

## Acid Enhancement Effect in the Clean Oxidation of Toluenes Photocatalysed by TiO<sub>2</sub>

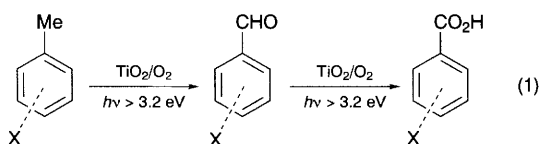
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The yield of substituted benzaldehydes and benzoic acids formed by the aerial oxidation of a range of substituted toluenes photocatalysed by titanium dioxide in acetonitrile is dramatically improved by the addition of small amounts of sulfuric acid.

In industrial synthetic organic chemistry, there is increasing environmental pressure to find cleaner methods of preparative synthesis. Heavy metal catalysed oxidations are a particular source of concern. Semiconductor photocatalysis in aerated non-aqueous solvents offers an alternative, novel, clean and simple approach to effecting organic oxidations.<sup>1</sup> Ultra-band gap irradiation of a semiconductor, such as TiO<sub>2</sub>, leads to the generation of an electron-hole pair. The photogenerated electron can reduce O<sub>2</sub> to superoxide anion (O<sub>2</sub><sup>•-</sup>), eventually forming H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O, and the photogenerated hole can oxidise many organic substrates. The oxidation of toluene and a range of substituted toluenes to their benzaldehyde and benzoic acid analogues is an important industrial synthetic process and is usually performed using high temperatures and pressures with air as the oxidant and potentially environmentally damaging metal catalysts such as cobalt and manganese.<sup>2</sup> This communication describes how TiO<sub>2</sub> photocatalysis can be used to convert toluene to benzaldehyde and benzoic acid cleanly and simply [eqn. (1)].



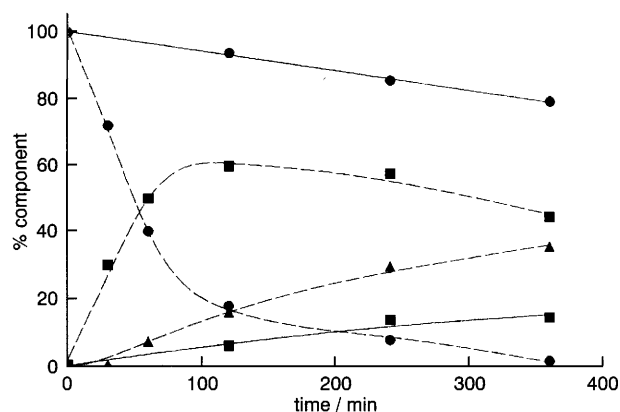
In semiconductor photocatalysis studies, the choice of solvent is an important consideration. Water is not suitable since toluene is barely soluble in it. Furthermore, in aqueous semiconductor photocatalysis, mineralisation of the organic to H<sub>2</sub>O, CO<sub>2</sub> and mineral acids due to OH<sup>•</sup> attack dominates the overall photocatalytic process,<sup>3-5</sup> and, as a result, a wide range of hydroxylated intermediate products are generated *via* Photo-Fenton type mechanisms.<sup>4,5</sup> In most of the work to date, on organic oxidation reactions sensitised by TiO<sub>2</sub>, acetonitrile has been used as the non-aqueous solvent.

In a typical experiment 100 cm<sup>3</sup> of an acetonitrile solution containing toluene (1 mmol dm<sup>-3</sup>) and a dispersion of 50 mg TiO<sub>2</sub> (Degussa P25) were oxygen purged for 15 min and then irradiated in a photoreactor comprising 12 × 8 watt black light UV lamps (λ<sub>max</sub> 365 nm and total output 4 × 10<sup>17</sup> photons s<sup>-1</sup>) as described fully elsewhere.<sup>6</sup> Samples of the irradiated solution were periodically withdrawn for analysis by HPLC.

In the absence of any acid in the acetonitrile it was found that the formation of benzaldehyde was slow and low yielding, as illustrated by the results in Fig. 1 (solid lines). Similar results have been reported elsewhere.<sup>7,8</sup> In contrast, both the reaction rate and yields of desired products [eqn.(1)] are improved dramatically through the addition of a small amount of an acid [H<sub>2</sub>SO<sub>4</sub> (50 μl, 5 mol dm<sup>-3</sup>)] (Fig. 1, dashed lines). Blank experiments showed that the addition of a similar quantity of water had no enhancement effect on the rate and yield of the reaction [eqn. (1)]. A study was carried out into the effect of increasing the concentration of the acid added to the initial reaction mixture on the amounts of toluene, benzaldehyde and benzoic acid present during the course of the reaction, and the results after 60 min irradiation are listed in Table 1. From these results and those of other experiments it appears that, overall, the product distributions were not affected by the change in

[H<sub>2</sub>SO<sub>4</sub>], whereas the rate of reaction [eqn. (1)] increases with increasing [H<sub>2</sub>SO<sub>4</sub>]. We have found that acids promote this reaction in the order: H<sub>2</sub>SO<sub>4</sub> > HNO<sub>3</sub> > HCl > HClO<sub>4</sub> > H<sub>3</sub>PO<sub>4</sub>. The order does not appear to relate directly to their different acidities in acetonitrile.<sup>9</sup> In addition we have found that KHSO<sub>4</sub>, when added in identical concentration to the acid, produces a rate enhancement similar to that of HCl suggesting that the anion, HSO<sub>4</sub><sup>-</sup>, may be involved in the reaction. It is known that HSO<sub>4</sub><sup>-</sup> strongly adheres to the TiO<sub>2</sub> surface and it is possible that this species acts as a surface trap for the photogenerated holes producing a highly oxidising sulphonyl radical, HSO<sub>4</sub><sup>•</sup>, which is likely to be very effective in the oxidation. This aspect is under current study.

For many aqueous photocatalytic reactions, the activation energy is usually low and positive.<sup>10</sup> In this work we have found that the activation energy for the oxidation of toluene is relatively large and positive (45 kJ mol<sup>-1</sup>). As a result, the yield of benzaldehyde in reaction (1) increases dramatically as the reaction temperature is increased. For example at 50 °C, after 1 h irradiation of a TiO<sub>2</sub>-toluene-acetonitrile reaction mixture, with a 50 μl sample of 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> acid present, the



**Fig. 1** Plot showing the variation in the percentage composition of reaction mixtures irradiated under identical conditions [toluene in acetonitrile (100 cm<sup>3</sup>, 1 mmol dm<sup>-3</sup>), TiO<sub>2</sub> (50 mg), 30 °C, O<sub>2</sub> at 10 ml min<sup>-1</sup>] in the absence (solid line) and presence (dashed line) of an addition of H<sub>2</sub>SO<sub>4</sub> (50 μl, 5 mol dm<sup>-3</sup>) in the initial reaction mixture. The % component vs. time profiles shown are for toluene (●), benzaldehyde (■) and benzoic acid (▲).

**Table 1** Typical yields of reaction products after 60 min irradiation under standard reaction conditions using different concentrations of a 50 μl H<sub>2</sub>SO<sub>4</sub> addition

H <sub>2</sub> SO <sub>4</sub> concentration/mol dm <sup>-3</sup>	Toluene (%) <sup>a</sup>	Benzaldehyde (%) <sup>a</sup>	Benzoic acid (%) <sup>a</sup>
0.5	75	25	—
5.0	35	50	7
18	24	60	18

<sup>a</sup> The percentages are calculated from the concentration of the material concerned, obtained by HPLC, compared to the initial toluene concentration.

yield of benzaldehyde was 80% (instead of 20% at 30 °C under otherwise identical conditions).

A set of parallel photocatalytic oxidations have been performed on a number of substituted toluenes [ $X = p\text{-CF}_3, p\text{-NO}_2, p\text{-Cl}, p\text{-F}, p\text{-Me}, p\text{-tert-butyl}, m\text{-NO}_2, m\text{-Cl}, m\text{-F}$  in reaction (1)] and in all cases the addition of a small amount of  $\text{H}_2\text{SO}_4$  improved the rate of semiconductor catalysed photo-oxidation markedly. The reaction shows a tendency to favour formation of the benzoic acid analogue in the case of more electron withdrawing substituents. The Hammett plot for the disappearance of substituted toluene shows good linear behaviour with a  $\rho$  value of  $-1.1$ . This is typical for a radical mechanism;<sup>11</sup> the rate-determining step may well involve hydrogen abstraction from the methyl group forming benzylic radicals. Scavenging of the benzylic radical by  $\text{O}_2$  would lead ultimately to benzyl hydroperoxides which are known to rearrange to benzaldehydes under the influence of acid. This pathway avoids the intermediate formation of benzyl alcohol, which has never been observed as a reaction product in our reactions. Indeed, control experiments indicate that, under the conditions used, benzyl alcohol should be observed if it is formed.

In conclusion, the rate of oxidation of a wide range of substituted toluenes by  $\text{O}_2$ , photocatalysed by  $\text{TiO}_2$ , to synthetically useful products is dramatically increased through the addition of a small amount of an acid to the reaction solution.

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