

# Synthesis of a coumarin compound from phenanthrene by a TiO<sub>2</sub>-photocatalyzed reaction†

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Phenanthrene was converted into a coumarin compound by a TiO<sub>2</sub>-photocatalyzed reaction in an acetonitrile solution containing 8 wt% water and molecular oxygen in 45% yield.

Photocatalytic reactions using TiO<sub>2</sub> particles have been widely studied, especially in the field of the decomposition of waste materials included in water and air. This function of a TiO<sub>2</sub> photocatalyst arises from the strong chemical activity of electrons and holes photogenerated in TiO<sub>2</sub> particles under irradiation with an ultraviolet beam. Due to the strong activity of these carriers, aromatic compounds can be mineralized.<sup>1–7</sup> Before their complete mineralization, partially oxidized products were often obtained, and the reactions have attracted interest as a means of organic synthesis.<sup>6–8</sup> For example, we have reported that naphthalene is efficiently oxidized to 2-formylcinnamaldehyde in a mixed solvent of acetonitrile and water bubbled with molecular oxygen.<sup>7</sup>

Here, we report the photocatalyzed reaction of phenanthrene on photoirradiated TiO<sub>2</sub> under conditions similar to those used in our previous study on the reaction of naphthalene. In the present study, we obtained a coumarin compound as the main product. The production of a coumarin compound is interesting because its formation from phenanthrene has not been reported and it may open new synthetic routes to coumarin compounds by a one-pot process.

Reactions in the present study were typically carried out in Pyrex test tubes (30 ml), each containing a mixture of acetonitrile (3.63 g), water (0.30 g), phenanthrene (115 mg) and TiO<sub>2</sub> powder (38 mg). P-25 TiO<sub>2</sub> powder (Japan Aerosil), which showed strong activity for the oxidation of naphthalene under similar conditions,<sup>7</sup> was used as the photocatalyst. During the reaction, the solution was magnetically stirred to suspend the TiO<sub>2</sub> particles, bubbled with oxygen gas at a rate of 2.0 ml min<sup>-1</sup> and externally photoirradiated. A 500 W super-high-pressure mercury lamp was used as the light source, and deep UV ( $\lambda < 340$  nm) light was removed with a UV34 glass filter (HOYA) to prevent photo-excitation of the phenanthrene molecules. All of the reactions were carried out at room temperature.

As the reaction proceeded, a small portion of the solution was repeatedly sampled and analyzed by a high-performance liquid chromatograph (HPLC: HITACHI L-6000) equipped with an

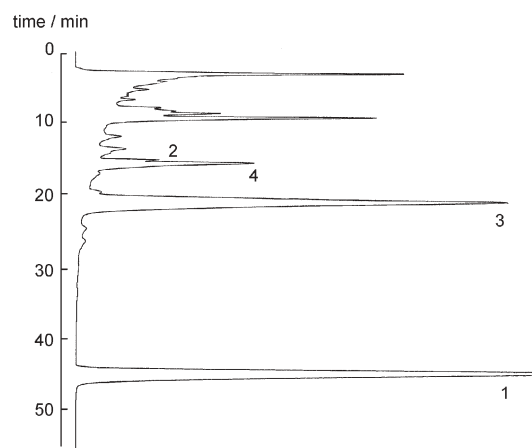
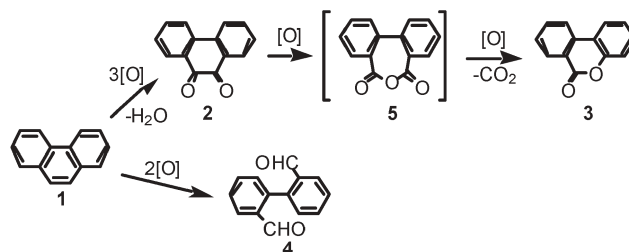


Fig. 1 A typical HPLC chart of a phenanthrene solution after continuing the TiO<sub>2</sub>-photocatalyzed reaction for 76 h.

ODS column. A mixture of acetonitrile and water (1 : 1) was used as the eluent. The HPLC chart showed four peaks with long retention times and some peaks with shorter retention times, as shown in Fig. 1 for the solution after photoirradiation for 76 h.

The peaks with long retention times are assigned to phenanthrene (1), phenanthraquinone (2), 6*H*-benzo[*C*]chromen-6-one (a coumarin compound) (3) and biphenyl-2,2'-dicarbaldehyde (4), which had retention times of 44.9, 15.0, 21.0 and 15.6 min, respectively. The structures of these products are described in the proposed reaction path shown in Scheme 1. The products were identified by the following procedure: We carried out the reaction on an enlarged scale in a 300 ml flask. The reaction solution was filtered to remove the TiO<sub>2</sub> powder and completely evaporated *in vacuo*. The residual mixture was added to hexane, in which some of the residue formed an oily suspension, and the liquid was poured into a silica gel column (Wakogel C-200). After eluting



Scheme 1

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phenanthrene from the column using hexane, the eluent was changed to mixed solutions consisting of hexane, chloroform and ethanol, and the content of chloroform and ethanol was gradually increased. Finally, the fractionalized effluents were completely evaporated under reduced pressure, and the reaction products were separately obtained. These products were recrystallized from hexane, and the structures of the isolated products were identified as **2**, **3** and **4** by  $^1\text{H}$  and  $^{13}\text{C}$  NMR using a JEOL JNM-AL400 NMR spectrometer.‡

The peaks of the HPLC chart of the mixed products were assigned to **1**, **2**, **3** and **4** by comparing their retention times with those of authentic samples. The peaks due to the polar compounds produced by the photocatalyzed reaction were not significant at its early stages, suggesting that they were oxidation products of **2**, **3** and **4**. We did not identify these compounds because we were more interested in those meaningful from the viewpoint of organic synthesis.

The time profiles of the amounts of **2**, **3** and **4** produced in the test tube were different, as shown in Fig. 2. During the initial 80 h, the amount of phenanthrene decreased linearly with reaction time, suggesting that the reaction rate is determined by the supply of photogenerated carriers to the surfaces of  $\text{TiO}_2$  particles. At the very initial stage of the reaction, the rates of production of **3** and **4** were nearly the same. However, the amount of **4** soon levelled off as the photoirradiation continued. The amount of **2** also levelled off at the early stage, and its amount was much less than the amounts of **3** and **4** throughout the reaction. The amounts of **2** and **4** were nearly constant during the period in which the amount of phenanthrene decreased linearly. This suggests that **2** and **4** were rapidly converted to other species by successive photocatalyzed reactions. In contrast, the amount of **3** continued to increase linearly during the period in which the amount of phenanthrene decreased linearly. As a result, **3** became the dominant product after photoirradiation for 10 h, and its yield reached 45% at 100 h. After reaching a maxima, the amount of **3** started to decrease at a rate slower than the initial decay rate of **1**. The sum of the initial slopes of the rise of **3** and **4** is nearly equal to the slope of the decay of **1**, as seen in Fig. 2. This suggests that the

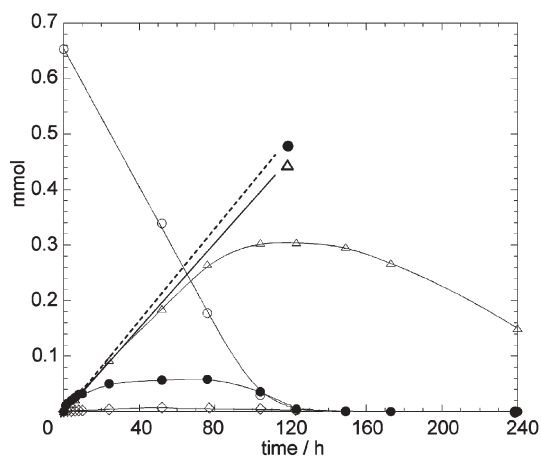


Fig. 2 Time courses of the change in the amounts of **1** ( $\circ$ ), **2** ( $\diamond$ ), **3** ( $\triangle$ ) and **4** ( $\bullet$ ) included in the solution as the  $\text{TiO}_2$ -photocatalyzed reaction continued. The amounts were determined by HPLC. The solid and dashed lines show the initial slopes of the rise of **3** and **4**, respectively.

polar compounds observed as peaks in the HPLC chart are mostly produced *via* **3** or **4**.

When we carried out the reaction without supplying oxygen gas practically no products were obtained. No products were obtained when the reaction was carried out in water-free acetonitrile bubbled with oxygen gas.

Lin and Valsaraj<sup>4</sup> studied the oxidation of phenanthrene by a  $\text{TiO}_2$ -photocatalyzed reaction in water in the presence of oxygen, and observed **2** and many other kinds of products, including **4**, before the mineralization. Kohtani *et al.* studied the reaction of phenanthrene on photoirradiated  $\text{BiVO}_4$  in acetonitrile, and obtained **2** and **4**.<sup>8</sup> However, these authors did not report the production of **3**, which was the main product in our study, carried out in a mixed solvent of acetonitrile and water, and using  $\text{TiO}_2$  as the photocatalyst.

In order to clarify the reaction paths of phenanthrene on photoirradiated  $\text{TiO}_2$  in our mixed solvent, we carried out photocatalyzed reactions using authentic samples of **2** and **4** under the same conditions as those used for the reaction of **1**. The results showed that **3** was produced from **2**, whereas only polar compounds were produced from **4**. On the basis of these results and other findings, we propose the reaction paths shown in Scheme 1. Production of **4** is equivalent to production of the dialdehyde from naphthalene, which was observed in our previous study.<sup>7</sup> This path seems to be unique to the photocatalyzed reactions of compounds with condensed aromatic rings. The production of **2** from **1** is a common practice in the chemical oxidation of **1**;<sup>9</sup> **2** is probably generated through the oxidation of **1** by positive holes on the surface of  $\text{TiO}_2$ .

The photocatalyzed production of **3** from **2** is the key step in the present system. This step was not driven by  $\text{O}_2^-$ , which was supplied as a mixture of  $\text{KO}_2$  and 18-crown-6, or by  $\cdot\text{OH}$  radicals, which were generated *via* the photo-Fenton reaction. Although we do not know the details of this process, we tentatively propose that **2** is converted into **3** *via* acid anhydride compound **5**, as shown in Scheme 1. Presumably **5** is generated from **2** by surface Ti peroxide, which is photogenerated in a manner similar to that of the Baeyer–Villiger reaction,<sup>10</sup> or by repeating the butterfly-type reaction with the surface hydroperoxo species.<sup>11,12</sup> However, the intermediate **5** was not isolated from the reaction solution, probably because **5** can easily be hydrolyzed to a dicarboxylic acid in a wet medium, such as the solvent used in the present study. We speculate that **5** is immediately converted to **3** upon its formation on the photoirradiated  $\text{TiO}_2$ .

The apparent quantum efficiency of the reaction, defined as the ratio of the number of molecules of **3** produced compared to the number of incident photon fluxes, was determined to be 1.7% using light of around 365 nm wavelength, selected from the super-high-pressure Hg lamp using a band-pass filter. The incident photon flux was determined by the standard photochemical actinometer method, based on the conversion of ferrioxalate ion into  $\text{Fe(II)}$ , using the same experimental setup as that used in the photocatalytic reaction. No corrections were made for the losses of incident photons due to reflection. By taking into account the fact that 10 electrons must be removed from **1** to produce **3**, the apparent quantum efficiency of the whole photooxidation process was estimated to be 17%.

In conclusion, we have found that a coumarin compound is synthesized from phenanthrene with considerably high efficiency

by a TiO<sub>2</sub>-photocatalyzed reaction in a mixed solution of acetonitrile and water. The production of **3** by a one-pot reaction is interesting because many steps are involved in its synthesis from commercially available reagents by conventional methods.<sup>13,14</sup> It is also interesting from the viewpoint of future applications because coumarin compounds are useful intermediate compounds in the synthesis of a variety of chemicals, including pharmaceuticals and fluorescent dyestuffs.

## Notes and references

‡ The authentic sample of **2** was purchased from Wako Pure Chemical Industries and that of **4** was synthesized from phenanthrene *via* ozonolysis.<sup>15</sup> Their NMR and chromatogram data were in agreement with the corresponding compounds isolated from the products of the photocatalyzed reaction. **3** was identified from the NMR data of the isolated compound. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.416 (1 H, dd, *J* = 8.0 and 1.2 Hz), 8.137 (1 H, d, *J* = 8.0 Hz), 8.075 (1 H, d, *J* = 8.0 Hz), 7.836 (1 H, td, *J* = 8.0 and 1.2 Hz), 7.594 (1 H, td, *J* = 8.0 and 1.2 Hz), 7.491 (1 H, td, *J* = 8.0 and 1.2 Hz), 7.380 (1 H, dd *J* = 8.0 and 1.2 Hz) and 7.349 (1 H, td, *J* = 8.0 and 1.2 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 161.06, 151.21, 134.75, 134.71, 130.52, 130.37, 128.81, 124.48, 122.69, 121.61, 121.23, 118.00 and 117.74.

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