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Dehydrogenation of Succinic Acid in Aqueous Solution and Isomerization of Its Products under Sonication

こはく酸からのソノケミカル的脱水素反応とその生成物の異性化

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1. Introduction

Sonolyses of C4 (Carbon number 4) dicarboxylic acids (succinic acid, maleic acid, and fumaric acid) were performed. Reactants of this work are symmetrical dimers and water soluble. Succinic acid is a straght-chain dibasic acid and it has saturated hydrocarbon chain. On the other hand, maleic aicd and fumaric acid have a double bond in their skeltal hydrocarbon chain, namely unsaturated compounds.

A systematic study of dicarboxylic acids has been carried out under ultrasonic irradiation in an argon (Ar) atmosphere. Studies about oxalic acid (C2) and malonic acid (C3) have been reported [1-3]. In the former case, almost all products were gaseous carbon compounds (CO & CO_2) and hydrogen. In the latter case, many kinds of gaseous and liquid products were obtained. As a result, more or less, their carbon numbers decreased compared with reactant (oxalic acid or malonic acid).

Saccinic acid plays a importnt role in tricarboxylic cycle (TCA cycle or Citric acid cycle), namely, it is transformed into malic acid via fumaric acid mediated by flavin adenine dinucleotitide (FAD). Through this transformation, carbon number of molecules does not change. In this presentation, we showed the sonication without changing carbon number. We also demonstrated isomerization between unsaturated dicarboxylic acids without mediators.

2. Experimental

The Pyrex glass reactor (short-neck Kjeldahl flask, 250 ～ 350 cm^3) containing the reactant solution was sonicated from the bottom surface with a ultrasonic generator (200 kHz, 200 W). It was placed in a temperature-controlled water bath throughout the reaction. Before sonication, pure argon gas (Ar) was passed through the reactant solution to expel the air. The solution was also saturated with Ar. All chemicals in this study were special grade and they used as received.

The amounts of gaseous and liquid products were determined by gas chromatography and liquid chromatography, respectively. Hydrogen peroxide in the solution was analyzed by colorimetry using a titanium sulfate solution [4].

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3. Results and discussion

Sonolysis of succinic acid

Products and their yields from succinic acid solution were shown in **Table I**. Malic acid and fumaric acid were obtained just like the case of TCA cycle.

Table I Sonolytical products from succinic acid solution (μ mol・(6h)$^{-1}$)

CO_2	12.7
CO	64.8
H_2	213
H_2O_2	51.6
Formic acid	15.9
Malic acid	5.23
Maleic acid	0.13
Fumaric acid	0.21

Ultrasound: 200 kHz, 200 W; Reactant: 10 mM, 50 mL; Bath temperature: 25°C; Atmospheric gas: Ar

Maleic acid was also detected. The production of fumaric acid and maleic acid is also interesting in spite of their lower yields in products because they are dehydrogenation products from succinic acid. The abstraction of hydrogen from skeletal hydrocarbon chain in succinic acid molecure would occur without mediators. In addition, maleic acid and fumaric acid are isomer each other; the former is a trans-type (*E*) and the latter is cis-type (*Z*) compounds. It is certain that more yields of them are desirable.

$$\underset{\text{(Succinic acid)}}{HOOCH_2C\text{-}CH_2COOH} \rightarrow \underset{\text{(Fumaric acid or Maleic acid)}}{HOOCHC{=}CHCOOH} + H_2$$

To get more yields, higher reactant concentration and longer reaction time were examined. Because of double bond in molecule, however, reducing rates of both acids under sonication were more rapid compared with succinic acid as shown in **Fig. 1**. Thus, it is difficult to

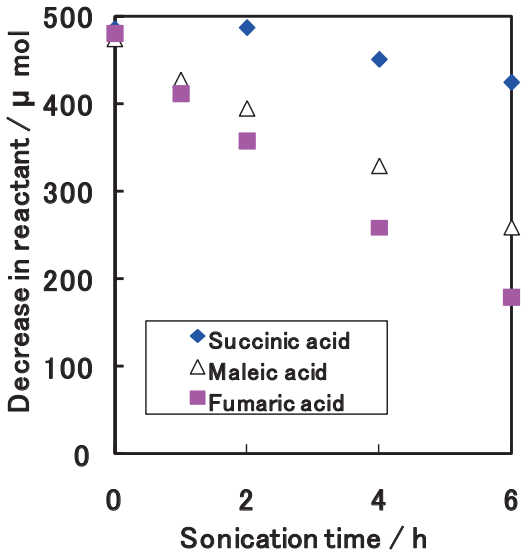

Fig. I Differences in sonochemical reaction rates of C4 dicarboxylic acids; Ultrasound: 200 kHz, 200 W; Reactants: 10 mM, 50 mL; Bath temperature: 25 °C; Atmospheric gas: Ar

accumulate great amounts at the present sonolytical conditions.

Mutual isomerization between maleic acid and fumaric acid

To consider the pathway of production for malic acid, fumaric acid and maleic acid were sonicated. **Table 2** indicated malic acid was produced not only from fumaric acid but also from maleic acid. As other hydroxy acids (hydroxycarboxylic acids), succinic acid and tartaric acid were obtained. Similar yields of malic acid and succinic acid were observed from both reactants. Those compounds are produced by addition of hydoxyl group (or radicals, ·OH) and hydrogen radicals (·H). Of course carbon number do not change. Because of aqueous solution, active chemical species, which are mainly ·OH and ·H radicals, are produced and they would play important role for the reaction.

$$\mathrm{HOOCHC{=}CHCOOH} + 2\cdot\mathrm{H} \rightarrow \mathrm{HOOCH_2C\text{-}CH_2COOH}$$

$$+ \; 2\cdot\mathrm{OH} \rightarrow \mathrm{HOOC(OH)HC\text{-}CH(OH)COOH}$$

(Tartaric acid)

$$+ \cdot\mathrm{H} + \cdot\mathrm{OH} \rightarrow \mathrm{HOOCH_2C\text{-}CH(OH)COOH}$$

(Malic acid)

As also shown in Table 2, interestingly, both reactants changed each other, namely mutual isomerization was confirmed. So far, sonolytical isomerization of those compounds had been reported [5]. However, additives were needed for

Table 2 Sonolytical products from unsaturated C4 dicarboxylic acids solution in an Ar atmosphere (μmol・(6h)$^{-1}$)

	Fumaric acid	Maleic acid
Succinic acid	31.7	28.6
Maleic acid	1.84	-279
Fumaric acid	-320	5.95
Formic acid	Detected	14.6
Malic acid	38.4	35.5
Tartaric acid	23.4	5.52
CO_2	16.8	12.7
CO	57.6	54.8
H_2	114	220
H_2O_2	58.6	87.3

Ultrasound: 200 kHz, 200 W; Reactant: 10 mM, 30 mL; Bath temperature: 25 °C

isomerization and the one-way isomerization (maleic to fumaric) was shown in the report. In our system, on the other hand, isomerization proceeded without additives. Although the mutual isomerization proceeded, the difference rate of the individual reaction was observed. The rate from maleic acid to fumaric acid (2.2 %) was higher than that from fumaric acid to maleic acid (0.6 %).

To confirm the role of hydroxyl radicals methanol as radical scavenger was added into the solution. In this condition, malic acid and tartaric acid could not be detected even after 24 h sonication.

4. Conclusions

Sonolyses of succinic acid, maleic acid, and fumaric acid were performed. We focused reactions without changing carbon number.

Dehydrogenation from succinic acid to maleic acid and fumaric acid was observed and vice versa.

Mutual isomerization was observed between maleic acid and fumaric acid.

Malic acid was produced from succinic acid. Because fumaric acid was also obtained, this reaction was similar to the part of TCA cycle.

5. References

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