Photochemistry in Organic Pigment Dispersions. Phthalocyanine-Mediated Photoproduction of Hydrogen Peroxide

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Abstract: The organic pigment x-phthalocyanine dispersed in aqueous medium has been shown to generate hydrogen peroxide photochemically. For this reaction to occur two conditions had to be fulfilled: the surface charge had to be positive (achieved through adsorption of cetyltrimethylammonium bromide) and an adequate reductant was required (ethylenediaminetetraacetic acid). The quantum efficiency for this reaction was determined as a function of pH, temperature, light intensity, O_2 concentration, phthalocyanine concentration, and surface charge. These results are discussed in relation to the application of pigment dispersions for solar energy utilization.

Introduction

Certain photoconducting pigments when dispersed in aqueous media are capable of useful photochemistry.[1] Perhaps the most widely cited example is the ZnO-mediated photosynthesis of H_2O_2.[2-4] In this case, light with energy greater than that of the band gap (3.2 eV) creates H_2O_2 from oxygen at the expense of a reductant. Other inorganic pigments (such as CdS, CdSe, and ZnS) have also been shown to be effective as generators of H_2O_2. However, no reports of H_2O_2 synthesis from organic photoconductors have appeared. This report will focus on the photoactive pigment x-phthalocyanine and its ability under certain conditions to photogenerate hydrogen peroxide.

The utilization of pigment dispersions for conversion of light energy to chemical free energy or for photocatalysis is an area which has recently been reconsidered.[5,6] This was earlier suggested by Rubin et al.[2] using aqueous dispersions of ZnO to generate H_2O_2. The system described here is intended as a model to reveal some of the limitations and problems which exist in this type of approach. In particular, the quantum efficiency, Φ, is discussed in terms of the variables of which it is a function. In using phthalocyanine, the potential application of organic pigment dispersions for solar energy utilization is demonstrated.

Experimental Section

α-Phthalocyanine (H_2Pc) was obtained from BASF and extensively ball milled[7] to yield the x form. The resultant x-H_2Pc had a surface area of 70 m^2/g and consisted of submicron-sized particles.[8] The aqueous suspensions used for these experiments contained 0.2% x-H_2Pc by weight, 0.1 M EDTA, and 0.2% surfactant (ensuring a monolayer adsorption), and were irradiated ultrasonically to achieve dispersion. Cetyltrimethylammonium bromide (CTAB) (Sigma), Aerosol OT (AOT) (American Cyanamide Co.), and ethylenediaminetetraacetic acid disodium salt (EDTA) (The British Drug House, Ltd.) were used as received.

Oxygen uptake measurements were accomplished with a YSI Model 53 oxygen monitor which is a closed system containing 5 mL of solution. Illumination was achieved using a Quartzline 300-W projection lamp with a Corning CS 3-66 filter. The enzyme catalase (Sigma) was added as a probe to determine whether hydrogen peroxide (H_2O_2) had been formed. An increase in O_2 concentration upon catalase addition reflects the catalytic dismutation of H_2O_2 to oxygen and water (Figure 1). Air-saturated H_2O contains $\sim 2 \times 10^{-4}$ M dissolved O_2 and typically the O_2 concentration was monitored until at least half had been consumed (see Figure 1).

The quantum efficiency (Φ) was measured by determining the initial rate of oxygen uptake (which is equivalent to the rate of H_2O_2 generation) and dividing by the number of photons per second incident upon the cell. This was measured with an Alphametrics Model dc 1010 radiometer and a Model P1100S silicon light probe. A broad band (700 nm) or a narrow band (630 nm) interference filter was used for the determination of Φ. This system was also used to measure the quantum efficiency of H_2O_2 formation in a ZnO/air-saturated dispersion containing formate and a value of $\Phi = 0.15$ was obtained. This can be compared to values in the literature of 0.1-0.5.[1] Microelectrophoresis measurements were made on a Rank Bros. Model II instrument using the flat-cell configuration.

Results

x-H_2Pc can be readily dispersed in aqueous media with surfactants such as CTAB or AOT.[8] However, under these conditions no H_2O_2 could be detected when the system was illuminated. This contrasts to the analogous ZnO/H_2O system, where in the absence of additives H_2O_2 is photosynthesized to a limiting concentration of $10^{-5} \rightarrow 10^{-4}$ M.[1,4] Addition of EDTA (reductant) to the x-H_2Pc system, however, resulted in H_2O_2 formation provided that CTAB was present as surfactant (Figure 1). The addition of catalase brings about the dismutation of H_2O_2 which is formed in the photoreaction ($2H_2O_2 \rightarrow 2H_2O + O_2$) with one O_2 being liberated for every two H_2O_2 molecules originally present. Hence a return of the O_2 level to one-half the original value implies 100% conversion of O_2 to H_2O_2. No H_2O_2 synthesis resulted when AOT was used as surfactant.

The quantum efficiency for this reaction, defined as the number of H_2O_2 molecules formed per photon absorbed by the pigment ($\lambda > 600$ nm), was determined as a function of the polarity of surface charge, temperature, pH, light intensity, O_2 concentration, and H_2Pc concentration. The data for T, pH, and light intensity are given in Figures 2-4.

Since this is a closed system, it is possible to determine the dependence of the rate of oxygen uptake on oxygen concentration. The conversion ratio (CR), which is the number of H_2O_2 molecules formed per number of O_2 molecules consumed, is close to one (pH ≤ 10) and therefore demonstrates that the rate of O_2 uptake is the same as the rate of H_2O_2 production. The results show that the rate is proportional to $\{O_2\}^{1/n}$ where $n = 1.8 \pm 0.3$.

Experiments in which the phthalocyanine concentration was varied showed that Φ reached a maximum at 0.05 wt % and remained constant as the concentration increased. The cell used for these measurements had a diameter of 2 cm.

It has previously been reported[8] that adsorption of CTAB on phthalocyanine gives a positive surface charge whereas AOT adsorption results in negatively charged particles. Since Φ was such a strong function of pH, the mobility of the particles was measured as a function of pH. It was found that no significant change ($\Delta\mu < 20\%$) in mobility was observed over the pH range of 4-11.

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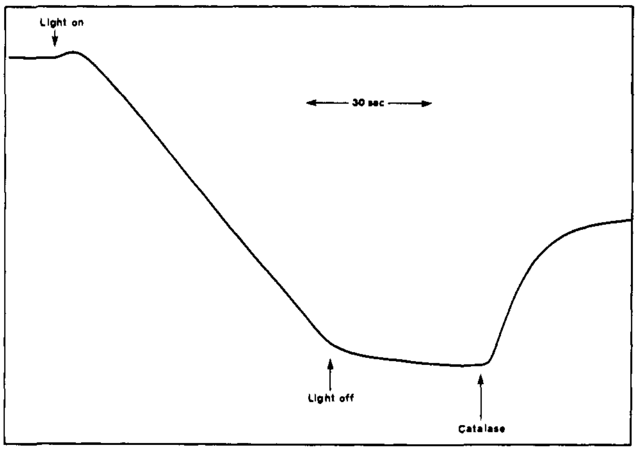

Figure 1. O_2 uptake of an x-phthalocyanine aqueous dispersion containing both CTAB and EDTA.

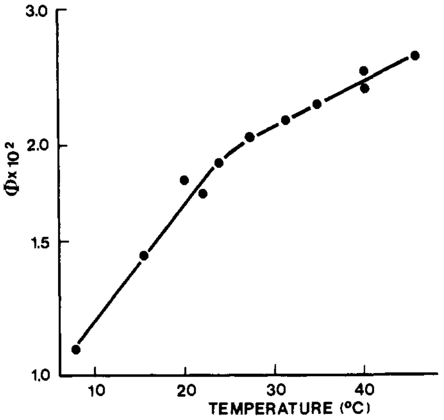

Figure 2. The temperature dependence of Φ for an x-phthalocyanine dispersion at pH 10 and a light intensity of 40 mW/cm^2.

Discussion

These results can be interpreted in terms of the band model for semiconductors.[9] The incident photon creates an electron–hole pair (e^--h^+) by exciting an electron from the valence band (VB) to the conduction band (CB), thus creating both a reducing and an oxidizing agent. Hence, with both oxidants and reductants in solution, photoinduced redox reactions can occur provided that the acceptor level lies below the level of the CB and the donor level above that of the VB.[9]

For O_2 the redox couple $E^0_{O_2/O_2}$ is -0.15 V[10] (all potentials vs. NHE), which is well below E_{CB} (-1.2 V),[11] and thus the O_2 can be reduced photochemically to the superoxide anion (O_2^-). This has previously been confirmed by spin trapping experiments.[8] The E_k^0 for the O_2^-/H_2O couple is $\geq +0.36$, where E_k^0 is the kinetic redox potential.[12] The thermodynamic potential is expected to be higher (i.e., more positive).[12] This is also below that of E_{CB} and can therefore complete the two-electron reduction to hydrogen peroxide.

EDTA was found to be unique in its capacity to act as an electron donor. For example, neither formate nor oxalate was oxidized in these systems, whereas both function as donors in the ZnO photogeneration of H_2O_2.[1] EDTA apparently functions by hole capture from the VB and the resultant electron flow from EDTA to O_2 is achieved by photopumping. The overall process can be summarized by eq 1–4. This most likely is an example of photocatalysis since decarboxylation of EDTA occurs with a large decrease in free energy.

$$\text{x-}H_2Pc \xrightarrow{h\nu} h^+ + e^- \qquad (1)$$

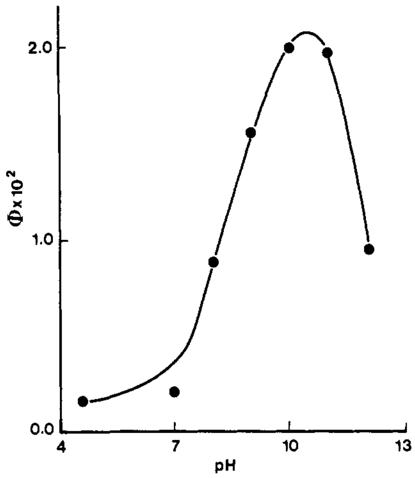

Figure 3. The pH dependence of Φ for the x-phthalocyanine dispersion at 22 °C and 40 mW/cm^2 light intensity.

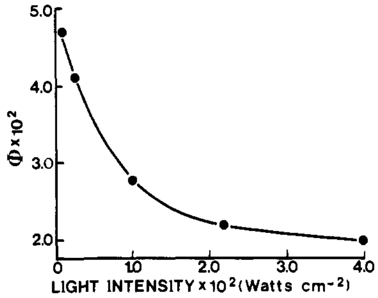

Figure 4. The dependence of Φ on light intensity for the x-phthalocyanine dispersion at pH 10 and 22 °C.

$$e^- + O_2 \xrightarrow{\{H^+\}} (HO_2) \qquad (2)$$

$$HO_2 + e^- \xrightarrow{\{H^+\}} (H_2O_2) \qquad (3)$$

$$\text{EDTA} + h^+ \rightarrow CO_2 + CH_3CHO + \text{amine residue}^{13} \qquad (4)$$

The Φ for this reaction is a function of several variables. These will each be discussed separately.

1. Surface Charge. It was found that it is necessary to have a positive surface charge in order for this reaction to occur. (This was achieved through adsorption of CTAB.) The mobility measurements showed that the surface charge did not vary significantly (<20%) from pH of 4 to 11. In this system the oxidant (O_2) is neutral and should not be affected by the surface charge, whereas the reductant (EDTA) is negative and should be electrostatically attracted to the positive surface. In addition (as pointed out by a referee), the positive surface can also stabilize the O_2^- intermediate formed during the two-electron reduction of O_2 to H_2O_2.

A second feature of the positive charge could be the creation of a space charge region in the H_2Pc. This would cause a downward bending of the bands and would establish an electric field in this region. This would more effectively separate the hole–electron pair and presumably increase Φ. However, there is a dilemma here resulting from the fact that both oxidation and reduction must occur at the same surface. The electrons should have an easy time interfacially transferring to adsorbed oxygen whereas the holes (which have a substantial mobility) will be driven toward the bulk of the particle and thereby be less reactive toward an adsorbed species (EDTA). If the space charge region is important in this type of system, then a determination of the wavelength dependence should reflect this.

That is, those photons which are strongly absorbed in the space charge region should have a higher Φ than those with a lower $\epsilon_{\max}$ ($\lambda \sim 470$ nm). This is a nontrivial experiment in the configuration currently employed but is presently being attempted.

2. pH. The ionization of EDTA is a strong function of the pH. It is only at pH >7 that significant quantities of HY^{3-} and Y^{4-} are present. Bonneau and Pereyre[14] have postulated that only HY^{3-} and Y^{4-} are effective reductants owing to the presence of a non-hydrogen-bonded nitrogen site on EDTA in both these anions. On the other hand, Fife and Moore[15] have shown that all the anionic forms of EDTA can be effective reductants in the photoreduction of riboflavin. However, the rate of their reaction increased as the degree of ionization increased. Both of these results suggest that the increased rate observed in our system as the pH is increased reflects the increased ionization of EDTA.

In addition, the Coulombic attraction between the positive surface and the EDTA anion will be increased as the degree of ionization is increased. It therefore appears that the pH dependence of this reaction is a function of both the total charge on the anion (Coulombic attraction) and the variation in ease of oxidation of the different anionic states. The drop in Φ at higher pH values must initially reflect the onset of the base-catalyzed destruction of H_2O_2. At extreme pH, there is obviously a change in the system as reflected by the low values of Φ.

3. Light Intensity. The fact that Φ decreases with increasing light intensity most likely reflects the fact that the rate of electron-hole recombination will be superlinear while the generation rate is linear with light intensity. In addition, band bending, if present, would be reduced under high light intensities which has the effect of increasing hole-electron recombination.

4. Temperature. Φ can also be limited by the rates of adsorption-desorption of reactants and products if they are slow compared to the previous steps. If H_2O_2 desorption is increased with an increase in temperature, then adsorption of O_2 can occur, thereby increasing the turnover rate. This will reduce the competitive hole-electron recombination reaction and increase Φ. The increased Φ of this reaction with temperature could only be measured to 45 °C and therefore the maximum value is unknown.

5. O_2 Concentration. The rate of the reaction was found to depend approximately on $\{O_2\}^{1/2}$. This dependence can be explained by considering the adsorption of O_2 onto the surface of x-H_2Pc. If the adsorption follows a Freundlich-type isotherm

$$y = kC^{1/n}$$

where y is the weight of the solute adsorbed per g of adsorbent and C is the concentration in the solution, then the rate of reaction, which is proportional to the amount adsorbed, y, will depend on $C^{1/n}$. Both k and n are empirical constants. In this case n is approximately 2. It should be noted that the Freundlich equation is empirical and applies only in dilute systems. This condition is certainly met by the present system where O_2 has a maximum value of 1×10^{-3} M. (The above discussion assumes that the equilibration of O_2 adsorption is rapid compared to the observed reaction and that the change in rate is primarily a reflection of the change in oxygen concentration.)

Assuming that all these effects are additive, a maximum value for Φ under our experimental conditions would be 0.12, corresponding to a photon efficiency of 0.24 (each H_2O_2 molecule generated requires two photons). Experimentally, the highest value we recorded in our experiments was ~0.1 for photon efficiency of 0.2. The maximum achievable value is unknown but most likely is higher as it appears limited by the temperatures which can be achieved with the present experimental configuration (Figure 2).

The results in these experiments are consistent with ESR results reported previously[8] which showed that O_2^- is photoproduced in these systems if both EDTA and CTAB are present. Since the spin traps used to detect the O_2^- in those experiments could react with O_2^- either on the surface or after desorption, the ESR experiments do not allow us to distinguish whether the H_2O_2 arises from a two-electron reduction of O_2 on the surface or a disproportionation of O_2^- in solution. However, as it is known that the rate constant for the reaction $O_2^- + O_2^- \rightarrow O_2 + H_2O_2$ is negligible at higher pH values,[16] a solution reaction appears unlikely.

Conclusions

It has been demonstrated that an organic pigment can effectively mediate the photochemical reduction of oxygen to hydrogen peroxide at the expense of the reductant, EDTA. No photochemical oxygen uptake occurs in the absence of EDTA, reflecting the known stability of phthalocyanine pigments. (Many inorganic pigments such as ZnO and CdS undergo self-oxidation in the absence of a reductant.) Surfactants are normally required to disperse organic pigments in aqueous medium and it is observed that the adsorption of a monolayer of surfactant for dispersability does not prevent the photochemistry. The surface charge of the pigment which is also controlled by the nature of the surfactant was found to be crucial in controlling H_2O_2 generation. In this system, a cationic surfactant was required to impart a positive surface charge since our reductant was negatively charged and the oxidant (O_2) neutral. This implies that the selection of oxidants and reductants must be compatible with the surface charge; e.g., a positively charged oxidant would require a negative surface and a neutral (or positive) reductant. In addition the products should desorb rapidly from the surface to allow for adsorption of reactants.

For solar energy utilization the reduction in Φ with increasing light intensity is a negative effect. However, the fact that Φ increases with temperature could be exploited in solar energy utilization systems. Finally, it is important to note that organic pigments can achieve high quantum efficiencies when dispersed in aqueous medium.

References and Notes

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