Study on Photocatalytic Organic Reactions Using Photocatalytic Microreactors

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Photocatalytic organic reactions were performed using automatic photocatalytic microreactor, where several open-end capillaries with photocatalytic materials coated inside were just soaked in a test tube including a reactant solution. Organic reactions of the alkyl radicals generated from carboxylic acids due to the photo-Kolbe reaction was studied, in analogy with the reactions using a photosensitizer. This methodology features the reusability of the reactor and an easy process for analysis due to easy separation of the reactant solution.

Keywords Photocatalytic reaction, microreactor, decarboxylation

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Introduction

Inorganic materials such as titanium oxide are well known as photocatalysts, and have been commercially utilized mostly for cleaning of walls, toilets, interior walls in tunnels, *etc.*^{1,2} Such inorganic photocatalysts have strong oxidation ability, causing the decomposition of organic molecules directly or indirectly *via* hydroxyl radicals generated by the oxidization of water. Photocatalysts can be utilized not only for such decomposition reactions, but also for organic syntheses or conversions, which in comparison have not been explored in depth. Oxidation of simple functional groups in aromatic compounds have been reported,³⁻⁸ and the result for the selective oxidation of various alcohols showed high yields.⁹ Although the oxidation ability of photocatalysts is often the focus, they also have reducing ability, which could be controlled by depositing noble metals on the surface^{5,10} and the reduction reaction of nitrobenzene has been well studied.¹¹⁻¹⁴

If inorganic photocatalysts could be utilized effectively for organic syntheses and conversions, it would be beneficial as 'green chemistry' since they are mostly non-toxic and also easily separated after reactions because they are particulate. Furthermore, a wide variety of new photocatalytic materials with the capability of visible-light reaction have been developed in recent years due to strong demand for light harvesting applications such as solar fuels and solar cells.¹⁵⁻¹⁷ Although these materials were not developed for organic syntheses, they would have considerable potential in this area because there are a variety of materials where the energy levels of the conduction and valence bands are modified, meaning that the oxidation and reduction abilities are controlled.

However, there has not been a standard methodology for screening or optimization of photocatalytic organic reactions. Recently, we proposed a new concept of a photocatalytic microreactor that does not require electrical resources to perform the photocatalytic reaction. Instead, our microreactor using a natural force such as capillary force and diffusion due to a

concentration gradient, and we successfully demonstrated decomposition reactions for dyes and organics.¹⁸ Since we suppose that this microreactor can be utilized not only for decomposition reactions but also for organic syntheses, we applied it for a survey of organic syntheses.

We applied a photocatalyst for an organic conversion instead of a photosensitizer, because of the similarity between the reaction processes, as shown in Scheme S1 (Supporting Information). In the case of photosensitizers, once they are photo-excited, which show a higher ability of oxidization or reduction, and they exchange electrons with reactants or sacrificial agents, causing the formation of radical ions. When they return back to the original state, they are oxidized or reduced again with reactants or sacrificial agents. The process is very similar for the TiO₂ photocatalysts, where water is oxidized and oxygen is reduced in aqueous solutions. In recent years, a variety of reactions of carboxylic acids using a photosensitizer were introduced, such as hydrogen atom transfer^{19,20} carbon bond formation with alkenes.²¹⁻²³ These reactions follow the process in Scheme 1, and the generated radical was used for various reactions utilizing their nucleophilic property. In these reactions, the photo-excited phenanthrene oxidizes the carboxylic anion, and the corresponding radical is generated, which follows carbon oxide release. The similar process is known for the TiO₂ photocatalyst, known as the photo-Kolbe reaction, where alkyl radicals are generated from various carboxylic acids.²⁴

In this study, we demonstrated how the photocatalytic microreactors can be utilized for the study for organic reactions, and clarified their feature. As a demonstration, we studied the reactions of carboxylic acids and the reactivity of the alkyl radicals generated from the carboxylic acids, in analogy with the reactions utilizing photosensitizers.

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Scheme 1 Photosensitizing carboxylic acid and the following decarboxylation.

Experimental

Photocatalytic reactions were performed using the automatic photocatalytic reactors, based on the principle proposed in a previous paper.¹⁸ The setup for organic reactions is shown in Fig. S1 (Supporting Information). Photocatalytic microreactors were prepared by coating photocatalytic materials inside a capillary with both ends open. Capillaries were bundled and the bottom was soaked in a reagent solution. Due to the capillary force, the solution is drawn up to a height on the order of several centimeters, where UV light was irradiated to initiate the reaction. Since the reactant decrease in the capillary due to light irradiation, a concentration gradient is formed inside the microreactors, driving the reactants beneath the capillary bundle up into the microreactors due to diffusion, and *vice versa* for the products. The reaction then continues until the concentration gradient disappears; namely when the reaction reached an equilibrium.

Fused silica capillaries (i.d. 1.1 mm, o.d. 1.4 mm) with a length of 6 cm were used. The capillaries were transparent, and were treated using an alkaline solution before coating. The capillaries were soaked in a photocatalyst paste and the inside was filled with the solution three times, and placed in a furnace at 450°C for 1 h. Six capillaries were bundled, and were placed in a test tube. The reactant solution typically rose up to a few centimeters above the solution surface due to the capillary forces.

TiO₂ powder (Degussa P25) was used as a photocatalyst. It was mixed with water (3.33 mL) and acetylacetone (0.33 mL) and mixed in a mortar for 30 min, to prepare a TiO₂ paste. Once the photocatalytic microreactor was prepared, it could be used for several months at least. (>20 times). To deposit metal nanoparticles on the photocatalyst, a metal colloid solution was put into the TiO₂ coated capillary three times, and then placed in a furnace at 450°C to deposit the metals firmly. The metal colloid solutions were prepared by irradiating a UV light for 3 h to a mixed solution of metallic precursor (chloroauric acid for gold, chloroplatinic acid for platinum, rhodium chloride for rhodium) and polyvinylpyrrolidone in a solvent (H₂O:EtOH = 1:1). The metal nanoparticles are typically deposited for enhancement of photocatalytic reactions by preventing the recombination of electrons and holes.

The test tubes were loaded on a merry-go-round type photoreaction stage with eight test tube holders (Fig. S1), and a light was shone from the side at a distance of about 10 cm for typically 18 h. A UV-LED with a wavelength of 365 nm and intensity of 360 mW/cm² was used. After the reaction, the photocatalytic microreactors were removed from the test tube, and only the solution was analysed by gas chromatography (Shimadzu, GC-2014) and GC mass spectrometer (Agilent, 6890N(GC), 5975B (inert XL EI/CI MSD)). There was no difficulty for the separation of the catalytic substance and reactant solutions, whereas the centrifugation or filtering process is typically necessary. The error of the yield was less than 10% for repeated experiments. Four kinds of carboxylic acids were used: benzoic acid (Ph-COOH), benzyloxyacetic acid (Ph-CH₂OCH₂COOH), phenoxyacetic acid (Ph-OCH₂COOH) and 3-phenylpropionic acid (Ph-CH₂CH₂COOH); and three kinds of alkenes were used for the reaction with the radicals generated from the carboxylic acids: acrylonitrile (CH₂=CHCN), crotononitrile (CH₃CH=CHCN), allyl cyanide (CH₂=CHCN). All the reagents were purchased from Wako Chemicals and used without further purification. All the reactions were made in acetonitrile, unless otherwise specified, and under ambient or

Table 1 Dimerization of benzyloxyacetic acid

Entry	Photocatalyst	Conversion, ^a %	Yields, ^b %	Selectivity, ^c %
1	TiO ₂	16	1.2	8
2	Pt/TiO ₂	22	4.5	20
3	Pt/TiO ₂ (AR)	10	2.7	27
4	Au/TiO ₂	22	2.7	12
5	Rh/TiO ₂	36	2.0	5.6

a. the ratio of the reactant consumed in the reaction, b. the ratio of the objective product divided by the reactant amount, c. the ratio of the objective product in the whole product amount. The amounts for each species are calculated by the GC peak intensity.

argon atmosphere. The concentrations of the reagents were 50 mM.

Results and Discussion

If a carboxylic acid will follow the reaction in Scheme 1 even if a photocatalyst is used instead of a photosensitizer, the radical species (R·) should be generated, and some amount of the radicals would be subject to dimerization.²³ Thus, we first investigated whether the dimer product was generated for each carboxylic acid, and the corresponding dimer products were found only for benzyloxyacetic acid (**1**) and phenoxyacetic acid (The GC-MS spectrum after the reaction of (**1**) is shown in Fig. S2 (Supporting Information). The byproducts were the molecules generated by which the corresponding radical abstract hydrogen or oxygen. No dimer product was confirmed without the photocatalysis. No dimer products were detected for benzoic acid and 3-phenylpropionic acid. Thus, it is considered that the oxygen in the alkyl chain worked to stabilize the radical (R·). The reason is still not clear but it is possible that the radical was stabilized by the resonance of the electrons in the pi orbitals in the C-O-C bond, and the abstraction of hydrogen or oxygen was delayed.

To find an appropriate condition for the reaction of benzyloxyacetic acid, we investigated the effect of metal deposition, and the result for the dimerization reaction is shown in Table 1. Platinum deposition gave the highest yield and selectivity, and the ambient condition did not have a strong influence on the result. Next, the dependence on the solvent was investigated for ethanol, dichloromethane, benzene and acetonitrile and the best result was obtained for acetonitrile.

Since we could confirm the radical formation only for benzyloxyacetic acid, we investigated the reactions using the corresponding radical. C-C bond formation with alkenes, by the reaction with acrylonitrile, crotonitrile, and allyl cyanide were studied (Table 2). In the reaction with acrylonitrile, we could detect the product (**4a**), and the selectivity was much enhanced by Pt deposition on TiO₂. Similarly for crotonitrile, the product (**4b**) was detected, but the Pt deposition did not affect the result. However, this reaction did not proceed for allyl cyanide, although benzyloxyacetic acid was converted into different species. It is considered that the double bond next to the nitrile group is necessary, because the electron deficient double bond tends to be attacked by the radical.²¹

Although we did not observe the dimerization reaction of 3-phenylpropionic acid, it was subject to C-C formation with

Table 2 Adduct to alkene by benzyloxyacetic acid

Entry	Alkene	Photocatalyst	Conversion, %	Yields, %	Selectivity, %
1	3a	TiO ₂	58	12	21
		Pt/TiO ₂	26	15	59
2	3b	TiO ₂	16	8	47
		Pt/TiO ₂	22	7	32
3	3c	TiO ₂	37	trace	—
		Pt/TiO ₂	35	trace	—

alkenes as shown in Table 3. Although the generated radical from 3-phenylpropionic acid was easily subject to the reaction of hydrogen or oxygen abstraction, it is supposed that the adduct reaction of alkene was faster than these processes.

Conclusions

We demonstrated the application of the automatic photocatalytic microreactor for the study of organic syntheses. We studied the decarboxylation of several carboxylic acids and the subsequent alkylation of the generated radicals. The yields were not good enough to replace the reactions using a photosensitizer. However, this reaction system is useful for the survey of photocatalytic organic syntheses because 1) it is not necessary to separate photocatalytic materials from the reactant solution, which is beneficial for the product analysis, and 2) the reactors can be re-used many times (>20 times). The screening by this method for a wide variety of photocatalytic materials would help identify organic syntheses that could be an alternative to the conventional syntheses.

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Supporting Information

General scheme of the organic reactions using a photosensitizer and a photocatalyst is shown in Scheme S1. The experimental setup for the photocatalytic microreactor is shown in Fig. S1. The GC-MS spectrum for benzyloxyacetic acid after the reaction is shown in Fig. S2. These materials are available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

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Table 3 Adduct to alkene of 3-phenylpropionic acid

Entry	Alkene	Photocatalyst	Conversion, %	Yields, %	Selectivity, %
1	3a	TiO ₂	58	9	15
		Pt/TiO ₂	56	14	25
2	3b	TiO ₂	38	3	9
		Pt/TiO ₂	48	4	8

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