Hydrogenolysis of disodium *trans*-epoxysuccinate in the solid-to-solid state with palladium catalysts

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Abstract

The hydrogenolysis of disodium *trans*-epoxysuccinate to the malate in the solid-to-solid state was investigated with supported Pd catalysts. The reaction was carried out at 100°C; the reaction temperature is much lower than the melting points of the epoxide, the malate, and their mixture. We observed nearly quantitative formation of the malate when carbon was used as the support for Pd. Moreover, this finding suggested that the organic components over Pd/C were in the solid state not only before and after the reaction but also during the reaction. This idea was supported by a microscopic study of the mixture of catalyst–organic components before and after the reaction. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Organic reactions in the solid-to-solid state have become a powerful tool for organic synthesis and have been studied in many laboratories. [2] Organic reactions in the solid-to-solid state have several advantages over those in solution: it is possible to use small reaction vessels and to decrease the consumption of reaction solvents. Moreover, we can expect that different products are obtained in two types of reactions, because the mobilities of organic molecules in the solid state are much lower than those in the liquid state.

There are many reports on the reactions in the solid-to-solid state between organic reagents [1]. For example, the syntheses of thiocarbonylimidazolides from solid alcohols and thiocarbonylimidazole were reported by Hagiwara et al. [2]. The thiocarbonylimidazolides were prepared by grinding both substrates with a pestle and mortar at room temperature in ambient atmosphere. Hagiwara et al. described that the preparation in the solid-to-solid state was simpler in operation than that in solution.

However, there have been only few papers on catalytic organic reactions in the solid-to-solid state. First, Lamartine and Perrin [3] reported

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[2] For example, see Ref. [1] and references therein.

the results of organic reactions with supported metal catalysts in the solid-to-solid state. They hydrogenated thymol to menthones and menthols in the solid-to-solid state at room temperature and under atmospheric pressure of hydrogen. They presumed that the hydrogen dissociated on the metal catalyst migrates onto the support and reacts with the solid thymol on the support. They also attempted the alkylation of solid phenol by isobutene gas using phosphoric acid supported on silica as a solid catalyst [4]. C-alkylation and O-alkylation of the phenol proceeded in the solid-to-solid state as well as in solution. The reaction rate in the solid-to-solid state was higher than that in solution. Lamartine et al. proposed that the organic reactions in the solid-to-solid state are helpful to react a substrate of low solubility with organic solvents.

As stated above, certain interesting features of catalytic reactions in the solid-to-solid state have been reported. However, there are no catalytic reactions in the solid-to-solid state, of which the products cannot be obtained by the reactions in the liquid state. The similarities of the products between the reactions in the solid-to-solid state and those in the solution can be interpreted based on an idea that catalytic reactions in the solid-to-solid state, reported so far, proceeded in the fused state. It can be assumed that molecular mobilities in the fused state are much higher than those in the solid state. Thus, in the reactions in the fused state, the intrinsic reactivity of a molecule is more important than the nature of the packing of the neighboring molecules around the reactants; this situation is similar to that in the reactions in the liquid state. This may be a reason for the similarities of the products between the reaction in the solid-to-solid state and that in the liquid state. We can expect to attain unique results in the reactions in the solid-to-solid state, when a mixture of the substrates and the products is kept in the solid state during the reactions. Based on this idea, we have sought a reaction in which substrates, products, and their mixture have higher melting points than the reaction temperature.

Kitamura et al. [5] reported the results of the hydrogenolysis of *trans*-epoxysuccinic acid to malic acid in the solid-to-solid state with supported palladium catalysts. The melting points of *trans*-epoxysuccinic acid, malic acid, and their mixture are much higher than the reaction temperature (100°C). It was found that the substrate was hydrogenated not only to malic acid but also to diglycolic and succinic acids. The formation of the by-products resulted in significant lowering of the melting point of the reaction mixture. It was assumed that the mixture was in the fused state during the reaction.

In the present paper, we describe the hydrogenolysis of disodium *trans*-epoxysuccinate (m.p. 258–262°C) to disodium malate (m.p. 180–185°C) in the solid-to-solid state with supported palladium catalysts. The reaction was carried out at 100°C, which is lower than the melting point of the epoxide-the malate mixture (weight ratio = 1:1, 173–177°C). Under these conditions, we can expect that the materials taking part in the hydrogenolysis, except for hydrogen gas, are in the solid state during the reaction.

2. Experimental

2.1. Preparation of disodium trans-epoxysuccinate

Sodium hydroxide (0.3 g) was dissolved in ethanol (100 ml) at room temperature. Insoluble materials in ethanol were removed by filtration. The filtrate was added dropwise to an ethanol solution (20 ml) of *trans*-epoxysuccinic acid (1.0 g), resulting in formation of a white fine precipitate. Stirring was continued for a total of 20 min, and the precipitate was collected by filtration. The product was dried overnight over calcium chloride. The yield was 1.3 g. M.p. 258–262°C. Anal. Calcd. for $C_4H_2O_5Na_2 \cdot 1.5H_2O$: C, 23.65; H, 2.45%. Found: C, 23.64; H, 2.46%.

2.2. Hydrogenolysis of disodium trans-epoxy-succinate in the solid-to-solid state

A supported palladium catalyst (0.50 g) was pretreated with hydrogen gas at 200°C for 30 min. The catalyst was mixed with disodium *trans*-epoxysuccinate (0.10 g), and the mixture was ground well with a mortar and pestle at room temperature. The mixture was placed in an autoclave and then shaken in the presence of hydrogen gas (9.0 MPa) at 100°C for 14 h.

2.3. Measurement of material balance and analysis of hydrogenolysis products

After the reaction in the solid-to-solid state, the autoclave was cooled to room temperature, and the hydrogen in the autoclave was replaced by argon gas. The catalyst–organic component mixture was removed from the autoclave, and its weight was measured. Deionized water (20 ml) was added to the mixture to extract the water-soluble organic components, and the resulting suspension was stirred magnetically for 5 min. After removal of the catalyst by filtration, the filtrate was concentrated to dryness in vacuo. The weight of the residue was estimated. The water-soluble materials were esterified with methanol (50 ml) and a cation exchange resin (Amberlist 15E, H^+ form, 0.5 g) at the reflux temperature for 3 h. The resulting esters were subjected to GC and GC/MS analyses. GC analysis: DB-17, 30-m column, 120°C. GC/MS analysis: DB-1, 30-m column, 90°C. GC and GC/MS analyses were carried out using a Shimadzu GC-15A and a Shimadzu GC-17A/QP-5000, respectively.

2.4. Examination of hydrogenolysis of disodium trans-epoxysuccinate under the product-analysis conditions

Disodium *trans*-epoxysuccinate (0.10 g) was dissolved in deionized water (5.0 ml). A hydrogen-pretreated Pd catalyst (0.50 g) was added to the solution. The suspension was stirred at room

temperature for 5 min. The catalyst was removed by filtration and the filtrate was evaporated in vacuo. The conditions of esterification and the product analysis were the same as those described in Section 2.3.

3. Results and discussion

3.1. Examination of thermolysis of organic components during the reaction in the solid-to-solid state

Epoxides are highly reactive and tend to decompose to gaseous compounds at a high temperature under non-solvent conditions. To investigate generation of the gaseous products during the reaction in the solid-to-solid state, we determined the amounts of the mixture of the catalyst-organic components after the reaction and compared to those of the mixture of the catalyst–substrate before the reaction. We found no remarkable weight loss of the catalyst–substrate mixture during the reaction. These findings indicate that thermolysis of the substrate is a minor reaction even if it occurred under the non-solvent conditions.

3.2. Examination of hydrogenolysis in water during the product analysis process

In an earlier paper, Harada and Osawa [6] suggested that, when a nickel catalyst was suspended in an aqueous solution of disodium fumarate, the salt was hydrogenated to the succinate by the adsorbed hydrogen on the catalyst. The product analysis in the present study includes an extraction of the substrate and the products with deionized water. There is a possibility that the substrate reacts with adsorbed hydrogen on palladium catalysts during the extraction procedure to afford hydrogenolysis products. Thus, we estimated the yields of hydrogenolysis under the substrate–product extraction conditions, and found no hydrogenoly-

Table 1
Hydrogenolysis of disodium *trans*-epoxysuccinate in the solid-to-solid state with Pd catalysts

Catalyst	Organic components (%)				
	trans-Epoxysuccinate	Malate	Succinate	Diglycolate	Unknowns
5%Pd/Al$_2$O$_3$	0	77	0	3	2
5%Pd/SiO$_2$–Al$_2$O$_3$	100	0	0	0	0
2%Pd/C	0	98	2	0	0
0.5%Pd/SiO$_2$	100	0	0	0	0
5%Pd/SiC	0	49	0	0	51

sis of disodium *trans*-epoxysuccinate proceeds during the extraction process.

3.3. Hydrogenolysis of disodium trans-epoxysuccinate in the solid-to-solid state with palladium catalysts

The hydrogenolysis of disodium *trans*-epoxysuccinate in the solid-to-solid state was attempted using 5%Pd/Al$_2$O$_3$ (N.E. CHEMCAT), 5%Pd/SiO$_2$–Al$_2$O$_3$ (N.E. CHEMCAT), 2%Pd/C, (N.E. CHEMCAT), 0.5%Pd/SiO$_2$ (Nikki Chemical), and 5%Pd/SiC (Kawaken Fine Chemicals). Table 1 shows the result of the hydrogenolysis in the solid-to-solid state. It can be seen that the hydrogenolysis of disodium *trans*-epoxysuccinate proceeded in the solid-to-solid state with 5%Pd/Al$_2$O$_3$, 2%Pd/C, and 5%Pd/SiC to convert the epoxide completely to the hydrogenolysis products (malate, succinate, and diglycolate) and unknowns, whereas no reactions occur in the solid-to-solid state with 5%Pd/SiO$_2$–Al$_2$O$_3$ or 0.5%Pd/SiO$_2$. It is noteworthy that the combination of disodium

trans-epoxysuccinate and 2%Pd/C afforded the malate in an excellent selectivity. As reported earlier, when *trans*-epoxysuccinic acid was employed as the substrate for the hydrogenolysis in the solid-to-solid state, the selectivities to malic acid were insufficient (in the case of 2%Pd/C, less than 50%) [5]. The low selectivity for malic acid would be attributed to the conversion for malic acid to succinic acid in the fused state. The C–C bond cleavage to diglycolic acid also decreases the yield of malic acid. We can explain the high selectivity for disodium malate with 2%Pd/C based on the following ideas; (1) the mobility of organic materials in the present study was lower than that of the acid type during the reaction, (2) the sodium ions function as protective groups for the C–C bond cleavage in the epoxide ring. Thus, we can say that the sodium salts of the epoxide and malic acid are maintained in the solid state during the reaction.

The results in Table 2 show that the hydrogenolysis in aqueous solution proceeded with all of the Pd catalysts examined in the present study. When C or SiC was used as the support for palladium, the hydrogenolysis in aqueous

Table 2
Hydrogenolysis of disodium *trans*-epoxysuccinate in water with Pd catalysts

| Catalyst	Organic components (%)				
	trans-Epoxysuccinate	Malate	Succinate	Diglycolate	Unknowns
5%Pd/Al$_2$O$_3$	0	78	4	0	18
5%Pd/SiO$_2$–Al$_2$O$_3$	81	10	0	0	9
2%Pd/C	26	66	4	4	0
0.5%Pd/SiO$_2$	8	84	7	0	0
5%Pd/SiC	66	22	7	0	5

solution did not proceed smoothly compared to that in the solid-to-solid state. However, the hydrogenolysis with 5%Pd/Al$_2$O$_3$ in aqueous solution afforded a result comparable to that of the reaction in the solid-to-solid state. It is difficult to explain the origin of the support effects based on a simple idea.

3.4. Micrographic observation of catalyst–organic component mixture after the reaction in the solid-to-solid state

Microscopic studies of the catalyst–organic component mixture after the reaction in the

Before the reaction in the solid-to-solid state
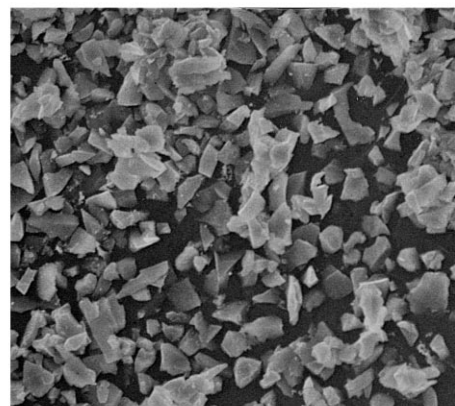
10 um
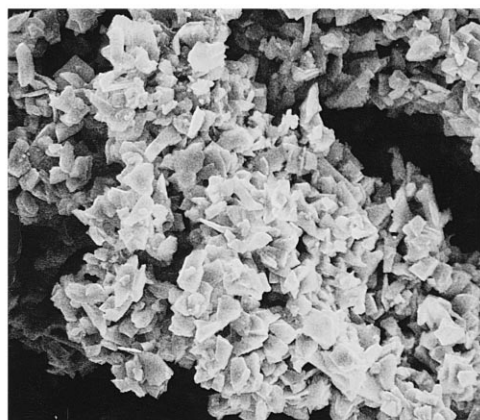
After the reaction in the solid-to-solid state

10 um

Fig. 1. Micrographs of 5%Pd/SiC–*trans*-epoxysuccinic acid mixture.

Before the reaction in the solid-to-solid state

10 um

After the reaction in the solid-to-solid state

10 um

Fig. 2. Micrographs of 5% Pd/SiC–disodium *trans*-epoxysuccinate mixture.

solid-to-solid state may provide significant information regarding fusion of the organic-component particles during the reaction in the solid-to-solid state. When the organic-component particles are fused during the reaction in the solid-to-solid state, some particles may merge to form fewer bigger ones with the catalyst. When bigger particles are observed after the reaction in the solid-to-solid state, it is reasonable to assume that the substrate was converted to products mostly in the fusion state. As reported earlier, the hydrogenolysis of *trans*-epoxysuccinic acid in the solid-to-solid state with

5%Pd/SiC resulted in the formation of large aggregates (Fig. 1), whereas no drastic changes in their appearance were observed with 0.5%Pd/SiO$_2$, 2%Pd/C, and 5%Pd/SiO$_2$–Al$_2$O$_3$ [5]. On the other hand, the use of disodium *trans*-epoxysuccinate as the substrate resulted in no remarkable growth of particles with all of the catalysts examined in this study. Fig. 2 shows the micrographs of the 5%Pd/SiC–organic component mixture before and after the reaction in the solid-to-solid state. It is clear that no remarkable aggregation of particles was observed, even when the 5%Pd/SiC was employed for the reaction in the solid-to-solid state. This finding suggests that the hydrogenolysis of the disodium salt proceeds in the solid state to a greater extent than that of the acid, despite the supports of the Pd catalysts.

The study on the reactions in the solid-to-solid state, of which products are completely different from those of the reactions in solution, is now under way.

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