

Photocatalytic Decompositions of Carboxylic Acid Derivatives by Semiconductors

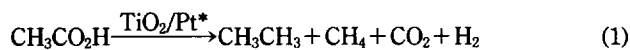
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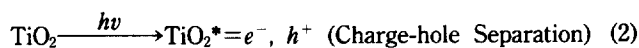
Each aqueous solution (pH=1) of acetic acid, acetamide, and acetonitrile produces carbon dioxide and hydrogen at 300 K when irradiated in the presence of semiconductors such as titanium dioxide, platinized titanium dioxide, etc. Similar results were obtained for each of benzoic acid, benzamide, and benzonitrile. Based on the relative amount of carbon dioxide, nitrile is believed to be transformed into carboxylic acid through the intermediacy of amide. A mechanism in which hydrogen atom and hydroxyl radical are involved is presented.

Introduction

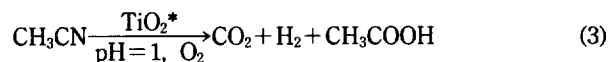
Semiconductor photocatalysts have been utilized in many areas of chemistry since the discovery of Photo-Kolbe reaction (Eq. 1) by Bard.¹



When photocatalysts are irradiated, the first event is the charge separation (Eq. 2) *i.e.* electron in the conduction band (CB) and hole (h^+) in the valence band (VB).²



The reduction and oxidation can be induced on the surface of photocatalysts depending on the redox potentials of substrates and the potential of CB and VB of photocatalysts. Particularly relating with organic chemistry, oxidations have been investigated extensively using many substrates.² It is well known that reaction products obtained are dependent on the reaction conditions. The present work was undertaken based on our earlier observation that acetonitrile in an aqueous solution of pH=1 and under air bubbling generates carbon dioxide, hydrogen, and acetic acid when irradiated in the presence of photocatalysts (Eq. 3).



Considering that acetonitrile is one of the most common solvents, the result of Eq. (3) made us to investigate this work in more detail. Correspondingly our concern was whether the reaction of Eq. (3) might be general for this type of compounds and what mechanism would be involved. For the purpose acetic acid (1), acetamide (2), acetonitrile (3), benzoic acid (4), benzamide (5), and benzonitrile (6) were employed.

Experimental

Materials. Acetamide (GR, Wako), acetic acid (99.8%, Aldrich), benzonitrile (EP, Junsei), benzamide (99%, Aldrich), and benzoic acid (EP, 99.5%, SCI) were used as received without further purification. Acetonitrile (Duksan) was distilled from calcium hydride just before use. In each experiment the solvent was either distilled water of pH=1 or 5% aqueous acetonitrile of pH=1. Anatase titanium dioxide was

Table 1. Amount of BaCO₃(mg) Obtained from the Photocatalytic Decompositions of Carboxylic Acid Derivatives

| Substrate | Amount of BaCO ₃ (mg) | | | |
|---|----------------------------------|-----------|----------------------|----------|
| | TiO ₂ | ZnS · CdS | TiO ₂ /Pt | Control* |
| CH ₃ COOH (1) | 10 | 5 | 43 | 2 |
| CH ₃ CONH ₂ (2) | 10 | 20 | 35 | 5 |
| CH ₃ CN (3) | 10 | 15 | 50 | 4 |
| C ₆ H ₅ COOH (4) | 12 | 20 | 38 | 5 |
| C ₆ H ₅ CONH ₂ (5)** | — | — | — | — |
| C ₆ H ₅ CN (6) | 5 | 10 | 30 | 2 |

Solvent: H₂O(pH=1), Atmosphere: N₂, Reaction time: 3 h, Light source: 450-w Hg arc lamp, Amount of semiconductor: 4.25 × 10⁻⁴ mol, Substrate: 0.03 mol Temperature: ~40°C, * Without TiO₂, ** Not determined.

used and ZnS · CdS and TiO₂/Pt (10% by weight) were made by known procedures.⁹

Apparatus. Most of all experiments were carried out in a Pyrex vessel (diameter 2 cm, length 19.5 cm) containing inlet and outlet tubes for gas bubbling. Irradiation was conducted mostly by a 450-W Hg arc lamp placed 12 cm away from the reaction vessel. In order to trap the gas products such as carbon dioxide and hydrogen, barium hydroxide and potassium permanganate solutions were used respectively. Also bubbling gas (nitrogen and air) was prepurified by passing into barium hydroxide solution to remove trace of carbon dioxide.

Procedure. Two methods were employed. In method A, all reactions were carried out under nitrogen in the presence of a semiconductor such as TiO₂, ZnS · CdS, TiO₂/Pt. Irradiation was performed without water jacket. In method B, reaction were carried out in the presence of TiO₂ under nitrogen or air. Irradiation was performed using water jacketed Hg arc lamp.

Method A. (i) *Reaction of Acetonitrile (Standard Procedure):* To a Pyrex vessel containing TiO₂(0.3g, 4.25 × 10⁻⁴ mol), water(pH=1, 20 ml) and acetonitrile(0.03 mol) were introduced. While nitrogen being bubbled through the reaction mixture, irradiation was continued for 3 h using a 450-W Hg arc lamp. Carbon dioxide evolving from the reaction was trapped by barium hydroxide solution. Hydrogen was detected by the formation of manganese dioxide from potas-

Table 2. Amount of BaCO₃(mg) Obtained from the Photocatalytic Decompositions of Carboxylic Acid Derivatives

| Substrate | Amount of BaCO ₃ (mg) | | |
|---|----------------------------------|----------------|----------|
| | N ₂ | O ₂ | Control* |
| CH ₃ COOH (1) | 30 | 86 | 6 |
| CH ₃ CONH ₂ (2) | 15 | 80 | 2 |
| CH ₃ CN (3) | 16 | 20 | 2 |
| C ₆ H ₅ COOH (4) | —** | 41 | 2 |
| C ₆ H ₅ CONH ₂ (5) | —** | 33 | 2 |
| C ₆ H ₅ CN (6) | —** | 25 | 1 |

* Without TiO₂ ** Not determined Experimental condition: Light source 450-w Hg arc lamp under O₂ bubbling for 3 h at 25°C. solvent was H₂O or 5% acetonitrile (pH=1). TiO₂ 4.25×10⁻⁴ mol, Substrate 0.03 mol.

sium permanganate trap solution. Barium carbonate trapped was dried in an oven at 80°C for 1 h and weighed. When either ZnS · CdS or TiO₂/Pt was employed respectively, similar procedure as above was employed. (ii) *Reaction of Other Substrates*: When each of acetic acid acetamide, benzoic acid, and benzonitrile was employed as a substrate similar procedure as previously described was employed. The results are listed in Table 1. (iii) *Control Experiment*: Each (0.03 mol) of substrates was subjected to this work as described in (i) except semiconductor. No semiconductor was used in this control experiment. The amount of carbon dioxide evolving from the reaction mixture was negligible.

Method B. (i) *Reaction of Acetonitrile under N₂*: Procedure was the same as in (Method A) (i) except the lamp. In this method irradiating lamp was placed into a quartz water jacket. The results are listed in Table 2. (ii) *Reaction of Acetonitrile under Air*; Procedure was the same as above except bubbling with air free of carbon dioxide. (iii) *Reaction of Other Substrate*; Procedure was the same as in (Method A) (i) and (ii). (iv) *Control Experiment* Procedure was the same as in (Method B) (iii) except bubbling with air free of carbon dioxide instead of nitrogen. The amount of carbon dioxide evolving from reaction was negligible. The results are listed in Table 2. (Detection of Intermediates) (i) *Acetic Acid from Acetonitrile*; Acetonitrile (0.03 mol) was introduced into a Pyrex cell containing titanium dioxide (0.3g, 4.25×10⁻⁴ mol) and water (20 ml) of pH=1. After reaction mixture was purged with nitrogen free of carbon dioxide, irradiation was continued for 36 h. During which time formation of acetic acid was observed by GC/MS as well as by strong characteristic odor. (ii) *Benzaldehyde from Benzoic Acid*; Experimental conditions were the same as in (Method B) (iii) except using Rayonet Photoequipment (350 nm) instead of a 450-W Hg arc lamp. After irradiation for 15 h, GC/MS showed the formation of benzaldehyde. (iii) *Benzoic Acid from Benzamide*: Experimental conditions were the same as previous one except using benzamide as a substrate. After irradiation for 15 h, GC/MS showed the formation of benzoic acid.

Results and Discussion

Based on the result of Eq. (3), one might suppose that acetonitrile is sensitized by semiconductors to yield acetic

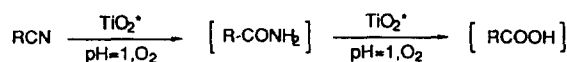
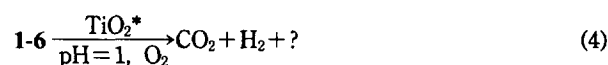


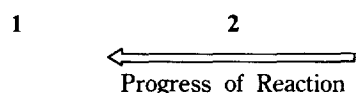
Photo-Kolbe Process

Scheme 1

acid *via* acetamide. To investigate this further, six substrates (1-6) were irradiated separately in the presence of semiconductors such as TiO₂, TiO₂/Pt, and ZnS · CdS under nitrogen bubbling (Method A). All of six substrates produced carbon dioxide and hydrogen (Eq. 4). In order to determine the progress of reaction, carbon dioxide



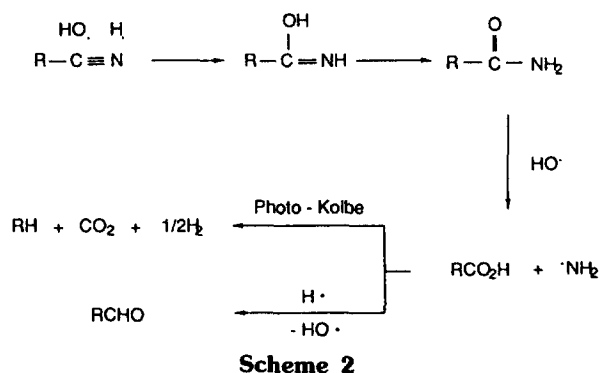
was converted to BaCO₃ using a trap of Ba(OH)₂ solution.¹⁰ The amounts of BaCO₃ obtained during 3 h in the presence of semiconductors are summarized in Table 1. It needs to be pointed out that the results in Table 1 were obtained by direct irradiation from a 450-W Hg arc lamp without water jacket. In this condition the steady-state temperature was 40-42°C. As can be seen in Table 1, among the three semiconductor photocatalysts, TiO₂/Pt showed the greatest effect. The result is consistent with the earlier reports that TiO₂/Pt is the best photocatalyst in generating H₂ by water splitting. Another series of experiments were also carried out using a quartz water jacket so as to maintain the temperature of the reaction mixture at around 25°C. The results are listed in Table 2. It can be seen in Table 2 that photocatalytic decomposition of substrates is more efficient in the presence of air (O₂) due to the efficient capture of electrons in the conduction band of semiconductors thus allowing hole (h⁺) to be used in the oxidation of nearby reductants (see later part). Also seen in Table 1 and 2, aromatic substrates (4-6) were more resistant than aliphatic ones (1-3) to photodecompositions. The progress of the reaction on aliphatic and aromatic substrates is shown in Eq. (5) and (6) respectively.



The sequence in Eq. (5) and (6) together with the result of Eq. (3) suggest that possible pathway for the photocatalytic decomposition of substrates might involve the pathway as shown in Scheme 1.

From the control experiments, it is evident that nitrile is not hydrolyzed to carboxylic acid in our reaction conditions. Instead a mechanism in which hydroxyl radicals and hydrogen atoms are involved is believed to be operating as shown in Scheme 2.

It is reported in many cases that hydroxyl radicals and hy-

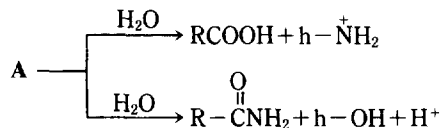
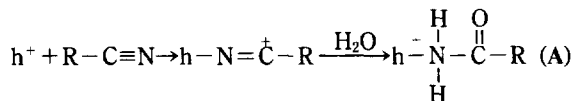


drogen atoms are formed¹¹⁻¹³ particularly in aqueous solution. Another supporting indication that our reaction condition (pH=1, aqueous under air bubbling) is effective in generating hydroxyl radicals¹⁴ and hydrogen atoms comes from the detection of benzaldehyde (Scheme 2) in the reaction of benzoic acid. Based on the results of this work, following conclusions can be stated. (1) Acetonitrile, a most common solvent, is decomposed photocatalytically. Hydroxyl radicals and hydrogen atoms formed on the surface of semiconductor are believed to be participating for this process. (2) A possible way in the conversion of nitrile compound to carboxylic acid involves intermediacy of amide. (3) The photocatalytic method might provide a way to remove nitrile present as an impurity.¹⁵

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- Hydroxyl radicals are believed to be obtained from the oxidation of water by hole ($h^+ + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{HO} \cdot$). Another possibility is the sensitization of nitriles by h^+ . Based on both the oxidation potential of acetonitrile¹⁶ (+2.9–3.0 V vs SCE) and valence band potential of TiO_2 in water at pH=1 (+3.1 V vs SCE),³⁰ following sensitization processes might be conceived.



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