

Ag–TiO₂/Clay Composite Photocatalyst for the Oxidation–Cyclization of 1,2-Diamine Compounds with Propylene Glycol or Alcohols

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Received December 3, 2009; E-mail: chemres50@gmail.com

Silver-loaded TiO₂ (Ag–TiO₂) and acidic clay (K10 montmorillonite) composite photocatalyst has been successfully applied for the light-induced conversion of *o*-phenylenediamine (OPD) and its derivatives to substituted benzimidazoles with various alcohols in acetonitrile using UV-A and solar light. The influence of the various photocatalysts, solvents, and substituents on the yield and selectivity of the products has been investigated. The mechanism of photocatalysis is proposed. Loading silver on TiO₂ enhances product yield and selectivity both in UV and solar light. In the presence of primary alcohols, 2-aminothiophenol forms only disulfide and hence Ag–TiO₂/clay can be used as a green catalyst for the synthesis of disulfides.

The development of highly selective and environmentally benign chemical conversion processes to synthesize chemical specialties is an important subject in chemistry. Unfortunately, the required selectivity often comes at the expense of specially designed metal catalysts or reagents which have adverse environmental effects. One encouraging approach is to use nontoxic catalysts such as TiO₂ in the presence of sunlight, which is a safe and sustainable energy source, as a driving force for the reaction.¹

Since the discovery of the photocatalytic properties of TiO₂, this heterogeneous photocatalyst has been mainly employed to degrade organic and inorganic pollutants in water or air.² Different from that, the application of this catalyst for organic synthesis is a very attractive and significant target of research, which however is not much explored. The fact that some chemical reactions occur only in photocatalytic systems is more significant for this application. A few examples, such as the photocatalytic cyclization of α,ω -diamines,³ the synthesis of unsaturated α -anilino esters⁴ and unsaturated α -cyano-homoallylamines,⁵ the light-induced carbon–carbon bond formation,⁶ the diastereoselective radical tandem addition–cyclization reactions of aromatic tertiary amines have been reported.⁷

Benzimidazoles and substituted benzimidazoles are very useful intermediates/subunits for the development of molecules of pharmaceutical or biological interest.^{8–10} The classical synthesis of benzimidazole and its derivatives involves the facile condensation of aromatic *o*-diamine and carbonyl compounds under strong acidic or harsh dehydrating conditions.¹¹ Far away from thermal synthetic routes to benzimidazoles, heterogeneous photocatalysts open a new way for the synthesis of heterocyclic compounds.¹² Combining the photocatalytic activity of TiO₂ with utility of zeolites for photo-induced cyclization is more advantageous¹³ because this integrated photocatalyst absorbent matrix utilizes adsorption with advanced oxidation by photocatalyst. Performance of these photocatalysts has been improved by loading and surface

modification to extend their light absorption to the visible region of the solar spectrum.^{14,15}

It was reported that composite catalyst TiO₂–acidic zeolite promotes photocatalytic cyclization of *o*-phenylenediamine (OPD) and propylene glycol to form 2-methylquinoxaline and quinoxaline.¹⁶ But we found that the photoreaction of OPD and propylene glycol employing a mechanical mixture of TiO₂ and 5% acidic clay (K10 montmorillonite) as photocatalyst, produced 2-methylbenzimidazole (60%) and benzimidazole (30%) in high selectivity without the formation of quinoxaline and 2-methylquinoxaline.¹⁷ Now we report a detailed study on the yield and selectivity of this photocatalytic cyclization in the presence of various solvents and photocatalysts and also the cyclization of substituted OPDs with propylene glycol, ethylene glycol, and various alcohols.

Experimental

Materials and Methods. *o*-Phenylenediamine, 4-fluoro-1,2-phenylenediamine, 4-chloro-1,2-phenylenediamine, 4-methyl-1,2-phenylenediamine, 4-methoxy-1,2-phenylenediamine, 4-nitro-1,2-phenylenediamine, 3,4-diaminobenzoic acid, 3,4-diaminobenzophenone, and 1,2-diaminoanthraquinone (Aldrich chemicals) were used as received. Titanium dioxide (anatase) with a BET surface area of 21.53 m² g^{−1} and perchloric acid were supplied by Qualigen. A gift sample of TiO₂–P25 (80% anatase:20% rutile) was obtained from Degussa (Germany). It has particle size of 30 nm and BET specific area 56 m² g^{−1}. Ag, Pt, Pd, and Au loading sources are silver nitrate (AR), hexachloroplatinic acid, palladium chloride, and hydrogen tetrachloroaurate(III) trihydrate (HAuCl₄·3H₂O) respectively. The metal-loaded TiO₂ catalyst was prepared by photoreduction of metal ions to metal on the TiO₂ anatase surface as per a procedure reported in our previous paper.¹⁴

The Ag-loaded TiO₂ catalysts were characterized by diffuse reflectance spectra, XRD, SEM, and BET surface area measurements.¹⁴ Diffuse reflectance spectra reveal that the loading of

silver on TiO₂ results in increase in absorbance from 400 nm to the entire visible region. The sizes of Ag–TiO₂ and TiO₂ anatase were determined from XRD data using the Scherrer equation. It was found that the catalyst is in the form of nanoparticulate with average crystallite size of 39.28 nm which is higher than the crystallite size of TiO₂ anatase (20.85 nm). Analysis of the SEM images of the catalyst reveals that the loading of silver metal does not leave any change in the topology of the catalyst surface.

The clay composite Ag–TiO₂ and TiO₂ catalysts were prepared by mechanical mixing of Ag–TiO₂/TiO₂ with K10 montmorillonite in low boiling solvent acetone and drying the catalysts to evaporate the solvent at 110 °C. Then they were activated at 200 °C for 2 h before use.

Photocatalytic Studies. All reactions were performed with a mole ratio 1:2 of *o*-phenylenediamine and propylene glycol or ethylene glycol or alcohols in 25 mL of acetonitrile using 200 mg of TiO₂/acidic clay (5%) catalyst under aerated conditions (airflow rate = 8.1 mL s^{−1}). The reaction mixture was irradiated with a Heber multilamp photochemical reactor (model HML-MP88) equipped with 8 lamps (365 nm) for the required time. After irradiation, TiO₂ was removed by centrifugation and filtration and the filtrate was subjected to GC analysis (GC-9000, Perkin-Elmer) using a capillary column (DB-5) and flame ionization detector (FID) for the determination of the yield. The separation of products was performed by column chromatography on a silica gel column by eluting with a co-solvent of dichloromethane and methanol (4:1 v/v). The structures of the products were confirmed with ¹H NMR, ¹³C NMR, and GC-mass spectra. For identification of acid derivatives, the oxidation of propylene glycol was determined by Shimadzu GC-17A gas chromatograph equipped with a HP-FFAP column (30 m × 0.25 mm) and a flame ionization detector (FID).

Solar light intensity was measured using a LT Lutron LX-10/A digital Lux meter every 30 min and the average light intensity over the duration of each experiment was calculated. The sensor was always set at the position of maximum intensity. The intensity of solar light (1100 × 100 Lux) was nearly constant during the experiments.

Results and Discussion

Photocatalytic Cyclization. The present study has been initiated keeping in view that heterogeneous photocatalysis happens on the surface of titanium dioxide catalyst and adsorption may be modified by the distribution of titania on clay and the acidity of the support. Figure 1 shows the time course of product formation and OPD consumption by 365 nm irradiation with the TiO₂/clay catalyst. The irradiation produced 2-methylbenzimidazole (2MBZ) and benzimidazole (BZ), the amount of each being increased with increase in irradiation time. No other oxidation product, such as azobenzene, was detected. Table 1 shows that photocatalytic cyclization reaction of OPD with propylene glycol (PG) using UV-A/solar light under different conditions. It was observed that photocatalytic formation of 2-methylbenzimidazole (2MBZ) and benzimidazole (BZ) from PG with OPD required light, TiO₂, acidic clay, and air. The reactions have been carried out with 200 mg of the catalyst. It was observed that further

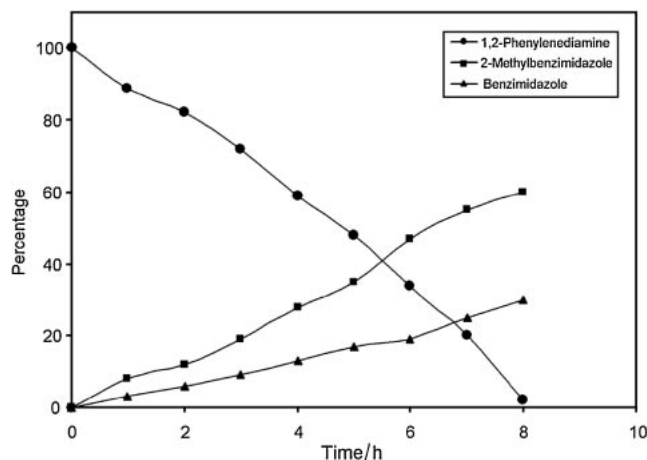


Figure 1. Time course of product formation and OPD consumption by irradiation of the 365 nm with TiO₂/clay catalyst. All reactions were performed with a mole ratio of 1:2 in acetonitrile (20 mL) solvent; TiO₂: 200 mg, airflow rate: 8.1 mL s^{−1}, $I_0 = 1.381 \times 10^{-3}$ einstein L^{−1} s^{−1} (4 lamps).

Table 1. Photocatalytic Cyclization of 1,2-Phenylenediamine with Propylene Glycol under Different Conditions

Conditions ^{a)}	Irradiation time/h	2MBZ /%	BZ /%	Conversion /%
Clay/TiO ₂ /dark/air	8	0	0	0
TiO ₂ /air/UV light	8	14	3	17
Clay/UV light/air	8	0	0	0
TiO ₂ /clay (2%)/air/UV light	8	48	18	66
TiO ₂ /clay (5%)/air/UV light	8	60	30	90
TiO ₂ /clay (5%)/air/solar light	8	52	26	78

a) All reactions were performed with a mole ratio of 1:2 in acetonitrile (20 mL) solvent; TiO₂: 200 mg, airflow rate: 8.1 mL s^{−1}, $I_0 = 1.381 \times 10^{-3}$ einstein L^{−1} s^{−1} (4 lamps).

increase of catalyst amount did not show better reaction yields. No reaction was observed in the absence of light, with bare clay and in the absence of air.

Photocatalytic Synthesis of Benzimidazole Derivatives in Different Solvents. The photocatalytic synthesis of benzimidazole derivatives was carried out in various solvents and the results are shown in Table 2. It was found that the solvent played a remarkable role in the conversion and the yield of products. The conversion efficiency is high in acetonitrile and it is low in 1,4-dioxane. The order of conversion efficiency is acetonitrile > dichloromethane > dichloroethane > ethyl acetate > chloroform > benzene > *n*-hexane > 1,4-dioxane. Among these solvents acetonitrile, dichloromethane, and dichloroethane selectively (Runs 1–3) formed benzimidazole derivatives whereas, chloroform, ethyl acetate, benzene, *n*-hexane, and 1,4-dioxane (Runs 4–8) favors the formation of by-products. In the alcoholic solvents like methanol, ethanol, and isopropyl alcohol, benzimidazole was not formed as the solvents underwent oxidation. Among these solvents, dichloromethane and acetonitrile are most efficient and 1,4-dioxane is least efficient for photocatalytic cyclization. Dichloromethane, being a low boiling solvent, is highly

Table 2. Percentages of Benzimidazoles and By-products Formed in Various Solvents with OPD and PG Using UV Light^{a)}

Run	Solvents	2MBZ /%	BZ /%	By-product /%	Conversion /%
1	Acetonitrile	50	30	5	85
2	Dichloromethane	51	26	7	84
3	Dichloroethane	48	23	5	76
4	Ethyl acetate	40	20	15	75
5	Chloroform	37	14	33	84
6	Benzene	35	20	17	72
7	<i>n</i> -Hexane	40	19	35	94
8	1,4-Dioxane	15	9	56	80

a) All reactions were performed with a mole ratio of 1:2 in acetonitrile (20 mL) solvent; TiO₂: 200 mg, airflow rate: 8.1 mL s⁻¹, $I_0 = 1.381 \times 10^{-3}$ einstein L⁻¹ s⁻¹ (4 lamps).

Table 3. Effect of Various Photocatalysts on Synthesis of Benzimidazoles in Acetonitrile^{a)}

Run	Photocatalysts	2MBZ /%	BZ /%	By-product /%	Conversion /%
1	CdS	13	11	5	29
2	Fe ₂ O ₃	15	5	8	28
3	ZnO (Merck)	38	28	15	81
4	ZrO ₂	5	2	33	40
5	ZnO (nano)	30	22	11	63
6	V ₂ O ₅	35	20	17	72
7	TiO ₂ (anatase)	53	30	2	85
8	Ag-TiO ₂	59	33	2	94
9	Pt-TiO ₂	45	28	5	78
10	Au-TiO ₂	49	31	4	84
11	Pd-TiO ₂	30	21	10	61

a) All reactions were performed with a mole ratio of 1:2 in acetonitrile (20 mL) solvent; TiO₂: 200 mg, airflow rate: 8.1 mL s⁻¹, $I_0 = 1.381 \times 10^{-3}$ einstein L⁻¹ s⁻¹ (4 lamps).

volatile at room temperature. Acetonitrile is less volatile and is inert to light radiation. Hence, we used acetonitrile solvent for cyclization processes. The yield of benzimidazole derivatives is high with polar non-reactive solvents and low with polar solvents.

Effect of Various Photocatalysts. The photocatalytic synthesis of benzimidazole in different photocatalysts with 5% clay using UV (365 nm) light was carried out in acetonitrile under identical conditions and the results are given in Table 3. The order of activities for overall conversion of benzimidazole with photocatalysts are Ag-TiO₂ > TiO₂ (anatase) > Au-TiO₂ > ZnO (Merck) > Pt-TiO₂ > V₂O₅ > ZnO (nano) > Pd-TiO₂ > ZrO₂ > CdS > Fe₂O₃. The other semiconductors such as SnO₂, ZnS, and CdO were either less active or inert as a catalyst.

Though CdS (2.4 eV), V₂O₅ (2.8 eV), and Fe₂O₃ (2.2 eV) have lower band gap energies when compared to TiO₂-P25, the electron-hole recombination may be faster and hence they are less efficient. The lower efficiencies of ZnO (nano) and ZnO may be due to the low BET surface areas, 15 and 12.16 m² g⁻¹, which are smaller than that of TiO₂-P25 (56 m² g⁻¹). Though the BET surface area of Ag-TiO₂ is around 18 m² g⁻¹, this

catalyst is efficient because Ag loading inhibits the electron-hole recombination.¹⁴ Furthermore, Ag-TiO₂ has increased absorption in the UV and visible region. Since Ag-TiO₂ is more efficient than the other photocatalysts, we had carried out the photocatalytic cyclization using this catalyst in acetonitrile under optimum conditions with UV and solar light.

In the case of ZrO₂, its band gap energy of 5.0 eV is equivalent to the energy of 250 nm light. As the light used in this study is only 365 nm, it is not efficient in the excitation of this catalyst.

With all photocatalysts the percentage of 2-methylbenzimidazole is higher than the percentage of benzimidazole. Conversion efficiency and benzimidazoles formation are higher and the by-product formation is lower with TiO₂ and loaded TiO₂. With ZrO₂ and V₂O₅ by-product formation is high. This difference in efficiency may be due to the differences in the adsorption of OPD and oxidizing power of semiconductors.

Synthesis of Benzimidazole Derivatives over Ag-TiO₂/5% K10 Montmorillonite. To demonstrate the generality and scope of this method, we examined this reaction with various structurally diverse *o*-phenylenediamines in different alcohols in the Ag-TiO₂ clay composite catalyst under UV and solar light and the results are summarized in Table 4. A series of *o*-phenylenediamine derivatives reacted with different alcohols at room temperature smoothly to afford a wide range of benzimidazole derivatives in moderate to good yields.

The percentage of conversion and yields of various products in the photocatalytic cyclization of substituted OPDs with propylene glycol in UV and solar light are given in Runs 1–7. The yields are high with CH₃- and OCH₃-substituted OPDs whereas Cl-, F-, and NO₂-substituted OPDs show lesser yield both in UV and solar light. In the case of 4-chloro and 4-fluoro OPDs (Runs 4 and 5), 2-methylbenzimidazole and benzimidazole are obtained in addition to the expected 5-halo (Cl and F) benzimidazole derivatives. This reveals the formation of OPD by oxidative dehalogenation before cyclization under the reaction conditions. Similarly 4-COOH-OPD undergoes complete oxidative decarboxylation to form OPD before cyclization and hence only 2MBZ and BZ are obtained in low yield.

The results of photocatalytic cyclization of OPD and substituted OPDs with the oxidized product of EG are given in Runs 8–13. Conversion efficiencies are less when compared to PG. In addition to the benzimidazoles and substituted benzimidazoles small amounts of quinoxaline and azoaniline and their derivatives are also formed with OPD, 4-CH₃-OPD and 4-OCH₃-OPD. As observed in PG, 4-NO₂-OPD has the least efficiency and both Cl- and F-OPDs undergo oxidative dehalogenation to form OPD before cyclization.

The photocatalytic cyclizations of OPD and substituted OPDs were carried out with the primary alcohols, ethanol, propanol, and butanol. The corresponding acids formed from these alcohols condensed with OPDs forming methyl-, ethyl-, and propylbenzimidazoles. A small amount of azobenzene derivatives (3%) were obtained along with these products. In all the three alcohols, the substituted OPDs follow the same trend as observed with PG. Among the three alcohols, the cyclization efficiency is high with propanol and low with ethanol. This is because of the presence of the electron donor methyl group in propanol. The low efficiency of butanol when

Table 4. Effect of Substituents with Different Alcohols in Photocatalytic Synthesis of Benzimidazoles with Ag–TiO₂ Catalysts in UV and Solar Light^{a)}

Run	Substrate	Irradiation time/h	Conversion/%		Products/% (Yield of UV, solar)
			UV	Solar	
1	OPD + PG	8	92	97	2-Methylbenzimidazole (59, 67), benzimidazole (33, 30)
2	4-CH ₃ OPD + PG	6	95	97	2,5-Dimethylbenzimidazole (65, 67), 5-methylbenzimidazole (30, 30)
3	4-OCH ₃ OPD + PG	8	91	94	5-Methoxy-2-methylbenzimidazole (55, 58), 5-methoxybenzimidazole (36, 36)
4	4-Cl OPD + PG	8	81	93	5-Chloro-2-methylbenzimidazole (45, 52), 5-chlorobenzimidazole (30, 33), 2-methylbenzimidazole (4, 5), benzimidazole (2, 3)
5	4-F OPD + PG	8	73	86	5-Fluoro-2-methylbenzimidazole (40, 45), 5-fluorobenzimidazole (21, 25), 2-methylbenzimidazole (8, 10), benzimidazole (4, 6)
6	4-NO ₂ OPD + PG	8	55	60	5-Nitro-2-methylbenzimidazole (45, 50), 5-nitrobenzimidazole (10, 10)
7	4-COOH OPD + PG	8	32	38	2-Methylbenzimidazole (22, 27), benzimidazole (10, 11)
8	OPD + EG	8	27	40	Benzimidazole (22, 35), quinoxaline (2), 2,2'-diaminoazobenzene (3)
9	4-CH ₃ OPD + EG	6	47	50	5-Methylbenzimidazole (32, 35), 5-methylquinoxaline (12), 4,4'-dimethyl-2,2'-diaminoazobenzene (3)
10	4-OCH ₃ OPD + EG	8	44	47	5-Methoxybenzimidazole (37, 40), 5-methoxyquinoxaline (4), 4,4'-dimethoxy-2,2'-diaminoazobenzene (3)
11	4-Cl OPD + EG	8	46	53	5-Chlorobenzimidazole (43, 50), benzimidazole (2, 3)
12	4-F OPD + EG	8	46	51	5-Fluorobenzimidazole (35, 45), benzimidazole (11, 9)
13	4-NO ₂ OPD + EG	8	30	35	5-Nitrobenzimidazole (35, 30)
14	OPD + EtOH	8	23	41	2-Methylbenzimidazole (26, 38), 2,2'-diaminoazobenzene (3)
15	4-CH ₃ OPD + EtOH	6	40	49	2,5-Dimethylbenzimidazole (49, 40)
16	4-OCH ₃ OPD + EtOH	8	30	36	5-Methoxy-2-methylbenzimidazole (30, 36)
17	4-Cl OPD + EtOH	8	34	39	5-Chloro-2-methylbenzimidazole (34, 39)
18	4-F OPD + EtOH	8	46	49	5-Fluoro-2-methylbenzimidazole (39, 40), 2-methylbenzimidazole (7, 9)
19	4-NO ₂ OPD + EtOH	8	33	37	5-Nitro-2-methylbenzimidazole (33, 37)
20	OPD + PrOH	8	78	84	2-Ethylbenzimidazole (75, 81), 2,2'-diaminoazobenzene (3)
21	4-CH ₃ OPD + PrOH	6	75	88	5-Methyl-2-ethylbenzimidazole (73, 88)
22	4-OCH ₃ OPD + PrOH	8	71	84	5-Methoxy-2-ethylbenzimidazole (71, 84)
23	4-Cl OPD + PrOH	8	60	76	5-Chloro-2-ethylbenzimidazole (57, 71), 2-ethylbenzimidazole (3, 5)
24	4-F OPD + PrOH	8	51	70	5-Fluoro-2-ethylbenzimidazole (45, 63), 2-ethylbenzimidazole (6, 7)
25	4-NO ₂ OPD + PrOH	8	40	59	5-Nitro-2-ethylbenzimidazole (40, 59)
26	OPD + BuOH	8	52	66	2-Propylbenzimidazole (55, 69), 2,2'-diaminoazobenzene (3)
27	4-CH ₃ OPD + BuOH	6	64	70	5-Methyl-2-propylbenzimidazole (64, 70)
28	4-OCH ₃ OPD + BuOH	8	59	65	5-Methoxy-2-propylbenzimidazole (59, 65)
29	4-Cl OPD + BuOH	8	44	53	5-Chloro-2-propylbenzimidazole (40, 50), 2-propylbenzimidazole (4, 3)
30	4-F OPD + BuOH	8	44	64	5-Fluoro-2-propylbenzimidazole (36, 38), 2-propylbenzimidazole (8)
31	4-NO ₂ OPD + BuOH	8	39	50	5-Nitro-2-propylbenzimidazole (39, 50)
32	OPD + toluene	8	30	43	2-Phenylbenzimidazole (16, 22), 2,2'-diaminoazobenzene (14, 21), <i>o</i> -phenylenediamine (60, 57)
33	OPD + 2-phenyl-1,2-propanediol	8	37	50	Benzimidazole (15, 15), 2-hydroxy-2-phenylpropionic acid (22, 35)
34	1,2-Diaminoanthraquinone + PG	8			No significant conversion
35	3,4-Diaminobenzophenone + PG	8			No significant conversion
36	3,4-Diaminopyridine + PG	8			No reaction

a) All reactions were performed with a mole ratio of 1:2 in acetonitrile (20 mL) solvent; TiO₂: 200 mg, airflow rate: 8.1 mL s⁻¹, $I_0 = 1.381 \times 10^{-3}$ einstein L⁻¹ s⁻¹ (4 lamps).

Table 5. Photocatalytic Cyclization of 2-Aminothiophenol (2-ASH) with Propylene Glycol, Ethylene Glycol, and Primary Alcohols^{a)}

Run	Substrate	Irradiation time/h	Conversion/%		Products/% (Yield of UV, Solar)
			UV	Solar	
1	2-ASH + PG	8	79	61	2-Methyl benzothiazole (38, 33), benzothiazole (15, 10), 2,2'-diaminodiphenyl disulfide (25, 18), 2-aminothiophenol (11, 38)
2	2-ASH + EG	8	61	46	Benzothiazole (15, 10), 2,2'-diaminodiphenyl disulfide (35, 28), 2-aminothiophenol (11, 38), 2-benzothiazolemethanol (11, 8)
3	2-ASH + EtOH	8	60	58	2,2'-Diaminodiphenyl disulfide (60, 58)
4	2-ASH + PrOH	8	73	76	2,2'-Diaminodiphenyl disulfide (73, 76)
5	2-ASH + BuOH	8	77	81	2,2'-Diaminodiphenyl disulfide (77, 81)

a) All reactions were performed with a mole ratio of 1:2 in acetonitrile (20 mL) solvent; TiO₂: 200 mg, airflow rate: 8.1 mL s⁻¹, $I_0 = 1.381 \times 10^{-3}$ einstein L⁻¹ s⁻¹ (4 lamps).

compared to propanol is due to the steric effect of the bulky propyl group.

The photocatalytic cyclization of OPD with 2-phenyl-1,2-propanediol gave 2-hydroxy-2-phenylpropionic acid and benzimidazole (Run 33). When OPD was irradiated with toluene, 2-phenylbenzimidazole and 2,2'-diaminoazobenzene were formed (Run 32).

In almost all OPDs, the benzimidazoles and 2-alkylbenzimidazoles were selectively obtained in moderate to good yields. However, when 1,2-diaminoanthraquinone (Run 34) and 3,4-diaminobenzophenone (Run 35) were employed instead of *o*-phenylenediamine with PG, only a trace amount of the respective condensation product was detected by GC-MS.

To extend the scope of this method, we also examined the coupling of 2,3-diaminopyridine (Run 36) and 1,2-diaminocyclohexane with propylene glycol under these conditions. Irradiation of these diamines with PG using Ag-TiO₂ failed to produce desired products. Although acids might have been formed in this reaction mixture, they could not precede further to form benzimidazole compounds as in the Philips synthesis.¹⁸

Similar to OPD, 2-aminothiophenol may also undergo cyclization with the oxidizing products of glycols and alcohols. We had carried out the reaction of 2-aminothiophenol with PG, EG, EtOH, PrOH, and BuOH and results are given in Table 5. 2-Aminothiophenol also underwent condensation with the oxidative products of PG and EG in presence of TiO₂/clay composite catalysts, affording the corresponding 2-methylbenzothiazoles and benzothiazole along with disulfide (Runs 1 and 2). 2-Aminothiophenol with other three primary alcohols (Runs 3–5) gave only sulfide and no benzothiazole was formed. This catalyst selectively oxidizes aminothiols to amino sulfides and the yield increases from ethanol (60%) to butanol (81%) both in UV and solar light.

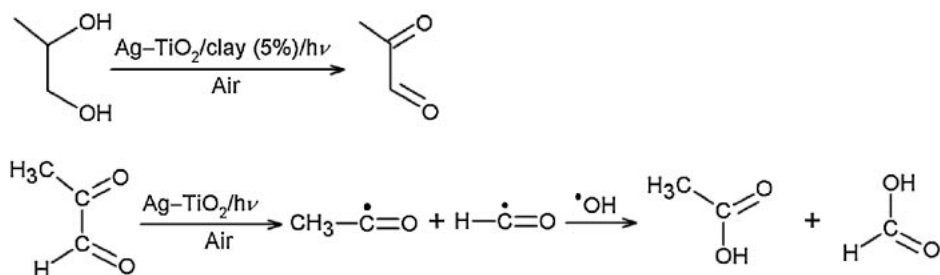
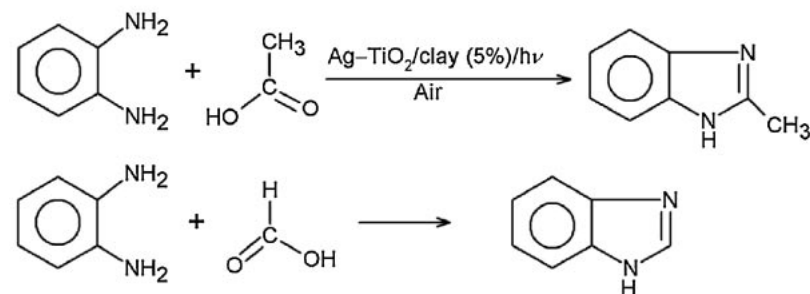
Selective oxidation of thiols to the corresponding disulfides is of interest from the point of view of biological and chemical process.^{19–22} Thiols are easily over-oxidized and therefore extensive study has been carried out for the controlled oxidation of thiols using iodine/hydrogen iodide,²³ bromine,²⁴ potassium dichromate,²⁵ potassium permanganate/copper(II)

sulfate,²⁶ hydrogen peroxide in trifluoroethanol,²⁷ and dimethyl sulfoxide.²⁸ Enzymatic²⁹ and electrochemical³⁰ methods are also known to perform this oxidative transformation. In this regard, this non-toxic clay composite catalyst is considered as an ideal “green” oxidant for the formation of disulfides by the controlled oxidation of 2-aminothiophenol without the formation of by-products.

But in the case of 2-aminophenol under the same reaction conditions, the desired benzoxazoles was obtained in very low yield along with several side products as identified from the GC-MS analysis. Hence no further attempts were made to optimize the reaction with this substrate.

When we compare the efficiency of this catalyst in UV and solar processes, Ag-TiO₂ is slightly more efficient in solar light than in UV light. The higher activity of Ag-TiO₂ catalyst in solar light has already been proved in the degradation of azo dyes.¹⁴ The Ag particles have increased absorption in the visible region and also act as electron traps, enhancing the electron-hole separation by the transfer of the trapped electron to the adsorbed O₂.³¹

Plausible Reaction Mechanism. A mechanism for the formation of 2-methylbenzimidazole and benzimidazole is proposed based on the experimental results (Scheme 1). When titanium dioxide is exposed to UV light, electrons are promoted to the conduction band and positive holes are formed in the valence band. It is already established that alcohols can be easily photooxidized on semiconductor surface to corresponding aldehyde or ketone.³² They may be further oxidized to acids by the hydroxyl radicals produced by irradiated semiconductors. It is also known that the oxidation depends on the acidity of semiconductor/clay composite catalyst. In this case *o*-phenylenediamines are adsorbed preferentially than PG (or alcohols) in the internal surface area of the clay pores. The preferential adsorption of OPDs causes PG to undergo oxidation to ketoaldehyde and then to acetic acid and formic acid (step 1). Acetic acid and formic acid formed undergo cyclization with OPDs to give 2-methylbenzimidazole and benzimidazole respectively (step 2). HCOOH is reported to be a hole scavenger and so it can undergo easy oxidation. This reduces the availability of free HCOOH for condensation.

Step 1**Step 2****Scheme 1.**

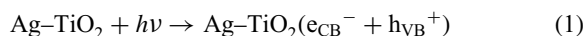
Hence the formation of 2-methylbenzimidazole is always higher than benzimidazole (Table 4). In all other reactions, the products are formed by a similar mechanism as shown in Scheme 1.

In the case of EG, formic acid is formed through glyoxal. Condensation of formic acid with OPD gives benzimidazole. A small amount of quinoxaline is also formed by the condensation of glyoxal with OPD. Primary alcohols on oxidation give acids, which condense with OPD giving alkyl benzimidazoles. In the case of alcohols, a small amount of 2,2'-diaminoazobenzene is also formed by the condensation of 2 OPD. When OPD is irradiated in toluene, toluene is oxidized to benzoic acid which condenses with OPD forming 2-phenylbenzimidazole. In toluene, the condensation of 2 molecules of OPD takes place giving 2,2'-diaminoazobenzene. 2-Phenylpropane-1,2-diol on irradiation gives 2-hydroxy-2-phenylpropionic acid and formic acid. Formation of 2-hydroxy-2-phenylpropionic acid has been confirmed by GC-MS. Formic acid condenses with OPD to form benzimidazole.

In order to confirm the formation of acetic and formic acids from propylene glycol, TiO₂-assisted oxidation of propylene glycol has been experimentally followed by GC and infrared spectroscopy. The oxidation of propylene glycol to acetic acid and formic acid in air-purged CH₂Cl₂ suspensions containing TiO₂ under UV irradiation was investigated. Acetic acid was identified as the major product of the reaction by comparing its retention time (1.95) with the retention time of the reference compound (1.95) by GC (data not shown). We do not have GC evidence for formic acid formation because this compound undergoes thermal decomposition during GC analysis. The formation of acetic acid and formic acid adsorbed on TiO₂ has also been confirmed by FT-IR studies. The FT-IR spectra of TiO₂ photocatalyst after the adsorption of PG in dark and

after completion of the reaction are shown in Supporting Information. Absorption bands in the range of 1700–1800 cm^{−1} on the absorption spectra of TiO₂ after the completion of the reaction indicated that PG was partially converted to acid derivatives.

Formation of disulfides by the oxidation of thiols can be explained by the following mechanism. Photogenerated hole (h⁺) readily accepts an electron from the thiol adsorbed on the surface of the photocatalyst to give the thiol radical cation (eq 3). The latter reacts with super oxide ion radical to yield disulfide (eq 4).



In the case of PG and EG, they undergo partial oxidation with holes forming acetic and formic acids. Hence they form benzothiazole along with disulfides. With primary alcohols, oxidation of thiols is more predominant and hence there is a selective production of disulfides.

Conclusion

Photocatalytic conversion of *o*-phenylenediamine to 2-methylbenzimidazole and benzimidazole on irradiation of propylene glycol using Ag-TiO₂/clay composite catalyst is more than 92% with UV and solar light. 2-Methylbenzimidazole formation is always higher than benzimidazole as the available free formic acid is reduced due to further oxidation. Acetonitrile is found to be the best solvent for cyclization. Conversion efficiency and benzimidazole formation are higher and the by-product formation is lower with TiO₂ and metal

loaded TiO₂. The yields of benzimidazole derivatives are higher with methyl- and methoxy-substituted *o*-phenylenediamines and lower with the chloro-, fluoro-, and nitro-substituted *o*-phenylenediamines both in UV and solar light. A mechanism is proposed for the formation of 2-methylbenzimidazole, benzimidazole, and other products for the cyclization of substituted *o*-phenylenediamine with propylene glycol, ethylene glycol, and various alcohols. 2-Aminothiophenol undergoes cyclization with propylene glycol and ethylene glycol with less yield along with the formation of sulfides. In the presence of alcohols, 2-aminothiophenol forms only disulfides and hence the Ag-TiO₂/clay can be considered as a green catalyst for the controlled oxidation of thiols. Hence, Ag-TiO₂/clay can be used as an efficient and ecofriendly catalyst for the cyclization of substituted *o*-phenylenediamines with glycols and alcohols in UV and solar light.

One of the authors, K. Selvam is thankful to CSIR, New Delhi for the award of Senior Research Fellowship. The authors thank Ministry of Environment and Forests (MOEF), New Delhi, for the financial support through research grant No. 315-F-36, F. No. 19/9/2007-RE. Authors also thank Trichy Distilleries & Chemicals Ltd., India for the detection of acid derivatives from propylene glycol oxidation using GC analysis.

Supporting Information

Spectral data of selected compounds and FT-IR spectra of the catalysts. This material is available free of charge on the web at <http://www.csj.jp/journals/bcsj/>.

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