Photocatalytic Oxidation of Organic Acids on Quantum-Sized Semiconductor Colloids

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A detailed analysis of the reaction products and mechanisms of the photocatalytic oxidation of acetate in the presence of quantum-sized ZnO colloids ($D_n \approx 40$ Å) is presented. The principal oxidation products and reaction intermediates are determined to be CO2, HCO2-, CHOCO2-, HCHO, CH₃OOH, CH₃COOOH, and H₂O₂. Formate and glyoxylate, which are found as intermediates in the photooxidation of acetate, also serve as effective electron donors on illuminated ZnO surfaces. The proposed relative reactivity of electron donors toward photooxidation is in the following order: $CHOCO_2^- > HCO_2^- > HCHO >$ $CH_3CO_2 > H_2O_2 \ge CH_3COOOH > CH_3OOH$. Observed product distributions are discussed in terms of pathways involving direct oxidation of surface-bound acetate by valence band holes (or trapped holes) and the indirect oxidation of acetate by surface-bound hydroxyl radicals. The product distribution observed at low photon fluxes is not consistent with oxidation primarily by free hydroxyl radicals. A mechanism involving the reaction of an intermediate carbon-centered radical with >ZnOH surface sites is proposed. When electron donors are strongly adsorbed to semiconductor surfaces, surface-mediated reactions appear to play a dominant role in the determination of the time-dependent product distributions.

Introduction

The application of illuminated semiconductors for the remediation of contaminants has been used successfully for a wide variety of compounds such as PCBs, simple aromatics, halogenated alkanes and alkenes, surfactants, and pesticides (1-8) as well as for the reductive deposition of heavy metals (e.g., Pt⁴⁺, Au⁴⁺, Rh³⁺) from aqueous solution to surfaces (9). In many cases, complete mineralization of organic compounds has been reported (1, 2, 8). In the case of photocatalytic acetate oxidation, complete mineralization would be described by the following stoichiometry:

$$CH_{3}COOH + 2O_{2} \xrightarrow{ZnO + h\nu} 2CO_{2} + 2H_{2}O$$

In addition, illuminated aqueous suspensions of semiconductors (CdS, CdSe, α -Fe₂O₃, TiO₂, and ZnO) have been shown to generate significant concentrations of hydrogen peroxide (10–15). Hoffman et al. (16) have recently shown that ZnO produces H₂O₂ more efficiently than TiO₂. This characteristic combined with the relatively benign environmental effects of ZnO make it an attractive potential source of H₂O₂ in contaminant destruction technologies.

Draper and Crosby (17) have reported a controlled field demonstration of the photocatalyzed destruction of molinate and thiobencarb by ZnO. The rate of loss of molinate is enhanced by a factor of 40, but it was not determined if degradation was mediated by photocatalytic oxidation, photocatalytically produced H_2O_2 , or the simultaneous operation of both pathways.

Semiconductors with band-gap energies in the range of UV and visible light exhibit photocatalytic activity because light absorption produces a conduction band electron (a reductant) and a valence band hole (an oxidant). Even though the mechanistic details of the processes are not fully understood, hydrogen peroxide is known to be produced from dioxygen by reduction with conductionband electrons. In contrast, most organic compounds are degraded via oxidation by valence band holes or OH. radicals. Because the electron and hole are produced simultaneously upon band-gap excitation, electron and hole transfer pathways that are competitive with bandgap recombination must be available for both electron donor and electron acceptor. For example, the coating of TiO_2 with Pt islands that act as electron traps increases the efficiency of the photooxidation of lactic acid presumably by short circuiting the band-gap recombination process (18).

In the present study, the photooxidation of acetate, formate, and glyoxylate was investigated together with the concurrent production of hydrogen peroxide by quantum-sized (Q-sized) ZnO. The products of acetate oxidation were chosen for detailed analysis; it is already present as a byproduct of the synthesis of Q-sized ZnO, and radiolysis studies of acetate oxidation have suggested that OH· and direct hole oxidation reactions would result in different products and product ratios (19, 20). Formate and glyoxylate were studied to gain insight on the behavior of acetate oxidation products as hole scavengers. Q-sized ZnO particles with particle diameters, $D_{p} \approx 40$ Å, were used as photocatalysts due to their negligible light scattering properties, higher specific surface areas, and larger band-gap energies relative to bulk-sized semiconductor particles $(D_{\rm p} \approx 0.1 \,\mu{\rm m})$. Because of these properties, Q-sized particles are ideal for optical measurements and mechanistic investigations. The objectives of this study, therefore, were to (i) identify efficient hole scavengers which could be used to maximize H_2O_2 production, (ii) determine whether acetate mineralization occurs via reaction with hydroxyl radical or direct interaction with valence band holes, and (iii) evaluate the implications of the results for the general mechanism of organic compound oxidation by semiconductor photocatalysts. Product distributions for the oxidation of acetate and for intermediate carboxylic acids are presented and discussed in terms of alternative reaction mechanisms.

Experiment Section

Synthesis of Q-sized ZnO particles and preparation of aqueous suspensions are described in detail in the pre-

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ceding companion paper (16). The electron donors added to the suspensions, sodium formate (Aldrich) and sodium glyoxylate (Sigma), were reagent grade and used as received. The pH of the ZnO colloidal suspensions was maintained at pH 7.8 by the inherent buffering capacity of the amphoteric ZnO surface (21).

Light sources, filters, actinometry procedures, oxygen saturation, and temperature conditions used in this study are described in the preceding paper (16). Reaction volumes varied from 3 to 50 mL. In some cases, aliquots of the irradiation mixture were withdrawn at various times for composition analysis. However, in most experiments, separate solutions were prepared for each data point in concentration-time space. This facilitated multiple and duplicate chemical analyses on identical solutions in addition to the trapping of CO_2 released during complete oxidation.

Hydrogen peroxide and organic hydroperoxide concentrations were determined by several independent methods. Calibration curves for the various methods were constructed using standards prepared by dilution of 30%hydrogen peroxide (Hunt), which had been standardized by titration with potassium permanganate. The first method is the spectrophotometric determination of triiodide, described in the preceding paper (16). Absorbance measurements were made using a Hewlett Packard 8451A diode array spectrophotometer. For the Hewlett Packard instrument, we found that the stability of the I_{3} absorbance was improved by using the 300-nm cutoff filter on the Hewlett Packard filter wheel to absorb excess UV light.

A second method for peroxide analysis is the fluorometric determination of the p-hydroxyphenylacetic acid (POPHA) dimer, also described earlier (16). Fluorescence measurements were made using a Shimadzu RF-540 spectrofluorimeter with excitation and emission wavelengths of 315 and 406 nm, respectively, and bandpasses of ≤ 10 nm. The two methods showed excellent agreement (within $\pm 5\%$) for the analytical determination of the sum of $[H_2O_2]$ and $[CH_3C(O)OOH]$. This method was also adapted for postcolumn derivatization enabling the chromatographic separation and determination of peroxides (22-24). A Dionex Bio-LC fitted with an Alltech Econosphere C18 column (5 μ m, 4.6 \times 250 mm) was used with 1 mN $H_2SO_4/0.1$ mM EDTA as the mobile phase. Postcolumn derivatization was performed with an Alpkem RFA-300 autoanalyzer using general procedures described by Igawa et al. (25). For peroxide determinations, an LC flow of 0.5 mL min⁻¹ was mixed with 74 μ L min⁻¹ streams of air, fluorescent reagent solution, and sodium hydroxide. The fluorescent reagent solution contained 0.35 M potassium hydrogen phthalate adjusted to pH 5.5, 26 mM recrystallized POPHA, 1×10^5 units L⁻¹ horseradish phthalate adjusted to pH 5.5, 26 mM recrystallized POPHA, 1×10^5 units L⁻¹ horseradish peroxidase and 0.1% (v/v) of Triton X-100. The Bio-LC air and fluorescent reagent flow lines were joined with tees and mixed with a 15-turn glass mixing coil. A solution of $0.4\,M\,NaOH$ was added and mixed with a tee and a 10-turn mixing coil. Fluorescence of the derivatized solution was measured with the Shimadzu RF-540 spectrofluorimeter using a quartz flow cell. Detection limits were $10 \,\mu M$ for hydrogen peroxide and are similar for organic hydroperoxides. Precise standard solutions of organic hydroperoxides such as peracetic acid (Aldrich) could not be prepared because

Table 1.Electrochemical Program Used To DetectHydrogen Peroxide by Ion-Exchange Chromatography							
potential ^a (V vs pH)	time (s)	potential ^a (V vs pH)					
+0.20	0.69	0.20					
0.20	0.74	0.20					
0.20	0.75	-0.33					
1.00	0.80	-0.30					
1.00	0.81	+0.10					
0.20							
	Peroxide by Ion-Ex potential ^a (V vs pH) +0.20 0.20 0.20 1.00 1.00 0.20	Peroxide by Ion-Exchange Ch potential ^a (V vs pH) time (s) +0.20 0.69 0.20 0.74 0.20 0.75 1.00 0.80 1.00 0.81 0.20 0.71					

^a Integrated amperometry with an integration time of 0.15–0.69

the solutions also contained H_2O_2 , preventing standardization by permanganate titration. Relative retention times of H_2O_2 and ROOH agreed well with retention times measured by Kok et al. (22). The retention times were 10.0, 10.4, and 12.0 min for H_2O_2 , CH_3OOH , and CH_3 -COOOH, respectively. Hydrogen peroxide and organic hydroperoxides can be distinguished by reacting the samples with catalase (Sigma) to destroy the H_2O_2 before the treatment with peroxidase to determine ROOH (22-24). This was necessary to observe low levels of organic hydroperoxides in the presence of often much larger H_2O_2 concentrations.

Hydrogen peroxide was also quantified by ion-exchange chromatography using a Dionex Bio-LC system equipped with the pulsed electrochemical detector and gold electrode. A Dionex OmniPac PAX-500 column and aqueous sodium hydroxide at pH 10 were used to separate hydrogen peroxide and organic hydroperoxides. The electrochemical approach used was modified from a procedure developed for hydroxy compounds (26-29). Table 1 shows the electrochemical program giving optimal sensitivity. Due to peroxide degradation in the mobile phase and on the column, the detection limits, $40 \,\mu$ M for hydrogen peroxide and peracetic acid, were high.

Carboxylic acid concentrations ($\geq 5 \ \mu M$) were determined on a Dionex Bio-LC with a Dionex OmniPac PAX-500 column (8 μ m, 5 × 250 mm) using a NaOH gradient coupled with conductivity detection. A total of 100 μ L of 0.01 M HF was added to each 5-mL aliquot of illuminated solution before treatment with a Dionex OnGuard-H filter to remove excess Zn^{2+} , which would otherwise precipitate at the high pH of the eluant. Typical retention times were 7, 9, 12, and 18.5 min for fluoride, acetate, formate, and glyoxylate, respectively. Retention times varied as much as 1 min depending on concentration of analyte, sample composition, and eluant reproducibility; standard additions allowed unambiguous identification of species. Formaldehyde ($\geq 5 \mu$ M) was detected using the Nash method (30, 31). Carbon dioxide was analyzed by scrubbing the oxygen gas used for bubbling into a NaOH solution. The amount of CO₂ absorbed was calculated from the drop in pH.

Neutral products were potentially lost as volatiles in the oxygen stream over the course of these experiments. As reported in the preceding paper (16), peroxide production was equal in closed and open systems, indicating negligible losses. An attempt to capture volatile organic hydroperoxides in cold aqueous scrubbers showed no loss from the irradiated solution. The Henry's law constant for formaldehyde, 2.97×10^3 M atm⁻¹ at 25 °C (32), is smaller than that for H₂O₂ at the same temperature [7.36 $\times 10^4$ M atm⁻¹ (33)], but significantly larger than methyl hydroperoxide or peracetic acid [220.5 and 467.6 M atm⁻¹



Figure 1. Two possible pathways for the oxidation of acetate in aqueous semiconductor colloids. Pathway (a) is the direct oxidation via the valence band holes. Pathway (b) is the indirect oxidation via hydroxyl radicals. Predicted products are those of von Sonntag and co-workers (*19, 20*).

at 25 °C (33)]. Therefore, losses of formaldehyde would be expected to be negligible also.

Results and Discussion

Background. Previous homogeneous radiolysis studies by von Sonntag and co-workers (19, 20) suggest that the oxidation of acetate should produce different product state distributions depending on whether the oxidation proceeds via H-atom abstraction by hydroxyl radicals (either adsorbed at the surface or free in solution) or via direct reaction with valence band holes (or surface-trapped holes) followed by CO_2 loss in a photo-Kolbe reaction. The two alternative pathways and expected products (after von Sonntag et al.) are outlined in Figure 1. Von Sonntag and co-workers found the final products of the radiolysis of acetate (OH • pathway) at pH 7.8 to be glyoxylic acid (2.7), glycolic acid (0.7), formaldehyde (1.4), carbon dioxide (1.4), total hydroperoxides (0.7), and hydrogen peroxide (2.5)(19). The G values, which are given in parentheses, are defined as the number of molecules of each product formed per 100 eV of absorbed energy. Loss of acetate occurred with a G value of 5.3 in this study. The products from the direct oxidation of acetate by valence band holes are expected to correspond to those observed for the aqueousphase radiolysis of CH_4 and N_2O . These products at pH 8 are (G values in parentheses) formaldehyde (2.8), hydrogen peroxide (2.1), methanol (1.5), methyl hydroperoxide (0.8), formic acid (0.3), and dimethyl peroxide (0.1) (20).

Evidence for both pathways exists in the semiconductor photooxidation literature. For example, intermediates detected during the photocatalytic degradation of halogenated aromatic compounds are typically hydroxylated structures (7, 34-37). These intermediates are consistent with those found when similar aromatics are reacted with a known source of hydroxyl radicals. In addition, an ESR study has verified the existence of hydroxyl and hydroperoxyl radicals in aqueous solutions of illuminated TiO_2 (38). Mao et al. (39) have found that the rate of oxidation of chlorinated ethanes correlates with the C-H bond strengths of the organics, which indicates that H-atom abstraction by OH[•] may be an important factor in the rate-determining step for oxidation. The strong correlation between degradation rates and concentration of the organic pollutant adsorbed to the surface (40, 41) also implies that the oxidizing species are adsorbed at the surface; however, evidence has also been presented for the



Figure 2. Photooxidation of 2 mM acetate using 1 mM Q-sized ZnO as photocatalyst. Curves guide the eye in distinguishing species. The inset shows the initial rate fits. Lines are linear least-squares fits over the range corresponding to the length of the line. The formate fit is shown by the dashed line; formaldehyde is shown by the dash-dot line. These two lines and the corresponding point symbols are offset from the zero *y*-intercept for clarity.

homogeneous-phase hydroxylation of furfuryl alcohol in aqueous ZnO suspensions (42). On the other hand, Mao et al. (39) have observed that trichloroacetic acid and oxalic acid are oxidized primarily by valence band holes on TiO₂ via a photo-Kolbe process. It should be noted that these compounds also have no hydrogen atoms available for abstraction by OH[•]. Likewise, Draper and Fox (43) were unable to find evidence of any hydroxyl radical adducts for the TiO₂ sensitized reactions of potassium iodide, 2,4,5trichlorophenol, tris(1,10-phenanthroline)iron(II) perchlorate, N, N, N', N'-tetramethyl-p-phenylenediamine, and thianthrene. In each case where the product of hydroxyl radical-mediated oxidation was known from pulse radiolysis studies to be different from that of direct electron transfer oxidation, Draper and Fox observed only the products of the direct electron transfer oxidation.

Products and Relative Rates of Oxidation. Loss of acetate and yields of several of the predicted stable products from the photooxidation of acetate by Q-sized ZnO were measured as a function of irradiation time at pH 7.8 [the surface of ZnO colloids provided the buffering capacity to maintain pH(21)]. Figure 2 shows the results obtained for a suspension of ZnO in which the electron donor is the in situ 2 mM acetate ion remaining from the synthesis of the colloids. H_2O_2 and ROOH analyses were performed using the iodide colorimetric method. The production of CO_2 was also measured; however, the pH changes were too small at early times to accurately determine the carbon dioxide concentration. Instead, the CO₂ concentrations were determined from longer irradiation times (1 h). As described in the experimental section, each data point is obtained from an independently irradiated solution. Variations in absorbance of the solution and in incident light intensity affect the rate of light absorption and thus the rate of change in concentration of these compounds. However, the data shown in Figure 2 have not been corrected or normalized for these variations because the effects were determined to be small. Adjusting for the 5-cm path length in the irradiation cell vields transmittances of less than 2% for all of the colloid suspensions. Actinometry results showed the variation in lamp intensity over approximately 12 h of continuous operation is about 5%. Figure 2 shows the major products



Figure 3. Photooxidation of 2 mM formate in the presence of 1 mM Q-sized ZnO. Legend arrows indicate appropriate axis scale. The solid lines represent non-linear least-square fits of the experimental data.



Figure 4. Photooxidation of 2.0 mM glyoxylate in the presence of 1 mM Q-sized ZnO. Legend arrows indicate appropriate scale. The solid lines represent non-linear least-square fits of the experimental data.

are H_2O_2 [also formed via the reductive pathway (16)], formaldehyde, and formate. From Figure 1, formaldehyde is expected in both mechanisms, but the presence of formate would indicate that pathway (a), the photo-Kolbe decarboxylation, is operative.

The results obtained when additional donors, formate and glyoxylate at 2 mM, were added are shown in Figures 3 and 4, respectively. The data were acquired and treated as described above for acetate alone. These species were chosen as additional donors because they are distinguishing products of the acetate oxidation mechanisms shown in Figure 1 and as such are potentially important donors. Figure 3 shows that, with added formate, the products are H₂O₂, a small amount of formaldehyde, and a very small amount of organic hydroperoxides. In Figure 4, glyoxylate is converted nearly quantitatively to formate: the firstorder rate constants for the loss and production are nearly equal $(0.067 \text{ and } 0.050 \text{ min}^{-1}, \text{ respectively})$. Note that peroxide production is near detection limits. Formaldehyde was measured, but we found that glyoxylate exhibits a positive response to the Nash method. This response is about 1/10 of the response observed with an equivalent concentration of formaldehyde and is dependent on the concentration of Zn²⁺. The data have been omitted because of the uncertainty associated with low levels of analyte in the presence of a large interference.

Table 2. Initial Rates of Reactant Loss (-) and Product Formation (+) in Photooxidation of Organic Acids by Q-Sized ZnO⁴

donors	species ($\mu M \min^{-1}$)						
	CH ₃ CO ₂ -	CH ₂ O	HCO2-	CHOCO2-	H_2O_2	RO ₂ H	
CH ₃ CO ₂ −	-9.6 ±1.7	+2.8 + 0.8	+4.2 ±0.4	N/0	$+13.9 \pm 2.6$	$^{+2.6}_{\pm 0.1}$	
HCO₂ [−]	-1.9 ± 0.7	$+1.5 \pm 0.5$	-22.3 ± 1.7	N/O	$+25 \pm 0.8$	+0.03 ±0.1	
CHOCO2⁻	-0.1 ±0.8	Ι	+74 ± 2.0	-79 ±6.0	+0.2 ±0.02	+0.03 ±0.04	

^a The quantum yields equal these rates divided by the absorbed light intensity of 440 μ Einsteins min⁻¹ L⁻¹. N/O = not observed; *I* = interference in analysis (see text). Uncertainty in slope of linear regression indicated by \pm values.

In order to compare relative rates of loss of electron donors, initial rates of loss or formation of species were determined from the data in Figures 2-4 and are given in Table 2; the linear least-squares fits for initial rates are shown for acetate as the donor in the inset to Figure 2. The use of initial rates is important because products of the donor-hole reaction may participate in subsequent donor-hole reactions. From comparison of the initial rates of loss and formation, and consideration of the reaction chemistries of other measured species, we propose the following relative selectivity of electron donors by excitedstate ZnO:

 $CHOCO_2^- > HCO_2^- > HCHO > CH_3CO_2^- > H_2O_2 \ge CH_3COOOH > CH_3OOH$

This ordering primarily reflects the observation that acetate performs only moderately well as an electron donor in this system, whereas glyoxalate and formate are the most effective donors studied. The net change in acetate concentration is nearly zero in irradiations with added formate and glyoxylate (Figures 3 and 4). A reasonable explanation for the small loss observed is that some acetate is closely associated with the ZnO matrix during the synthesis and this acetate is quickly reacted. The decreases in acetate concentration are on the order of the experimental uncertainty and are less than 200 μ M, which is the amount of acetate which was found to be nondialyzable in 2-propanol (16). That in situ acetate is not preferentially oxidized supports free competition for oxidizing species by electron donors in solution. This is corroborated in the preceding paper (16), in which the rate of hydrogen peroxide formation decreased in the following order of electron donors: $HCO_2^- > C_2O_4^{2-} > CH_3CO_2^-$.

The observed rates of donor loss or H_2O_2 production in the presence of various donors do not correlate with redox potentials or complex formation constants. The oneelectron redox potentials of oxalate, acetate, formate, hydrogen peroxide, and formaldehyde are 2.43, 2.33, 2.16, 1.78, and -1.22 V (vs NHE), respectively (44). For comparison, at pH 8, the redox potentials of the electron and hole in ZnO are approximately -0.33 and 2.87 V (vs NHE) (45). The Zn(H₂O)₅CO₂R⁺ formation constants, given by log β , are as follows: 3.9 (oxalate), 1.1 (acetate and glyoxalate), and 0.7 (formate) (46).

Glyoxylate. Based on the results of Table 2, glyoxylate appears to exhibit the fastest rate of degradation of all the added donors. However, the very low production rate of H_2O_2 in the presence of glyoxylate suggests that either

glyoxylate interferes with the reduction of dioxygen by conduction band electrons or glyoxylate rapidly degrades H_2O_2 . Yokota et al. (47) investigated the homogeneous reaction of radioactively labeled $HCOCO_2^-$ and H_2O_2 :

$$H^{14}COCO_2^- + H_2O_2 \rightarrow H^{14}CO_2^- + CO_2 + H_2O$$
 (1)

The reaction was found to be second order at pH 8.0 and 25 °C, with a rate constant of 2.27 M⁻¹ s⁻¹. Applying this rate constant to the results in Figure 4, the initial concentration of H_2O_2 necessary to give the observed rate of glyoxylate loss is 313 μ M. Since initial hydrogen peroxide concentrations in Figures 2 and 3 were below detection limits, this value appears unlikely. However, in this heterogeneous photocatalytic system, H₂O₂ produced at the semiconductor surface experiences a high local concentration of adsorbed glyoxylate which may explain the rate of glyoxylate degradation in Figure 4. The observation that the rate of glyoxylate degradation equals the rate of formate production and that the limiting formate concentration approaches the initial glyoxylate concentration suggests that formate is a direct product of glyoxylate degradation. Furthermore, the observation that glyoxylate loss continues at longer irradiation times in the presence of a high concentration of formate indicates that glyoxylate is a better hole scavenger than formate.

The homogeneous reaction given in eq 1 is insufficient to explain all our observations unless the product CO_2 donates electrons to ZnO, allowing the production of equimolar H_2O_2 . This is unreasonable because CO_2 is fully oxidized. The following mechanism is proposed to explain the results presented in Figure 4:

$$HCOCO_2^- + H_2O \leftrightarrow HC(OH)_2CO_2^-$$
(2)

$$\mathrm{HC(OH)_2CO_2^-} + \mathrm{h^+_{vb}} \to \mathrm{HC(OH)_2CO_2^-} \tag{3}$$

$$\mathrm{HC(OH)}_{2}\mathrm{CO}_{2}^{\bullet} \rightarrow \mathrm{HC(OH)}_{2}^{\bullet} + \mathrm{CO}_{2} \tag{4}$$

$$HC(OH)_{2}^{\bullet} + h^{+}_{vb} \rightarrow HCO_{2}^{-} + 2H^{+}$$
(5)

$$O_2 + e_{cb}^{-} \rightarrow O_2^{\bullet -}$$
 (6)

$$O_2^{\bullet -} + H^+ \to HO_2^{\bullet} \tag{7}$$

$$\mathrm{HO}_{2}^{\bullet} + \mathrm{e}_{\mathrm{cb}}^{-} \to \mathrm{HO}_{2}^{-} \tag{8}$$

$$\mathrm{HO}_{2}^{-} + \mathrm{H}^{+} \to \mathrm{H}_{2}\mathrm{O}_{2} \tag{9}$$

The net reaction occurring on ZnO, obtained by summing the oxidative (eqs 2-5) and reductive (eqs 6-9) steps, is then:

$$HCOCO_2^- + O_2 + H_2O \rightarrow HCO_2^- + CO_2 + H_2O_2$$
 (10)

Combining eq 10 with the homogeneous reaction studied by Yokota et al. (47)

$$HCOCO_{2}^{-} + H_{2}O_{2} \rightarrow HCO_{2}^{-} + CO_{2} + H_{2}O$$
 (11)

results in the following overall reaction:

$$2\text{HCOCO}_2^- + \text{O}_2 \rightarrow 2\text{HCO}_2^- + 2\text{CO}_2 \qquad (12)$$

The key aspects of this mechanism are electron donation

to ZnO by dissolved glyoxylate (eq 3) with production of CO_2 (eq 4), analogous to pathway (a) of Figure 1, and by the remaining radical (eq 5) in a "current doubling" process discussed in a later section of this paper. Steps 6-9 are the production of H_2O_2 by valence band electrons. The same net reaction could be achieved by postulating slightly different steps (e.g., $2HO_2 \rightarrow H_2O_2 + O_2$); however, it may be impossible to determine which of several parallel pathways, if any, predominates. With the stoichiometry of eq 12, glyoxylate loss by reaction with ZnO followed by reaction with H₂O₂ results in equimolar production of formate, explaining the 1:1 conversion of glyoxylate to formate with equivalent rate constants and the low H_2O_2 levels. The corrected initial rate of glyoxylate loss via hole scavenging alone would then be half of the value given in Table 2 or $39.5 \,\mu M \text{ min}^{-1}$, still the highest rate of donor loss observed.

Formaldehyde. Formaldehyde is difficult to rank as an electron donor in the ZnO system, because it is observed in low concentrations compared to acetate and added formate. However, in irradiations with acetate, the concentration of formaldehyde builds up to a higher level than formate, indicating a higher rate of formation and/or a slower rate of degradation. Formaldehyde has been shown to be a major product, formed in large excess over formate, in both studies by von Sonntag and co-workers (19, 20). This supports a higher rate of formation of formaldehyde in the ZnO system. When acetate is the only electron donor present initially, the formate concentration levels off more quickly than does formaldehyde. This is consistent with a higher rate of oxidation of formate. At pH 7.7, formate would be expected to be attracted to the net positively charged ZnO surface $(pH_{zpc} = 9.3)$ and therefore exhibit a higher rate of degradation. Based on these electrostatic considerations, formate is ranked above formaldehyde as an electron donor. Additional experiments would be required to confirm this hypothesis, but formaldehyde would not be expected to be an important initial electron donor in a practical application, due to potential air contamination by volatilization.

Peroxides. Hydrogen peroxide is apparently a poor electron-donating agent. The buildup of hydrogen peroxide to over $500 \,\mu M$ does not prevent acetate degradation, and hydrogen peroxide is observed to reach the highest concentrations of any products detected. It is difficult to assess the relative positions of CH₃OOH and CH₃COOOH in this scheme because they are always observed in very small amounts. This is at least partially because they are formed in such small amounts, but could also be because of significant reactivity as an electron donor. However, hydroperoxides are less reactive than hydrogen peroxide and peracetic acid as oxidizing agents in reactions with catalase (22-24). As reducing agents in the iodide/ molybdenum reaction, hydrogen peroxide and peracetic acid are again more reactive (15, 16). Therefore, CH₃-OOH is placed as the poorest electron-donating agent observed.

Significant concentrations of organic peroxides are produced only when acetate is used as the hole scavenger. Essentially no organic peroxides are produced when formate, oxalate, or citrate are used as hole scavengers (16). The organic peroxides from acetate oxidation were identified via LC retention times to be methyl hydroperoxide and peracetic acid. Figure 5 shows the time evolution of peroxides produced upon illumination of a



Figure 5. Peroxide production in an irradiated Q-sized ZnO suspension of 1 mM ZnO and 2 mM acetate. The solid lines represent non-linear least-square fits of the experimental data.

Q-sized ZnO suspension containing 2 mM acetate as the hole scavenger. Formation of these peroxide products is consistent with the following mechanism:

$$CH_3COO^- + h_{vb}^+ \rightarrow {}^{\bullet}CH_3 + CO_2$$
(13)

$$CH_3 + HO_2 \rightarrow CH_3OOH$$
 (14)

$$CH_3^{\bullet} + O_2 \rightarrow CH_3O_2^{\bullet}$$
 (15)

$$2CH_{3}O_{2}^{\bullet} \rightarrow CH_{3}OOH + HCO_{2}H$$
(16)

$$CH_3COO^- + H_2O_2 \rightarrow CH_3COOOH + OH^- \quad (17)$$

In the case of formate, no organic peroxides would be expected to form since the oxidation of formate leads to the formyl radical, which is rapidly oxidized to CO_2 as follows:

$$HCOO^{-} + h_{vh}^{+} \rightarrow HCOO^{-}$$
(18)

$$HCOO^{\bullet} \rightarrow CO_2 + H^+ + e^-$$
(19)

Similarly, organic peroxides are not expected with the glyoxylate donor. Steps 4 and 5 of the proposed mechanism for glyoxylate oxidation predict only formate and CO_2 .

Mass Balance Analysis. The absence of sensitive carbon dioxide measurements at short illumination times precludes an exact time-resolved mass balance in our systems. In the case of acetate, comparison of the values in Table 2 for the initial rate of loss of acetate and the rates of formation of all the observed products gives a 46% recovery on the basis of carbon (assuming hydroperoxides contain a single carbon). The G values reported by von Sonntag and co-workers (see Background) (19, 20) can be used to predict how much carbon dioxide should be produced for a given rate of acetate degradation in indirect oxidation of acetate by hydroxyl radical. The Gvalues for acetate loss and CO₂ production are 5.3 and 1.4, respectively. Combined with the observed rate of acetate loss, -14.7 μ M min⁻¹ (Table 2), the CO₂ production rate is predicted to be $3.9 \,\mu M \, min^{-1}$, bringing the carbon mass balance to 59%. For direct oxidation or the photo-Kolbe mechanism, the rate of CO_2 production should be equal

to acetate loss, bringing the mass balance to 96%. The validity of this correction is demonstrated in 1-h irradiation experiments, in which the rate of loss of acetate was observed to be equal to the rate of production of CO_2 and to the rate of production of H_2O_2 . In these experiments, H_2O_2 and ROOH concentrations were measured using several of the techniques described in the Experimental Section. The irradiations with added formate and gly-oxylate also achieve carbon balance if one assumes that formate and formaldehyde are oxidized to CO_2 .

Implications for Reaction Mechanism. Hydrogen peroxide may be produced by either the reduction of molecular oxygen and/or the oxidation of water. We have shown by 18 O isotopic labeling experiments (16) that the production of H_2O_2 by photoexcited ZnO results from the two-electron reduction of dissolved molecular oxygen (16, 48). The concurrent one-electron oxidation of a donor results in the formation of a radical species which can give an array of stable products via subsequent one-electron reduction or oxidation reactions or by radical-radical combinations. The experimental results and mechanisms proposed by von Sonntag and co-workers are under conditions in which the former is minimized and their mechanisms predict that products arise almost solely through dimerized radical precursors. Thus, for the radiolysis product yields to be quantitatively applicable here, the stoichiometry of CH_3CO_2 -: H_2O_2 should be 2:1. In the case of acetate and formate as donors, the initial rate of loss of these donors is 10-30% less than the initial rate of hydrogen peroxide formation.

To explain the observed stoichiometry of nearly 1:1, it is necessary to postulate a mechanism in which the donor is doubly oxidized. Two such possibilities will be considered here. In the first scheme, a donor undergoes a one-electron oxidation, and the resulting radical is trapped until a second reactive site is formed by absorption of a second photon. Thus, the original donor undergoes two sequential one-electron oxidations. In the second pathway, the radical species formed is oxidized by reaction with the ZnO particle via electron injection, producing a second conduction band electron that can further reduce oxygen. The net result is that one photon produces a two-electron reduction of O_2 and a two-hole oxidation of the donor, or equivalently, current-doubling. This effect would cause the maximum quantum yield for hydrogen peroxide formation to be 1.0 instead of 0.5 (16).

In the first scheme, the amount of time between excitation events could be crucial in limiting the distance the radical diffuses, assuming that the oxidation steps must occur on or very near the semiconductor particle surface. Calculations by Turchi and Ollis (49) have indicated that a hydroxyl radical formed at the TiO₂ surface could diffuse 100 Å or more before reaction with some solution species. In the present experiments, the irradiation rate ($\approx 440 \ \mu M$ photons min⁻¹) and the concentration of particles [1 mM ZnO and ~3000 molecules/ particle (21)] give a rate of photon absorption of 22 photons particle⁻¹ s⁻¹. This flux then gives the maximum possible rate of valence band hole formation. It should be noted that the actual rate is probably much lower because of electron hole recombination. However, this maximum rate would allow an acetate or other radical species a minimum of 45 ms to diffuse from the ZnO surface. Assuming a diffusion coefficient of 10⁻⁹ m² s⁻¹, a radical could potentially diffuse 13 μ m between successive photon hits.

Thus, a singly oxidized donor must be trapped on or bound to the surface in order to explain two successive oneelectron oxidations of acetate.

Lawless et al. (50) studied the reaction of Q-sized TiO₂ and 'OH generated using pulse radiolysis. They determined the rate constant of this reaction to be 6.0×10^{11} M⁻¹ s⁻¹, near the diffusion-controlled limit, and point out that hydroxyl radical desorption is unlikely. The product of the reaction was found to be an oxidant, not a reductant. and the authors argue that it is indistinguishable from a trapped hole. Oxygen had no effect on the reaction rate. Radicals other than the hydroxyl radical could be expected to exhibit high reactivities, generating a surface-trapped species that may exist until another valence band hole is produced. However, a surface-trapped acetate or other carbon-centered radical should be distinguishable from a trapped hole by its tendency to react as a reductant rather than as an oxidant. The surface trap for the carboncentered radical could be the reaction with surfaceadsorbed oxygen, which may be present in abundance. This is analogous to homogeneous radiolysis reactions in oxygenated solutions in which carbon-centered radicals immediately add dissolved oxygen.

The following example illustrates both the precedent of postulating a surface carbon radical species and electron injection. A surface carbon radical intermediate was postulated by Morrison and Freund (51, 52) to explain a current-doubling effect observed in photocatalytic studies using single-crystal ZnO electrodes and formate. They proposed the following steps:

$$h_{vb}^{+} + HCOO^{-} \rightarrow HCOO^{-}$$
 (20)

$$HCOO^{\bullet} \rightarrow CO_2 + H^+ + e_{cb}^-$$
(21)

This scheme accomplishes two-electron oxidation of the donor by reaction with a valence band hole and injection of an electron into the conduction band, resulting in electron-paired products. Morrison and Freund found O_2 to quench current-doubling in the external circuit, presumably by the reaction:

$$HCOO^{\bullet} + O_2 \rightarrow CO_2 + H^+ + O_2^{\bullet}$$
 (22)

Thus, either the electron may be injected into the semiconductor and then transferred to adsorbed oxygen or the electron may be transferred directly to oxygen. Either pathway produces a net two-hole oxidation of the electron donor and two-electron reduction of oxygen per photon absorbed. Additional evidence for this electron injection scheme is seen in the observation that the quantum yields of peroxide production approach 1.0 in concentrated 2-propanol solutions (16). Furthermore, pulse radiolysis studies of Q-sized TiO2 in 2-propanol have demonstrated that the isopropyl radicals, (CH₃)₂COH•, initially produced by the reaction of OH[•] are strong reductants (-1.23 V vs NHE) and that they are capable of rapidly injecting electrons into the conduction band of TiO_2 (53). Acetaldehyde, formate, and many aliphatic alcohols have exhibited current-doubling effects in semiconductor electrode systems; however, acetate has not previously exhibited this effect (52).

Returning to the original question, are the oxidation products observed to be similar to products obtained by hydroxyl radical attack or direct hole transfer? The direct decarboxylation of acetate and other carboxylic acid donors in supported by the following: (1) no glycolic acid was observed by anion chromatography even though radiolysis G values indicate it should be formed at half the rate of formaldehyde; (2) the assumption of one CO_2 per acetate lost closes the carbon mass balance; (3) the observed 1:1 stoichiometric ratio of the electron donor to H₂O₂ cannot be explained without invoking surface reactions. Quantitative agreement with the array of products elucidated by von Sonntag and co-workers is unlikely since the hole scavengers are proposed to donate two-electron equivalents. The major argument against direct or surface oxidation is that differences in adsorption capacity and kinetics should be reflected in rates of disappearance of the donors. We have shown that while for acetate and formate there are differences in the rates of loss, the rates fail to correlate to the relative magnitude of the $Zn(H_2O)_5$ -CO₂R⁺ formation constants or redox potentials of the donors. In our preceding paper (16), we have shown that the quantum yields of H_2O_2 production are relatively insensitive to the nature of the hole scavenger [i.e., the quantum yield decreased from 5.4% to 4.2% as the strength of the Zn²⁺ binding constant increased from 0.7 (formate) to 3.9 (oxalate)]. Furthermore, if the differences between many types of donors are relatively small, it implies that surface adsorption of the donor is not the limiting step.

Thus, in this system in which the electron donors are strongly adsorbed, surface-mediated reactions play a significant role in the stoichiometry and observed product distribution. However, in other systems such as alkane oxidations in which adsorption is weak, homogeneous OH• reactions in the bulk solution may play a greater role. Determining the influence of donor chemistry and of other solution species on this mechanism is an important tool in designing rational and effective treatment processes based on photocatalytic redox reactions.

Conclusions

We have shown that while the results of homogeneous radiolysis of acetate give invaluable information in planning experiments and understanding radical reactions, the details of the product array in the heterogeneous system studied here did not agree with either of the two comparable homogeneous systems. The proposed source of the differences is that donor radicals react with the semiconductor surface, forming trapped intermediates which are further oxidized via semiconductor holes or by injecting a second electron into the conduction band. The mechanisms presented here, along with supporting evidence, should lead to studies in which direct evidence of more types of surface intermediates is sought, rather than free hydroxyl radical-donor adducts.

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