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Synergistic effect of sonolysis combined with photocatalysis for the reaction of carbon chain elongation

超音波および光触媒反応の協同効果によるマロン酸からコハク酸への炭素鎖伸長反応

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1. Introduction

Sonophotocatalysis has been proposed as an attractive process for new category of sonochemistry. Nowaday, in almost all the cases, this combined system is applied for effective degradation of harmful compounds in the solution. It is certain that sonolysis in an aqueous solution is a degradation process of reactants. In other words, the molecular weight of a reactant decreases with ultrasonic irradiation. Active chemical species, which are made by a cavitaiton phenomenon in water under ultrasonic irradition, play effective role for the degradation. Hydrogen peroxide is key material for improvement of a reaction rate in sonophotocatalysis. This field of research increases larger and larger.

To gain the position as a conventional tool for chemical reactions in near future, we should be trying to not only degradation but also reactions for increasing molecular weight; *i.e.* elongation of carbon chain. Dimerization is a typical example for increasing molecular weight. Because of many radical reactions occurs in cavitation field, radical coupling reaction is easy to understand in sonolysis.

In this paper, we try to elongate the carbon chain of a dicarboxylic acid. In this system of reaction, combining radical coupling in sonolysis and oxidation in photocatalysis was studied.

2. Experimental

A Pyrex glass short-neck Kjeldahl flask (actual volume approximately 300 cm3) was used as a reactor. In the case of sonolysis, this reactor containing the reactant solutions was sonicated using by a 200 W and 200 kHz ultrasonic generator. It was placed in a temperature-controlled water bath all time of the reaction. Before sonication, pure argon gas (Ar) was passed through the reactant solution in order to expel the air. The solution was also saturated with Ar.

In the case of photocatalysis, a similar procedure was performed in the presence of powdered photocatalyst. We selected two kinds of TiO_2s (Rutile, or Anatase rich, Degussa P-25) as photocatalysts. The solution was irradiated with a 500-W Hg lamp.

In the case of sonophotocatalysis, a simultaneous irradiation was performed from one side of the reactor using Hg-lamp and from the bottom of the reactor using ultrasonic generator.

The amounts of products were determined by gas chromatography for gaseous products and liquid chromatography for liquid products. Hydrogen peroxide in the solution was analyzed by colorimetric method using a titanium sulfate solution [1].

3. Results and discussion

Malonic acid could be decomposed by both sonolysis and photocatalysis, as shown in **Fig. 1**. Furthermore, the decomposition rate of combined system was larger than the sum of the rates of sonolysis and photocatalysis. Namely, synergistic effect was observed under Ar atmosphere.

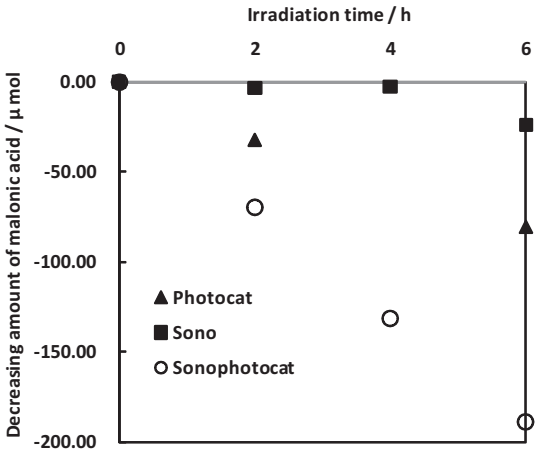

Fig. 1 Synergistic effect of combining sonolysis and phtotocatalysis of malonic acid solution.

Table I shows products and their yields from malonic acid solution under three types of irradiations. On the bottom line of this table, the rates of decomposition of malonic acid were also

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Table I Amounts of products(μ mol/6h) from 10mM malonic acid solution.

	Photocatalysis	Sonolysis	Sonophotocatalysis
CO_2	82.51	11.46	103.17
CO	0	28.74	210.27
CH_4	0.42	0	0.38
H_2	0	193.47	133.33
H_2O_2	0	80.78	15.00
Formic acid	0	11.62	38.33
Acetic acid	76.81	0	94.91
Oxalic acid	0	11.52	0.28
Malonic acid	−80.58#	−24.17#	−181.63#

Reducing amount of reactant

indicated. Carbon amounts of products almost balanced with those of consumed reactant (malonic acid).

Synergistic effect about each product reveals in this table. Active chemical species, which are mainly radicals such as hydrogen radical (・H) and hydroxyl one (・OH) play important role for the improvement of yields. The stable dimers of those radicals, especially hydrogen peroxide H_2O_2 is also important for degradation of reactant. It has been reported that photocatalytic evolution of CO_2 is accelerated in the presence of H_2O_2 [2].

$$H_2O + US \rightarrow \ ・H + ・OH \quad \text{--- (1)}$$
$$・H + ・H \rightarrow H_2 \quad \text{--- (2)}$$
$$・OH + ・OH \rightarrow H_2O_2 \quad \text{--- (3)}$$

As also shown in Table I, different distribution of products was observed with different systems. In liquid phase, acetic acid was the main product under photo-irradiation. On the contrary, oxalic acid and formic acid were obtained under ultrasonic irradiation. We summarize the products distribution including major gaseous products at each system.

Photocatalysis: $CH_2(COOH)_2$
$\cdots\rightarrow$ **CH_3COOH,** CO_2

Sonolysis: $CH_2(COOH)_2$
$\cdots\rightarrow$ $HCOOH$, $(COOH)_2$, CO, CO_2

Figure 2 shows products from acetic acid solution during 6-hour sonication. Interestingly, elongation of carbon chain was observed; *i.e.* certain amount of succinic acid was detected even in 1% acetic acid solution. Because succinic acid was obtained in low concentration of acetic acid solution, we proceed to the issue of the next step; *i.e.* elongation of carbon chain for malonic acid in the sonophotocatalytic system.

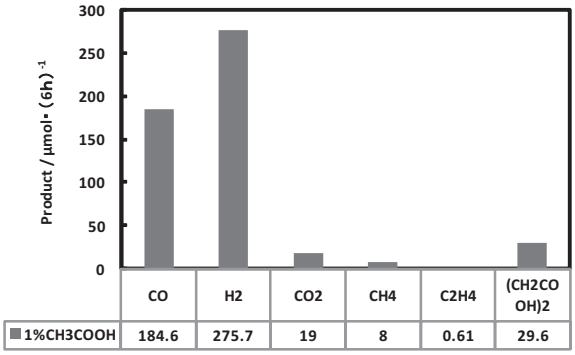


Fig. 2 Sonolytical products (μ mol / 6h) from acectic acid solution (1%).

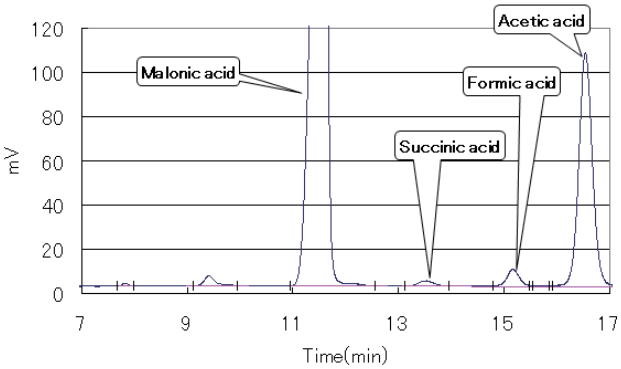


Fig. 3 Production of succinic acid from malonic acid by sonophotocatalysis.

Figure 3 shows liquid chromatogram of malonic acid solution after simultaneous irradiation for 46 hours. A little amount of succinic acid could be detected.

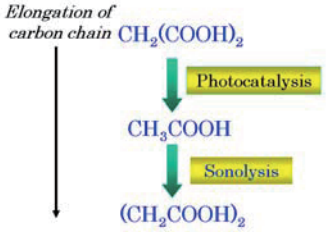
Therefore, elongation of carbon chain for malonic acid was achieved by sonophotocatalysis.

4. Conclusions

Firstly, synergistic effect combining between sonolysis and photocatalysis about the reaction of malonic acid was observed.

Secondly, we summarized our conclusion for the elongation of carbon chain, as shown below.

Sonophotocatalytic reaction of malonic acid



5. References

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