Electronic Supplementary Information

Selective Aerobic Oxidation of Amines to Imines by TiO₂ Photocatalysis in Water

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Materials and instruments:

All reagents and solvents used were obtained commercially and used without further purification. Gas chromatography (GC) measurements were made with a Hitachi GC 3900 equipped with a flame ionization detector (FID) detector and a DM-5 AMINE capillary column (5% polysilarylene, 95% polydimethylsiloxane, 30 m, 0.5 mm×0.25 µm, Dikma) using nitrogen as the carrier gas. Standard analysis conditions: Injector temperature 250 °C, FID detector temperature: 300 °C, column temperature program: 80 °C (hold 3 min) to 280 °C (hold 5 min) at a elevating rate of 20 °C/min. Gas chromatography–mass spectrometry (GC-MS) (Thermo-Finingan Trace 2000/Trace DSQ) analyses were carried out with a DB-5MS capillary column (5% polysilarylene, 95% polydimethylsiloxane, 30 m, 0.5 mm×0.25 µm, Dikma) and high pure helium as the carrier gas with a same temperature program as that of GC.

General procedure for the oxidation of amines:

The photocatalytic reactions were carried out under irradiation by a 100 W high-pressure Hg lamp (Toshiba SHL-100UVQ) with continuous stirring in a 10 mL Pyrex glass bottle (cut-off light below 300 nm, thus TiO_2 but not the substrates can be excited). The Pyrex glass bottle was connected to air with a syringe needle. A typical reaction system contained 0.1 mmol substrate

and 10 mg TiO₂ (Degussa P25) in 2 mL H₂O (Millipore 18.2 M Ω •cm). The substrates (benzylamines) could completely soluble in H₂O. The products (imines) are much less soluble in H₂O. Since some of imine products are white solids at room temperate, white solid imine products could be obtained directly on the surface of H₂O along with TiO₂ photocatalyst. After photocatalytic reaction, a given amount of CH₃CN was injected into whole suspension to dissolve the immiscible products, and dried over Na₂SO₄. The products were analyzed by GC using bromobenzene as the internal standard. The products were confirmed by comparison the retention time with standard samples and further confirmed with mass spectrometry by GC-MS.

Detailed procedure for the scale-up for the oxidation of 4-methoxybenzylamine:

The high yields and the easy separation for the photocatalytic coupling of benzylamines in water make it feasible to prepare imines in a large scale. To demonstrate the practical application and the synthetic potential of the photocatalytic imination reaction, 5 mmol (0.69 g) of 4-methoxybenzylamine was dissolved in 150 ml water in the presence of 0.5 g Degussa P25 TiO_2 photocatalyst. After 5 h of irradiation, the solid obtained by simple filtration was flushed by 30 ml of CH₃CN. 0.22 g product, corresponding to a yield of 35%, was isolated after removing the solvent by rotary evaporation. The collected TiO_2 was put back into the Pyrex glass reactor for reusing. In the followed two runs, additional 16% of the imine was further obtained. Thus, combined 0.32 g (51% isolated yield) of imine was successfully obtained in this preliminary attempt for scalable preparation. Both the mass spectrometry of GC-MS and NMR (Bruker Avance 400 M, ¹H, ¹³C) reveal that the isolated product is imine with purity of larger than 95%. Little 4-methoxybenzaldehyde is observed in the isolated product, probably because the 4-methoxybenzaldehyde could react with the remaining 4-methoxybenzylamine to the imine product during the evaporation.



Figure S1 A comparison of the suspensions before (right) and after (left) the photocatalytic oxidation reaction of 4-methoxybenzylamine. Both of the suspensions were left stand for 1 h before taking the photograph.



Figure S2 Distribution of the reactant (amine), product (imine) and intermediate (aldehyde) in the filtrate (A) and filter residue (B) during the photocatalytic oxidation of 4-methoxybenzylamine. Reaction conditions: amine (5 mmol) in 150 mL water, TiO_2 (Degussa P25, 0.5 g), Hg lamp (100 W), in 1 atm of air.



Figure S3. Gas chromatogram analysis for components in the filtrate (top) and filter residue (bottom) during the photocatalytic oxidation of p-methoxy-benzylamines after irradiation of 10 hours. Condition: amine (5 mmol, 0.6859 g) in 150 mL water, TiO_2 (P25, 0.5 g), Hg Lamp (100 W), in open air.





Figure S4. GC (top) and NMR (bottom) of the final products in a gram-scale preparation.