Near-u.v.-light-induced Competitive Hydroxyl Radical Reactions in Aqueous Slurries of Titanium Dioxide

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Photolysis of oxygenated benzoic acid and sodium benzoate aqueous slurries of titanium dioxide (anatase) with near-u.v. light gives hydroxybenzoic acids; hydroxyl radicals are shown to be involved.

Aqueous slurries of semiconductors are attracting increasing attention because of their ability to split water into hydrogen and oxygen when illuminated[1] and also because of their possible usefulness in other photosynthesis[2] and photocatalysis[3—5] reactions. Evidence has been accumulating that OH radical reactions are involved in illuminated aqueous slurries of titanium dioxide[6,7] and tungsten oxide.[8] We report here additional evidence for OH radical production from competition kinetic studies of benzoic acid and benzoate ion with various added solutes in illuminated aqueous slurries of titanium dioxide, and also the results of measurements of the hydroxy-isomer distribution.

Titanium dioxide (La Porte, Tiona grade) was sieved and the 125—500 μm fraction was retained and heated at 550 °C for 30 min to facilitate centrifuging. The *X*-ray diffraction pattern showed lines characteristic of anatase but no trace of rutile. Aqueous slurries were prepared from 1 g of this TiO_2 in 400 ml of 1×10^{-3} M benzoic acid at pH 3, or 5×10^{-4} M sodium benzoate at pH 7, and various known OH radical scavengers. All compounds used as scavengers were of at least reagent grade and were used as supplied. The slurries were illuminated in a Hanovia photochemical reactor of approximately 450 ml capacity fitted with a sintered glass frit at the base, through which oxygen was bubbled during illuminations, and an outlet

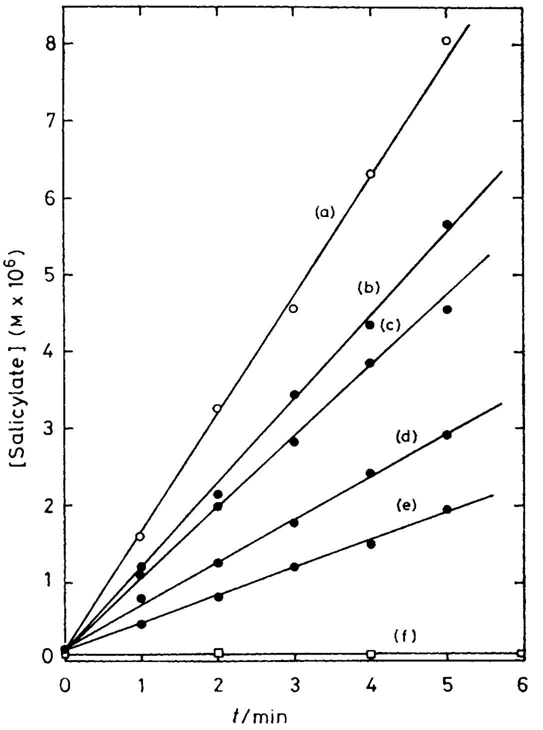

Figure 1. Formation of salicylate species in illuminated aqueous slurries of 1×10^{-3} M benzoic acid–TiO_2 containing various concentrations of ethanol. (a) No ethanol, (b) 1.25×10^{-3} M ethanol, (c) 2.50×10^{-3} M ethanol, (d) 6.25×10^{-3} M ethanol, (e) 12.5×10^{-3} M ethanol, and (f) no ethanol, no TiO_2.

tube from which portions of the slurry could be rapidly removed by pressurising the apparatus. The light source was a 100 W medium pressure Hg lamp surrounded by a Pyrex glass sheath through which a filter/coolant solution of 50 g l^{-1} $Cu(NO_3)_2 \cdot 3H_2O$ was continuously circulated. Portions of the slurry were removed at given times during the photolysis and, after being centrifuged, were analysed for salicylic acid. In a smaller number of experiments the other hydroxy-products, *m*- and *p*-hydroxybenzoic acids, were also determined. The determinations were made using a Farrand spectrofluorimeter and a modification of the procedure used by Armstrong *et al.*[9]

Representative data for the rate of formation of salicylate in 1×10^{-3} M benzoic acid solutions containing various concentrations of ethanol are shown in Figure 1. In the absence of TiO_2, no significant concentration of salicylate was formed. In the presence of TiO_2, the salicylate concentration increased at a linear rate over the period of the experiments. Increasing concentrations of ethanol depressed the rate progressively. At the highest ethanol concentration, there was no quenching effect of ethanol on the salicylate fluorescence.

It has been suggested[4] that OH radical formation occurs at the surface of illuminated TiO_2 particles *via* reaction with water and the positive holes of the valence band, equations (1) and (2).

$$TiO_2 \xrightarrow{h\nu} e^- + h^+ \quad (1)$$

$$h^+ + H_2O \rightarrow \cdot OH + H^+ \quad (2)$$

If OH radicals are formed in the above reactions, they should react with solutes known to be OH radical scavengers. Thus, the formation of hydroxy-aromatic compounds in aqueous

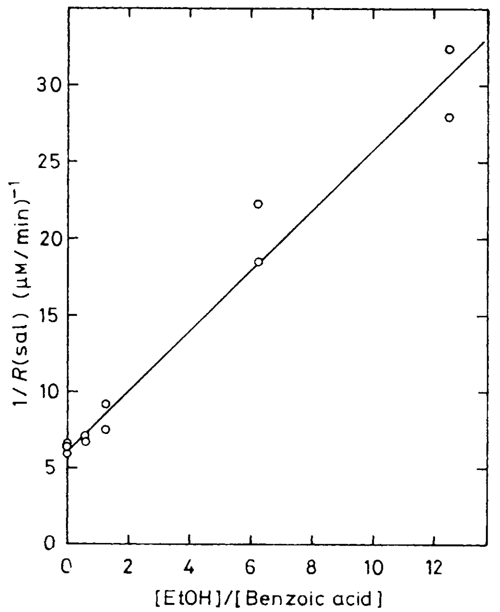

Figure 2. Reciprocal of the rate of salicylate formation *vs.* ratio of ethanol to benzoic acid. 1×10^{-3} M benzoic acid; *R*(sal) determined by regression analysis of salicylate concentration *vs.* time data as per Figure 1.

slurries of TiO_2 provides evidence for OH radicals as reactive intermediates.[6] Additional evidence would be provided by the determination of relative rate ratios of known OH radical scavengers. The formation of salicylate can be readily followed and, since the reaction between OH radicals and benzoate species has been thoroughly studied,[9–12] the decrease in the yield of salicylate in the presence of other solutes should allow the determination of the OH radical relative rate constants *via* equations (3)—(5), where *R*(sal), *R*°(sal) = the rate of

$$\begin{array}{c} C_6H_5CO_2H + \cdot OH \rightarrow \cdot C_6H_5(OH)CO_2H \\ \downarrow O_2 \\ C_6H_4(OH)CO_2H + HO_2\cdot \end{array} \quad (3)$$

$$S + \cdot OH \rightarrow \text{products other than salicylate} \quad (4)$$

$$\text{Thus, } R(\text{sal}) = R^{\circ}(\text{sal})/(1 + k_4[S]/k_3[B]) \quad (5)$$

formation of salicylate species in the presence and absence of added solutes, respectively, k_3, k_4 = the specific rate constants for reactions (3) and (4), and [S], [B] = the concentrations of solute and benzoate species, respectively. Hence, if the competition between reactions (3) and (4) is as shown, a plot of $1/R(\text{sal})$ *vs.* [S]/[B] should yield a straight line whose slope/intercept value is k_4/k_3.

Such a plot, from the data shown in Figure 1 and some additional results, is shown in Figure 2. The rates of formation of salicylate species were determined by regression analysis of salicylate concentration *vs.* time. The data are well described by a simple competition between reactions (3) and (4). The ratio of rate constants, k_4/k_3, determined by least squares analysis of the data and expression (5), gave a ratio of 0.30 ± 0.03 in reasonable agreement with 0.47 ± 0.38, the mean of the literature values for this ratio.[13]

Similar studies have been carried out with the solutes listed in Table 1. The means of published rate constants for the reaction of OH radical with these solutes[13] are also shown in Table 1 and compared with those determined in this work.

Table 1. Comparison between rate constants determined with illuminated aqueous slurries of TiO_2 and mean published OH rate constants.

Solute	pH	k_4[a]/l mol^{-1} s^{-1}	k(OH + S)[b]/ l mol^{-1} s^{-1}
Benzoic acid	3	3.4×10^9 [c]	$(3.4 \pm 1.9) \times 10^9$
Ethanol	3	$(1.0 \pm 0.1) \times 10^9$	$(1.6 \pm 0.4) \times 10^9$
Propan-2-ol	3	$(1.0 \pm 0.1) \times 10^9$	$(2.2 \pm 1.2) \times 10^9$
Methanol	3	$(4.1 \pm 0.7) \times 10^8$	$(9.2 \pm 4.0) \times 10^8$
Benzoate	7	4.8×10^9 [c]	$(4.8 \pm 1.3) \times 10^9$
Iodide	7	$(1.0 \pm 0.1) \times 10^{10}$	$(1.6 \pm 0.9) \times 10^{10}$
Formate	7	$(2.4 \pm 0.3) \times 10^9$	$(3.0 \pm 0.8) \times 10^9$
Bromide	7	$(8.6 \pm 1.9) \times 10^8$	$(1.3 \pm 0.8) \times 10^9$
Hydrogen carbonate	7	$(3.7 \pm 0.7) \times 10^7$	$(4.0 \pm 2.5) \times 10^7$
Chloride	7	$<2.4 \times 10^7$	10^6

[a] This work. [b] Ref. 13. [c] Assumed value from which other rates are calculated.

Possible quenching of salicylate fluorescence or loss of excitation intensity by inner filter action was tested with all solutes. No corrections were necessary at the highest concentrations of the solutes listed. The plots of salicylate conc. *vs.* time of illumination were linear in all cases, and the reciprocal plots *vs.* [S]/[B] were also linear within experimental error. The absolute rate constants evaluated in this way are in reasonable agreement with the literature values.

Additional evidence for OH radicals comes from the observed isomer distribution of the hydroxy-aromatic acids formed. A slurry of 1×10^{-3} M benzoic acid–1 g TiO_2 (400 ml) gave the isomer distribution *o*:*m*:*p* of (2.0 ± 0.05):(1.03 ±0.05):(0.98 ± 0.07). This agrees within experimental error with the distribution of 2.0:1.10:1.10 found by Armstrong *et al.*[9] and the distribution of 2.0:1.13:0.89 found by Matthews and Sangster[11] for the hydroxybenzoic acids from ^{60}Co γ-ray-generated OH radical attack on aqueous benzoate and benzoic acid solutions. These results provide strong evidence that the OH radical is the hydroxylating species. It seems unlikely that any other possible hydroxylating agent would show the same reactivity pattern.

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