CHEMISTRY LETTERS, pp. 1075-1078, 1985.

PHOTOCATALYTIC FORMATION OF SCHIFF BASES FROM PRIMARY AMINES BY PLATINIZED-TiO_2 SUSPENSION IN ACETONITRILE

Bunsho OHTANI, Haruyoshi OSAKI, Sei-ichi NISHIMOTO, and Tsutomu KAGIYA*
Department of Hydrocarbon Chemistry, Faculty of Engineering,
Kyoto University, Sakyo-ku, Kyoto 606

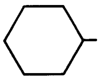
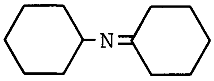
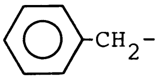
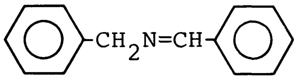
Photoirradiation ($\lambda_{ex} > 300$ nm) of platinized TiO_2 suspended in Ar-purged acetonitrile solution of aliphatic and aromatic primary amines produced Schiff bases together with H_2 and NH_3 at room temperature. Solvent acetonitrile was partly reduced on the Pt site to inhibit the reduction of the Schiff bases into secondary amines.

Aqueous suspension of semiconductor powders exhibits efficient photocatalytic activity for redox-related reactions of a variety of organic and inorganic substrates.$^{1)}$ The semiconductors are also operative as photocatalysts in organic solvents,$^{2-11)}$ thus being applicable to synthetic chemistry.$^{12)}$ Previously, we have demonstrated the photocatalytic formation of secondary amines from primary amines by platinized titanium dioxide (TiO_2/Pt) suspended in Ar-purged aqueous solution.$^{13)}$ This communication describes a formation of Schiff bases via the TiO_2/Pt photocatalytic reaction of primary amines dissolved in acetonitrile (CH_3CN), and provides novel information on the reactivity of non-aqueous solvent.

Anatase TiO_2 (Merck, 50 mg) powdered with platinum black (Pt, 5 wt%)$^{14)}$ was suspended in CH_3CN (5.0 cm^3, dried over molecular sieves 3A) in a glass tube (transparent for the exciting light of wavelengths > 300 nm). The suspension was purged with Ar for > 30 min and sealed off with a rubber septum through which primary amines (100-200 μmol) were injected. Photoirradiation was performed with a 400-W high-pressure mercury arc (Eiko-sha 400) under magnetic stirring at room temperature.

Table 1 shows the typical results of the photocatalytic reaction. H_2 evolution (GC: molecular sieve 5A, 100 °C, TCD) and NH_3 formation in both gas phase (GC: chromosorb 103, 80 °C, TCD) and liquid phase (indophenol-blue method) of the reaction system were commonly observed. Main carbon-containing products were Schiff bases (GC-MS: chromosorb 103, 210 °C, and polyethylene glycol 20 M, 180 °C, FID) while negligible amounts of secondary amines could be detected in contrast to the aqueous system.$^{13)}$ Propylamine and isopropylamine are converted into N-propylidenepropylamine ((1), M^+ 99)$^{13)}$ and N-isopropylideneisopropylamine ((2), M^+ 99), respectively. An equimolar mixture of propylamine and isopropylamine gave not only (1) and (2) but also two types of crossed Schiff bases, N-propylideneisopropylamine and N-isopropylidenepropylamine. In a similar manner,

Table 1. Photocatalytic reaction of primary amines by platinized TiO_2 suspended in acetonitrile[a)]

Run	Substrate (RNH_2) R =	Conversion	Product/µmol			
		%	H_2	NH_3	Schiff base	
1	$CH_3CH_2CH_2$-	65	42	13	$CH_3(CH_2)_2N=CHCH_2CH_3$	40
2	$(CH_3)_2CH$-	49	40	13	$(CH_3)_2CHN=C(CH_3)_2$	30
3[b)]	$CH_3CH_2CH_2$-	46	57	16	$CH_3(CH_2)_2N=CHCH_2CH_3$	20
	$(CH_3)_2CH$-	44			$(CH_3)_2CHN=C(CH_3)_2$	3
					$CH_3(CH_2)_2N=C(CH_3)_2$	16
					$(CH_3)_2CHN=CHCH_2CH_3$	18
4	$CH_3(CH_2)_5$-	46	25	16	$CH_3(CH_2)_5N=CH(CH_2)_4CH_3$	32
5		31	18	14		7
6		≃ 100	44	25		41

a) On irradiation ($\lambda_{ex} > 300$ nm) of Ar-purged suspension of TiO_2/Pt (52.5 mg) in acetonitrile solution (5.0 cm^3) of amines (200 µmol) for 20 h at room temperature by a 400-W high-pressure mercury arc.
b) An equimolar (200 µmol each) mixture was irradiated for 20 h.

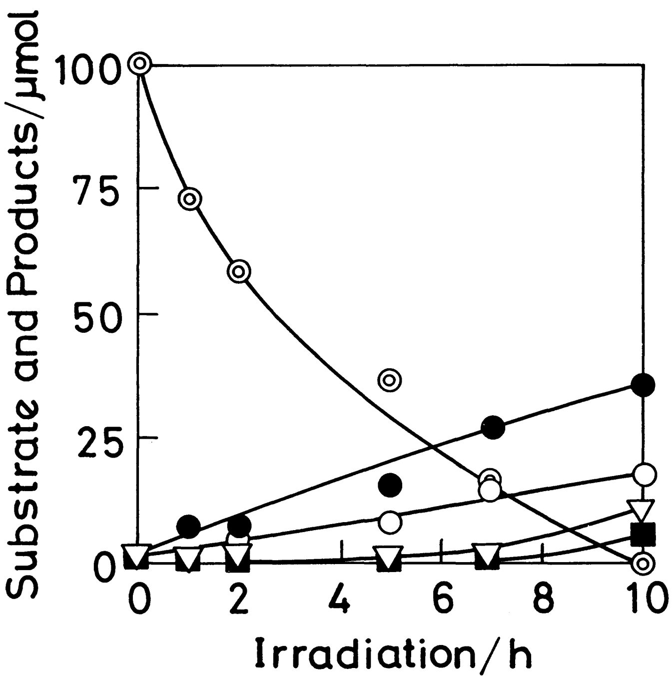


Fig. 1. Time course of the photocatalytic reaction of benzylamine by TiO_2/Pt (52.5 mg) in CH_3CN (5.0 cm^3); ◎ : benzylamine, ● : N-benzylidenebenzylamine, ○ : H_2, ▽ : N-ethylidenebenzylamine, and ■ : N-ethylbenzylamine.

cyclohexylamine and benzylamine were converted into N-cyclohexylidenecyclohexylamine and N-benzylidenebenzylamine (see also Fig. 1), respectively. The main reaction in these systems may be given as follows.

$$2R^1R^2CHNH_2 \xrightarrow[h\nu\ >\ 300\ nm]{TiO_2/Pt} R^1R^2CHN{=}CR^1R^2 + NH_3 + H_2 \qquad (1)$$

The observed NH_3 yield was smaller than the Schiff base or H_2 yields, probably due to the photocatalytic decomposition of NH_3.15)

The H_2 yield increased by the addition of small amount of H_2O (5 mm^3) prior to irradiation; e.g. 1.3- and 1.2- times larger yields were observed in the cases of propylamine and isopropylamine, respectively. This suggests that H_2 is partly originated from contaminant H_2O in the solvent and/or residual H_2O adsorbed on the TiO_2 surface. Conduction-band electron (e^-) generated in TiO_2 particles by photoabsorption has sufficient ability to reduce H^+ to H_2 on Pt.1,16)

$$TiO_2 + h\nu \longrightarrow h^+ + e^- \qquad (2)$$

$$e^- + H^+ + Pt \longrightarrow Pt{-}H \rightleftharpoons \frac{1}{2}H_2 + Pt \qquad (3)$$

The positive hole (h^+) generated simultaneously oxidizes the amines to imines with the H^+ release.

$$R^1R^2CHNH_2 + h^+ \xrightarrow{-H^+} R^1R^2C\overset{\bullet}{H}NH \xrightarrow{+h^+} R^1R^2C{=}NH + H^+ \qquad (4)$$

The imine (and/or its hydrolyzed derivative, aldehyde) undergoes condensation with the substrate amine to yiled the Schiff base.17-19)

$$R^1R^2C{=}NH + R^1R^2CHNH_2 \longrightarrow R^1R^2C{=}NCHR^1R^2 + NH_3 \qquad (5)$$

The failure to obtain secondary amine in CH_3CN indicates that the Pt exhibits no catalytic activity for hydrogenation of Schiff base. By the dark treatment with H_2 (20 μmol) overnight, propylidenepropylamine (100 μmol) in CH_3CN (5.0 cm^3) was little reduced to dipropylamine (< 0.1 μmol) in the presence of TiO_2/Pt (52.5 mg). This is not the case for the aqueous suspension of TiO_2/Pt.13) Adsorption of solvent CH_3CN on the Pt and its reduction to ethylimine may account for such an inhibitory effect. The formation of N-ethylidendbenzylamine and N-ethylbenzylamine as by-products in the later stage (> 5 h) of the benzylamine system (see Fig. 1) is attributable to the condensation of benzylamine with ethylimine, and H_2-reduction of the former on the Pt site, respectively.20)

Another characteristic of the CH_3CN system is the formation of Schiff base from α-substituted primary amines such as isopropylamine and cyclohexylamine, which are oxidized to acetone and cyclohexanone, respectively, in the aqueous system.

In summary, we have demonstrated that the photocatalytic reaction of primary amines by platinized-TiO_2 suspension in CH_3CN leads to the formation of Schiff bases without hydrolysis. The solvent CH_3CN is partly reduced by the photocatalytically liberated H_2 to yield N-ethyl and N-ethylidene derivatives, as by-products.

We thank Drs. Toshimi Sawano and Koichi Sakano for GC-MS measurement.

References

1) For recent review see A. J. Bard, J. Phys. Chem., 86, 172 (1982).
2) M. A. Fox and C. C. Chen, J. Am. Chem. Soc., 103, 6757 (1981).
3) M. A. Fox and C. C. Chen, Tetrahedron Lett., 24, 547 (1983).
4) M. A. Hema, V. Ramakrishnan, and J. C. Kuriacose, Indian J. Chem., 15B, 947 (1977).
5) B. Kraeutler and A. J. Bard, J. Am. Chem. Soc., 100, 5986 (1978).
6) R. B. Cundall, R. Rudham, and M. S. Salim, J. Chem. Soc., Faraday Trans. 1, 72, 1642 (1976).
7) P. R. Harvey, R. Rudham, and S. Ward, J. Chem. Soc., Faraday Trans. 1, 79, 1381 (1983).
8) K. Okada, K. Hisamitsu, and T. Mukai, J. Chem. Soc., Chem. Commun., 1980, 941.
9) R. A. Barber, P. de Mayo, and K. Okada, J. Chem. Soc., Chem. Commun., 1982, 1073.
10) K. Okada, K. Hisamitsu, Y. Takahashi, T. Hanaoka, T. Miyashi, and T. Mukai, Tetrahedron Lett., 46, 5311 (1984).
11) H. Al-Ekabi and P. de Mayo, J. Chem. Soc., Chem. Commun., 1984, 1231.
12) M. A. Fox, Acc. Chem. Res., 16, 314 (1983).
13) S. Nishimoto, B. Ohtani, T. Yoshikawa, and T. Kagiya, J. Am. Chem. Soc., 105, 7180 (1983).
14) This simple method of Pt loading was of good reproducibility (ca. ± 5%) for the photocatalytic reaction. TiO_2/Pt prepared by photoirradiation on TiO_2 suspension in aqueous solution of H_2PtCl_6 and 2-propanol (a modified photodeposition method, see B. Kraeutler and A. J. Bard, J. Am. Chem. Soc., 100, 4317 (1978)) was also used in this study, and exhibited comparable activity for the Schiff base formation.
15) Q. S. Li, K. Domen, and S. Naito, Chem. Lett., 1983, 321.
16) Negligible amount of products was obtained in the absence of Pt.
17) D. G. Norton, V. E. Haury, F. C. Davis, L. J. Mitchell, and S. A. Ballard, J. Org. Chem., 19, 1054 (1954).
18) K. N. Campbell, A. H. Sommers, and B. K. Campbell, J. Am. Chem. Soc., 66, 82 (1966).
19) W. S. Emerson, Org. React., 4, 174 (1948).
20) The expectation that most of N-ethylidenebenzylamine is produced on the Pt site and reduced successively while benzylidenebenzylamine on TiO_2 or in the solution, interprets the fact that N-ethylbenzylamine but not dibenzylamine was obtained in the photocatalytic system.

(Received May 10, 1985)