

Preliminary Note

Photocatalytic production of amines from alcohols and aqueous ammonia

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Amines were produced photocatalytically from alcohols and aqueous ammonia by using platinized TiO₂ as a photocatalyst. Increasing amounts of amines were produced in the order ethanol > methanol > isopropanol > *t*-butanol. H₂ enhanced the formation of amines whilst O₂ inhibited it. A reaction mechanism for the formation of the series of primary, secondary and tertiary amines from ethanol and aqueous ammonia is discussed on the basis of the experimental results.

Photocatalytic synthesis of organic compounds using semiconductor powders has recently attracted the attention of many researchers [1, 2]. Some of their work deals with compounds which contain nitrogen. Reports have been published on the synthesis of amino acids from methane, ammonia and water [3]. Reports have also been published on the synthesis of amino acids from ammonia and ketoacids or oxyacids [4], and also of the synthesis of secondary amines from primary amines [5, 6]. All these organic compounds contain nitrogen. However, no report has been published on the synthesis of amines from alcohols and ammonia. Therefore, we tried to synthesize amines from alcohols and ammonia using platinized TiO₂ powder as a photocatalyst. We identified the amines by using nuclear magnetic resonance (NMR) spectroscopy.

The platinized TiO₂ was prepared by mixing powders of anatase (Kojundo Kagaku Co., of purity 99.9%, 1 μm in diameter) with an aqueous solution of PtCl₄·5H₂O, drying and firing at 400 °C in a flow of argon. The powder was then reduced in H₂ at 400 °C for 4 h and washed with pure water. The amount of platinum compounded with TiO₂ was 5 wt.%. Photocatalytic reactions were performed using 20 ml aqueous solutions containing 50 vol.% of the alcohol, 35.6 mmol ammonia and 0.2 g of the platinized TiO₂ powder. Reagent grade alcohols and aqueous ammonia were used. The 90 ml capacity reaction vessel was made from Pyrex. After irradiating the vessel for 7 h in an argon atmosphere with a 500 W high pressure mercury

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lamp, the products were analysed. The reaction temperature was kept at about 40 °C by filtering out IR radiation by passing the light through a Pyrex flask filled with water. The analysis of the gaseous products was performed by gas chromatography (columns of 5A molecular sieves and active carbon, argon being used as the carrier gas), and that of the liquid products was carried out by ¹H NMR spectroscopy (JEOL JNM-GX 270). In the latter the reacted mixture was acidified with hydrochloric acid, dried by vacuum freezing to remove water and alcohols and dissolved in D₂O. The liquid products were identified as amines by comparison with authentic samples. The amounts of the products calculated from the NMR spectra are given in Table 1. The amounts of amines produced increase in the order ethanol > methanol > isopropanol > *t*-butanol. The order is similar to that for the oxidizability of alcohols on a metal electrode [7]. The amines appeared about 30 min after the start of the irradiation and their concentration increased almost in proportion to the irradiation time. As the reaction proceeded the fraction of diethylamine present increased, followed by an increase in the amount of triethylamine. When the photocatalytic reaction of ethanol with ammonia was carried out under an atmosphere of H₂, the amounts of amines produced increased appreciably compared with those formed under an argon atmosphere, as shown in Table 1.

TABLE 1

Amounts of amines produced by the photocatalytic reaction between ammonia and alcohols or acetaldehyde

<i>Alcohols or aldehyde</i>	<i>Amounts of products (μmol)</i>		
<i>Ar atmosphere</i>			
CH ₃ OH ^a	83 CH ₃ NH ₂	17 (CH ₃) ₂ NH	23 (CH ₃) ₃ N
C ₂ H ₅ OH ^b	49 C ₂ H ₅ NH ₂	87 (C ₂ H ₅) ₂ NH	46 (C ₂ H ₅) ₃ N
(CH ₃) ₂ CHOH ^c	87 (CH ₃) ₂ CHNH ₂	<0.05 ((CH ₃) ₂ CH) ₂ NH	
(CH ₃) ₃ COH ^d	<0.05 (CH ₃) ₃ CNH ₂		
CH ₃ CHO ^e	28 C ₂ H ₅ NH ₂	19 (C ₂ H ₅) ₂ NH	7 (C ₂ H ₅) ₃ N
<i>H₂ atmosphere</i>			
C ₂ H ₅ OH ^f	175 C ₂ H ₅ NH ₂	138 (C ₂ H ₅) ₂ NH	100 (C ₂ H ₅) ₃ N

^aTotal amount of amines, 123 μmol; yield of total amines based on ammonia fed, 0.346 mol.%.

^bTotal amount of amines, 182 μmol; yield of total amines based on ammonia fed, 0.511 mol.%.

^cTotal amount of amines, 87 μmol; yield of total amines based on ammonia fed, 0.244 mol.%.

^dTotal amount of amines, less than 0.05 μmol; yield of total amines based on ammonia fed, 0 mol.%.

^eTotal amount of amines, 54 μmol; yield of total amines based on ammonia fed, 0.152 mol.%.

^fTotal amount of amines, 413 μmol; yield of total amines based on ammonia fed, 1.17 mol.%.

TABLE 2

Amounts of gaseous products in the photocatalytic reaction between ammonia and ethanol

Atmosphere	Gaseous products (μmol)				
	H_2	CH_4	CO_2	N_2	Total
Ar	1100	5	<0.01	14	1119
O_2	11	35	160	7090	7296

The gaseous products from the reaction between ammonia and ethanol are given in Table 2. Here the main product is H_2 . When the reaction was performed under O_2 , the total amount of gaseous products and the amounts of CH_4 , CO_2 and N_2 increased appreciably; in this case almost no amines were produced. As shown in Table 1, amines were also produced in the reaction of acetaldehyde with ammonia; the photocatalytic reaction was carried out by using 20 ml aqueous solutions containing 2.5 vol.% acetaldehyde, 35.6 mmol ammonia and 0.2 g of the platinized TiO_2 .

From the experimental results described above, it is considered that aldehyde produced photocatalytically [8] produces primary amines via 1-hydroxylamine [9]. The primary amine produces a secondary amine on reaction with aldehyde via a Schiff base [5], and the secondary amine produces a tertiary amine similar to that produced by thermal reaction [9]. The participation of H_2 in the production of the primary amine is supported by the increased amounts of amines produced under H_2 . The effect of O_2 (Table 2) suggests the occurrence of the photo-Kolbe reaction reported by Kraeutler and Bard [10].

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