58}(OH)_4]^{8-} \qquad (19)$$

An increase in the concentration of DEAS up to 0.83 M led to a progressive lowering of pH and small positive shifts in peak potentials (Figure 8, Supporting Information, Table S1). Increases in ΔE_p values due to an increase of uncompensated resistance, and decreases in diffusion coefficient values due to the increase in viscosity were also observed, as the concentration of DEAS increased.

No significant shift of absorption bands of $[P_2W_{18}O_{62}]^{6-}$ (oxygen-to-d^0-metal charge transfer) occurred upon addition of DEAS to the aqueous solution (Supporting Information, Figure S7). Yet, in contrast to purely aqueous media, UV illumination of solutions (pH 3.0) containing DEAS (0.21 M) as electrolyte led to visual detection of a blue color after 10 min. The position of zero current in RDE voltammograms confirmed the presence of a significant concentration of reduced $[P_2W_{18}O_{62}]^{7-}$ anions after 60 min of irradiation (Figure 9). The pH had decreased to 2.8.

A Clark-type electrode was used to monitor the dioxygen concentration in aqueous solutions during the course of photochemical experiments with the experimental arrangement detailed in Figure 1b and Supporting Information, Figure S2. Prior to each experiment, the solution was degassed with nitrogen for a few seconds to achieve an oxygen concentration level that would allow either an increase or a decrease in its concentration to be detected readily. The cell was then sealed tightly (Supporting Information, Figure S2). An aqueous solution containing DEAS (0.09 to 0.18 M) was irradiated with white light for 1 h. No change in dioxygen concentration was detected (Supporting Information, Figure S8), nor in an aqueous solution (Figure 10a) containing KCl (0.1 M) and $[P_2W_{18}O_{62}]^{6-}$ (0.36 mM). In contrast, when $[P_2W_{18}O_{62}]^{6-}$ was added to the aqueous DEAS solution, the dioxygen concentration increased upon irradiation (Figures 10b, 10c and Supporting Information, Figure S8b) and the solution turned blue. RDE voltammograms confirmed the presence of reduced anion equivalent to ~10% of

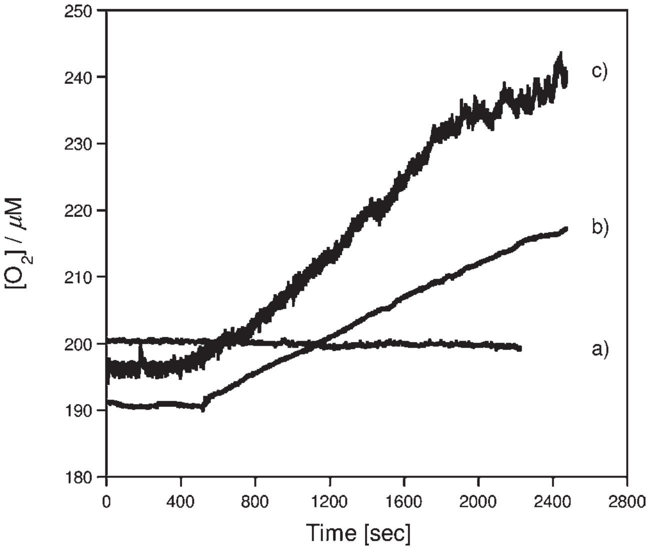


Figure 10. Time dependence of the dioxygen concentration for $[P_2W_{18}O_{62}]^{6-}$ (0.3 mM) in water with added electrolyte during the course of irradiation with UV light (λ = 275−320 nm) using the setup described in Figure 1b and Supporting Information, Figure S2. (a) KCl, 0.1 M; (b) DEAS, 0.09 M; (c) DEAS 0.14 M. The induction period before O_2 is detected due to the time taken for O_2 generated in solution to diffuse to the Clarke-type oxygen electrodes.

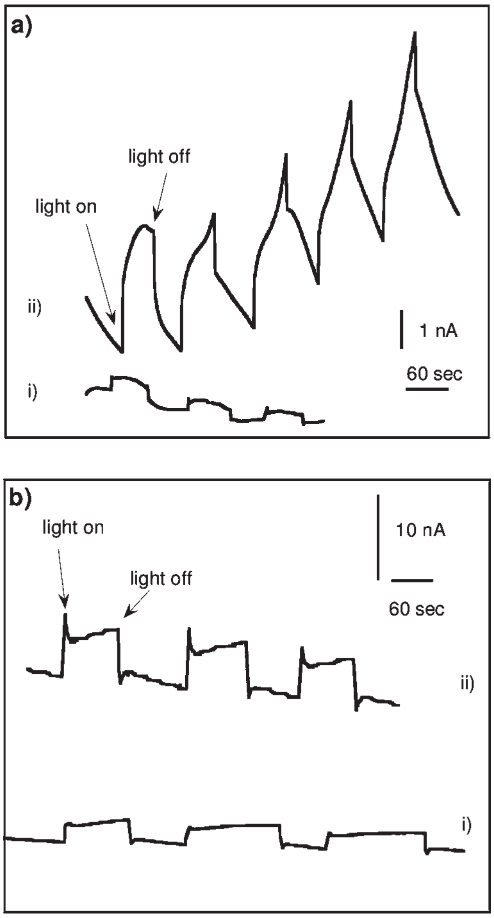
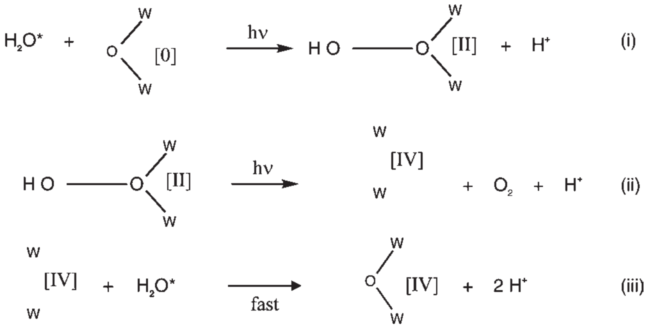


Figure 11. Photocurrents detected at (a) −100 mV vs $Fc^{0/+}$ from 0.2 mM $[P_2W_{18}O_{62}]^{6-}$ upon irradiation of a GC electrode with UV light (275−320 nm) (i) pH 5.75 acetate buffered aqueous solution, (ii) after addition of 9% (v/v) 2-propanol. (b) 0 V vs $Fc^{0/+}$ in (i) "wet" [Bmim][BF_4] (2000 ppm water), (ii) after addition of 0.1 mM $[P_2W_{18}O_{62}]^{6-}$ and irradiation with UV light (275−320 nm).

its one-electron reduced form (Supporting Information, Figure S9). This result combined with the pH decrease and the increase of dioxygen concentration (Supporting Information, Figure S7) are consistent with water being oxidized to O_2 during irradiation in the presence of $[P_2W_{18}O_{62}]^{6-}$ as a sensitizer. Control experiments conducted with diethanolamine (DEA) (0.38 M) in aqueous solution containing $[P_2W_{18}O_{62}]^{6-}$ (1.3 mM) did not lead to detection of changes in $[P_2W_{18}O_{62}]^{6-}$ or H^+ or O_2 concentration under these conditions. Thus, both $K_6[P_2W_{18}O_{62}]$ and DEAS appear to be essential to induce dioxygen evolution.

It could be envisaged that DEAS, which has an alcohol as its cation component, could be photooxidized in the presence of $[P_2W_{18}O_{62}]^{6-}$, as is the case with 2-propanol. However, oxygen found in the photochemical experiments would not be an anticipated product. Furthermore, a decrease in the potential window available in the positive potential region at a GC electrode was observed in DEAS upon addition of water. Since, no reduction of $[P_2W_{18}O_{62}]^{6-}$ in DEA was observed upon irradiation with white light for 2 h it may be concluded that water is more easily oxidized than DEA. The protonated form present in the protic IL cation is predicted to be even more difficult to oxidize than DEA.

Scheme 2. Possible Model to Account for the Photooxidation of Water in "wet" ILs upon Irradiation with UV or White Light



Karl Fischer titrations of solutions of $[P_2W_{18}O_{62}]^{6-}$ (1.3 mM) in DEAS (with deliberately added water) showed a decrease in water concentration of ~2000 ppm (from an average initial value of 61×10^3 ppm to a final value of 59×10^3 ppm) after 2 h irradiation with white light. A control experiment in the absence of the polyoxometalate salt showed no change in the water concentration (at the 20 ppm error level).

Photocurrent Measurements. These were initially undertaken in neutral aqueous solution containing 0.1 M KCl before and after the addition of 2-propanol as an electron donor. The measurements were then applied to ILs containing adventitious water and in aqueous solutions having an IL as the electrolyte. In each case the solution was degassed with dinitrogen and the cell was sealed from the atmosphere. Photocurrent detection was undertaken with the experimental arrangement shown in Figure 1c. The glassy carbon working electrode was held at a potential of 230 mV, which is more positive than the reversible potential for the $[P_2W_{18}O_{62}]^{6-/7-}$ process but less positive than the solvent oxidation limit. No increase of temperature (±0.2 °C level) was detected during the irradiation experiments. Significant photocurrent was detected when the solution contained both 2-propanol and $[P_2W_{18}O_{62}]^{6-}$ (Figure 11a).

Photocurrents in [Bmim][BF_4] containing approximately 2000 ppm of water were significantly higher (Figure 11b) than found in aqueous solutions containing 2-propanol. The current generated by photoreduction of 0.4 mM $[P_2W_{18}O_{62}]^{6-}$ in aqueous solution containing 0.2 M DEAS as electrolyte is ≥ 10 times higher than the current (≤ 0.01 μA) measured in control experiments in water containing 0.4 mM $[P_2W_{18}O_{62}]^{6-}$, 0.1 M Na_2SO_4 and 0.2 M DEA or 0.4 M DEAS and 0.4 mM $[P_2W_{18}O_{62}]^{6-}$ and 0.1 M Na_2SO_4. The photocurrent increased with DEAS concentration.

From Water Oxidation to Water Splitting. Photooxidation of water has been demonstrated to occur when $[P_2W_{18}O_{62}]^{6-}$ is dissolved in "wet" IL and aqueous solutions containing ILs as the electrolyte. In principle, an indirect form of water splitting could be achieved with a suitable polyoxometalate if protons preferentially act as the oxidizing agent for the oxidation of the reduced forms of the polyoxometalate. This could be achieved if dioxygen, produced during water oxidation, is rapidly removed from the solution to prevent the back reaction occurring with the reduced polyoxometalate, as in eq 7.

Transition metal cobalt[32] and copper[33] complexes are known to react rapidly with dioxygen in aqueous solution. Thus using a complex that is stable under acidic conditions and that could reversibly trap dioxygen might be a plausible route to achieve indirect water splitting. In a solution now lacking dioxygen, $[P_2W_{18}O_{62}]^{7-}$ also could be further reduced by using a more powerful light source, to achieve reduction of protons with $[P_2W_{18}O_{62}]^{8-}$ and the more highly reduced anions and complete the catalytic cycle (eq 20).

$$[P_2W_{18}O_{62}]^{(7+n)-} + 2mH^+ \rightarrow [P_2W_{18}O_{62}]^{(7+n-m)-} + mH_2 \qquad (20)$$

However, the present studies with $[P_2W_{18}O_{62}]^{6-}$ describe a model reaction with minimal catalytic capacity.

CONCLUSIONS

The photocatalytic activity of $[P_2W_{18}O_{62}]^{6-}$ shows a strong dependence upon medium (water, organic solvent, IL). In aqueous media and in conventional molecular organic solvents, addition of an alcohol such as 2-propanol is required to achieve photochemical reduction of $[P_2W_{18}O_{62}]^{6-}$. The reaction with light is influenced by the nature of the solvent. In "wet" aprotic or protic IL media, photoreduction occurs when water is present as the electron donor. Photoreduction of $[P_2W_{18}O_{62}]^{6-}$ also occurs in aqueous solutions containing relatively high concentrations of protic ILs as the electrolyte. In the dark, $E^0{}_F$ values (Table 1) associated with the polyoxometalate redox couple are far more positive than in organic solvents, and the same scenario probably prevails in the photoactive state. However, $E^0{}_F$ values are even more favorable in neat water so thermodynamic changes probably do not provide the full story to account for photochemical oxidation of water in an IL medium. It is plausible that a combination of the modified structure of water and more favorable $E^0{}_F$ values for the photochemistry in the excited state than applies in the cases of neat water or molecular organic solvents[16,31] facilitates the oxidation of water to O_2 and H^+ and allows H_2O to occupy the role of an electron donor. Spectroscopic data imply that water in an IL is embedded in the "free" state (no self-aggregation via strong hydrogen bonding with other water molecules). These modified properties and implications have been reviewed in ref 16.

The data for water oxidation approximate a net one electron process in the stoichiometric sense (eq 21) but a simple outer sphere process is unlikely.

$$2[P_2W_{18}O_{62}]^{6-} + H_2O \rightarrow 2[P_2W_{18}O_{62}]^{7-} + \frac{1}{2}O_2 + 2H^+ \qquad (21)$$

Two or four electron/photon reactions are mechanistically more probable. Multielectron reduced anions $[P_2W_{18}O_{62}]^{n-}$ (n = 8−10) formed in this way would react more rapidly with O_2 and H^+ in IL media than $[P_2W_{18}O_{62}]$.$^{7-}$ This could lead to rapid scavenging of highly reduced polyoxometalate products. However, an even faster reaction may occur via reaction with $[P_2W_{18}O_{62}]^{6-}$ as in eqs 22 and 23 for example

$$[P_2W_{18}O_{62}]^{6-} + [P_2W_{18}O_{62}]^{8-} \rightarrow 2[P_2W_{18}O_{62}]^{7-} \qquad (22)$$

$$3[P_2W_{18}O_{62}]^{6-} + [P_2W_{18}O_{62}]^{10-} \rightarrow 4[P_2W_{18}O_{62}]^{7-} \qquad (23)$$

with $[P_2W_{18}O_{62}]^{7-}$ effectively being the kinetically inert state. Equivalent reactions using water as the electron donor to produce O_2 and H^+ do not occur in liquid water or in molecular solvents such as MeCN and MeCN/CH_2Cl_2 containing water although they do occur for solid $K_6[P_2W_{18}O_{62}]$ in contact with water vapor.

Mechanisms postulated for the overall 2e$^-$ photooxidation of alcohols by polyoxometalate anions have involved both 1e$^-$ or 2e$^-$ transfers to these anions and give rise to $[P_2W_{18}O_{62}]^{7-}$ as the photoproduct (e.g., eqs 5 and 6).[7,8] However, this 1e$^-$ reduced anion is stable to O_2 and H^+ on the time scale of hours[11] while multiply reduced anions $[P_2W_{18}O_{62}]^{n-}$ (n = 8−10) react much more rapidly with both O_2 and H^+. Consequently, effective catalysis requires photoactivated $[P_2W_{18}O_{62}]^{6-,*}$ mediating the 2e$^-$ oxidation of alcohols R_2HCOH to produce 2e$^-$ reduced species such as $[P_2W_{18}O_{60}(OH)_2]^{6-}$. This pathway may be viewed as involving hydrogen atom extraction or proton-coupled electron transfer. The transfer may be either an outer sphere process or an inner sphere process (with an intermediate such as $R_2HC{-}O{-}O{-}W$).

An extension of the inner sphere model to the oxidation of water gives rise to Scheme 2 (protons are most likely bound to the reduced anions):

Step (i). Proposes reaction between two activated water molecules, one via interaction with the IL ions (H_2O^*) and a second as a μ-oxo ligand in the photoactivated anion. This leads to a hydro-peroxo ligand bound to a 2e$^-$ reduced anion (indicated by the label II).

Step (ii). The reduced intermediate may, in turn, be photoactivated to release O_2 and generate a 4e$^-$ reduced lacunary anion $[P_2W_{18}O_{61}]^{8-}$ (indicated by the label IV).

Step (iii). Such a reduced lacunary species would be rapidly scavenged by solvent water, generating an intact 4e$^-$ reduced anion $[P_2W_{18}O_{62}]^{10-}$.

Subsequent Reactions. Highly reduced anions can react rapidly with $[P_2W_{18}O_{62}]^{6-}$ and with both the proposed products of water oxidation (O_2, H^+). In the present case, reaction with $[P_2W_{18}O_{62}]^{6-}$ may be faster, giving rise to $[P_2W_{18}O_{62}]^{7-}$ and O_2 and H^+ as the finally detected kinetically stable products. However, it must be emphasized that the detection of these particular final products does not allow a distinction to be made between an outer sphere or an inner sphere mechanism. Details of the photophysics and other experiments are needed to provide definitive mechanistic details.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Further details are given in Figures S1−S9 and Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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