

Regioselective Direct Carboxylation of 2-Naphthol with Supercritical CO₂ in the Presence of K₂CO₃

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ABSTRACT

A direct regioselective preparation of 2-hydroxynaphthalene-6-carboxylic acid, a useful industrial intermediate of aromatic polyester from 2-naphthol was conducted by use of excess amount of K₂CO₃ (10-fold molar to 2-naphthol) under supercritical CO₂ at 10 MPa and 473 K. The obtained yield under this condition was *ca.* 20 mol% to 2-naphthol. The further investigations may provide an alternative process to the conventional Kolbe-Schmitt reaction, because of no use of strong alkali and recoverability of K₂CO₃. Theoretical explanation about the regioselectivity was achieved by means of DFT calculations.

Keywords: Supercritical CO₂; CO₂ Utilization; Kolbe-Schmitt Reaction; Carboxylation; 2-Naphthol; Potassium Carbonate; 2-Hydroxynaphthalene-6-carboxylic Acid; DFT Calculation

1. Introduction

Aromatic hydroxyl carboxylic acids have been prepared over a long period of time via Kolbe-Schmitt reaction [1], utilizing CO₂ as a carbon resource. However, the conventional process, which is a heterogeneous reaction in the gas-solid phase, requires a high temperature and a long reaction time. The process consists of three steps: 1) the preparation of alkali metal salts of hydroxylarenes with strong alkali; 2) their desiccation; and 3) the carboxylation with CO₂ in a pressure device. A number of ameliorating trials for its process have been examined up to the present, because aromatic hydroxyl carboxylic acids have been widely utilized for various purposes by now, for example, as valuable raw materials or intermediates in the production of pharmaceutical and fine chemicals.

It is well known that the carboxylation can be carried out under moderate temperatures and pressures when an organic solvent is used [2-6]. One of the authors (TY) found that the reaction readily occurred at atmospheric pressure of CO₂ at 333 K in benzene with small amount of crown ether or polar solvent, which created a ho-

mogenous solution with alkali metal 2-naphtholate [7]. However, in view of the contemporary concept of so-called “green chemistry” or “sustainable society”, it is required to get rid of organic solvent from the chemical process as much as possible. The development of utilization of CO₂ is commendable under the same sort of intentions. This prompts us to make use of supercritical CO₂ as a medium and a reagent of the carboxylation. As a result, comparative studies of the reaction between sodium phenolate and CO₂ under the gaseous and supercritical conditions have demonstrated the preferential effect of the supercritical condition for promoting the reactivity of CO₂ [8]. Furthermore, the direct carboxylation of phenol to salicylic acid, namely without the preparation of the alkali metal salt, has been observed regioselectively with AlBr₃ under supercritical CO₂ condition [9]. The direct selective synthesis of salicylic acid from phenol with K₂CO₃ has been performed in a similar way [10].

In this paper, the examination of the similar direct carboxylation of 2-naphthol with K₂CO₃ under supercritical CO₂ conditions will be reported shortly with respect to the regioselective synthesis of 2-hydroxynaphthalene-6-carboxylic acid (2-H-6-NA), which is a useful chemical intermediate of aromatic polyesters.

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2. Experimental

2.1. Material

2-Naphthol (Kanto Chemical Co., Inc., Tokyo, Japan) and K_2CO_3 (Kanto Chemical Co., Inc., Tokyo, Japan) of reagent grade were used without further purifications. The standard 2-hydroxynaphthalene-6-carboxylic acid (2-H-6-NA), 2-hydroxynaphthalene-1-carboxylic acid (2-H-1-NA) and 2-hydroxynaphthalene-3-carboxylic acid (2-H-3-NA) were supplied from Tokyo Chemical Industry Co., Ltd and employed as gas-chromatography standards.

2.2. Carboxylation

The experimental system was basically the same with the previous report [10], using a stainless steel autoclave reactor (AKICO Corporation; Tokyo, Japan). After CO_2 was introduced to the reactor, the reaction started under the prescribed conditions. After the reaction, the resulting product was dissolved in tetrahydrofuran. The solution was filtered and removed the solvent by a rotary evaporator.

2.3. Analysis

The reaction product of 0.10 g was collected and silylated with 500 μL of *N*-trimethylsilylimidazole solvation (GL Sciences Inc., Tokyo, Japan) at 313 K for 3 h. Then the pyridine solution was analyzed by gas-chromatography, using dodecane as an internal standard.

2.4. Computational Method

A quantum chemical calculation was performed by means of the Gaussian 03 program package in this study. The DFT method was selected, using the function commonly called as B3LYP. The geometrical optimization was carried out using the LANZL2DZ basis set.

3. Results & Discussion

The topicality of this communication is an inexplicable effect of the coexistent K_2CO_3 on the carboxylation of 2-naphthol in supercritical condition of CO_2 . The increase of the molar ratio of K_2CO_3 to 2-naphthol resulted in the increase of the yield and hence the regioselectivity to 2-hydroxynaphthalene-6-carboxylic acid (2-H-6NA). Its maximum yield of *ca.* 20% was obtained currently with the ratio of 10 at 10MPa and 473 K. The increase of product yields with the ratio is presented in **Figure 1**. The reduction of pressure and temperature from this attained conditions retarded significantly the yields as shown in **Table 1**.

As it has been reported in our previous paper [10], the similar effect of the molar ratio of K_2CO_3 has been ob-

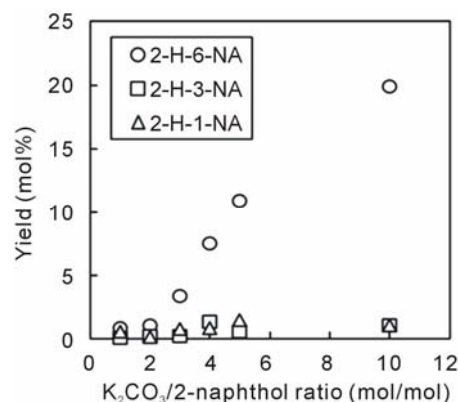


Figure 1. Effect of molar ratio of K_2CO_3 to 2-naphthol on the yield of 2-hydroxynaphthalene carboxylic acid under the pressure of 10 MPa, 473 K, duration 8 h.

Table 1. Effect of reaction pressure and temperature on the carboxylation of 2-naphthol with carbon dioxide at molar ratio 10 of K_2CO_3 , duration 8 h.

Molar ratio of K_2CO_3	Pressure (MPa)	Temperature (K)	Yield (mol %)		
			2-H-6-NA	2H-3-NA	2-H-1-NA
10	6	473	2.20	0.40	0.00
10	8	473	3.40	0.61	1.10
10	10	473	19.91	1.04	1.04
10	10	453	2.00	0.00	1.10

served with respect to the carboxylation of phenol in the supercritical CO_2 condition. In this case, the salicylic acid yield increases with an increase of K_2CO_3 up to the equimolecular amount with phenol. The catalytic action of K_2CO_3 , formerly proposed, should be withdrawn, because its performances are not catalytic in the strict meanings. Of course, K_2CO_3 may form a potassium salt with phenol to some extent to activate the carboxylation. But the formation would be a little because of its lower basicity than potassium hydroxide, conventionally used for Kolbe-Schmitt reaction.

The requirement of the presence of excess K_2CO_3 under supercritical CO_2 condition might be matter of solvation. It has been pointed out [11,12] that the reaction rates are maximal near the critical pressure of CO_2 when CO_2 is used as a reactant and a solvent. This is in accordance with our former results [8,10]. These phenomena may be explained by the local augment effect, namely the reaction rate increases because of the clustering solvent molecule around the solute species [13]. On the contrary, excessively high CO_2 pressures may retard the interaction between reactants because of increasing the density by clustering of CO_2 molecules [14-16]. As CO_2 has a lower dielectric constant, K_2CO_3 may behave as a substitute to cluster around 2-naphtholate in the present case, separating each 2-naphthol molecule from others as

a strainer does in the extraction with supercritical fluids. The aggregation of reactants would become a serious problem in the supercritical condition.

Previously, it has been shown that the carboxylation of 2-naphtholate readily occurs through the addition of crown ethers or polar solvents in a nonpolar solvent, affording the selective production of 2-hydroxynaphthalene-1-carboxylic acid (2-H-1-NA) under ordinary conditions [7]. This is because the separation of alkali cation from 2-naphtholate by the solvation enhances greatly its reactivity toward CO_2 . As shown in **Figure 2(a)**, the HOMO distribution of the naked 2-naphtholate is localized on 1-position of naphthalene ring, making it possible to attack by CO_2 directly to this position. On the other hands, a carbonate like complex formation between potassium phenolate and CO_2 has been proposed for the conventional Kolbe-Schmitt reaction [17,18]. The reac-

tion mechanism is considered as the migration of carbonate group to the ortho-position. The HOMO distribution of potassium 2-naphtholate (**Figure 2(b)**) is decreased by the direct binding of K^+ , which causes the requirement for the higher reaction temperature in the conventional methods.

The possibility of complex formation of 2-naphthol with K_2CO_3 , as speculated above, was examined by DFT calculations. The resulting optimized geometry is shown in **Figure 2(c)**, being K^+ found at the region between O and C of 1-position of 2-naphthol molecule. A CO_3^{2-} moiety is located nearby. Obviously, these situations might prohibit the attack of CO_2 molecule toward C of 1-position. The additional calculations on the complex formation with CO_2 molecule gave no geometry optimization. This suggests the difficulty of salvation by CO_2 in the supercritical state.

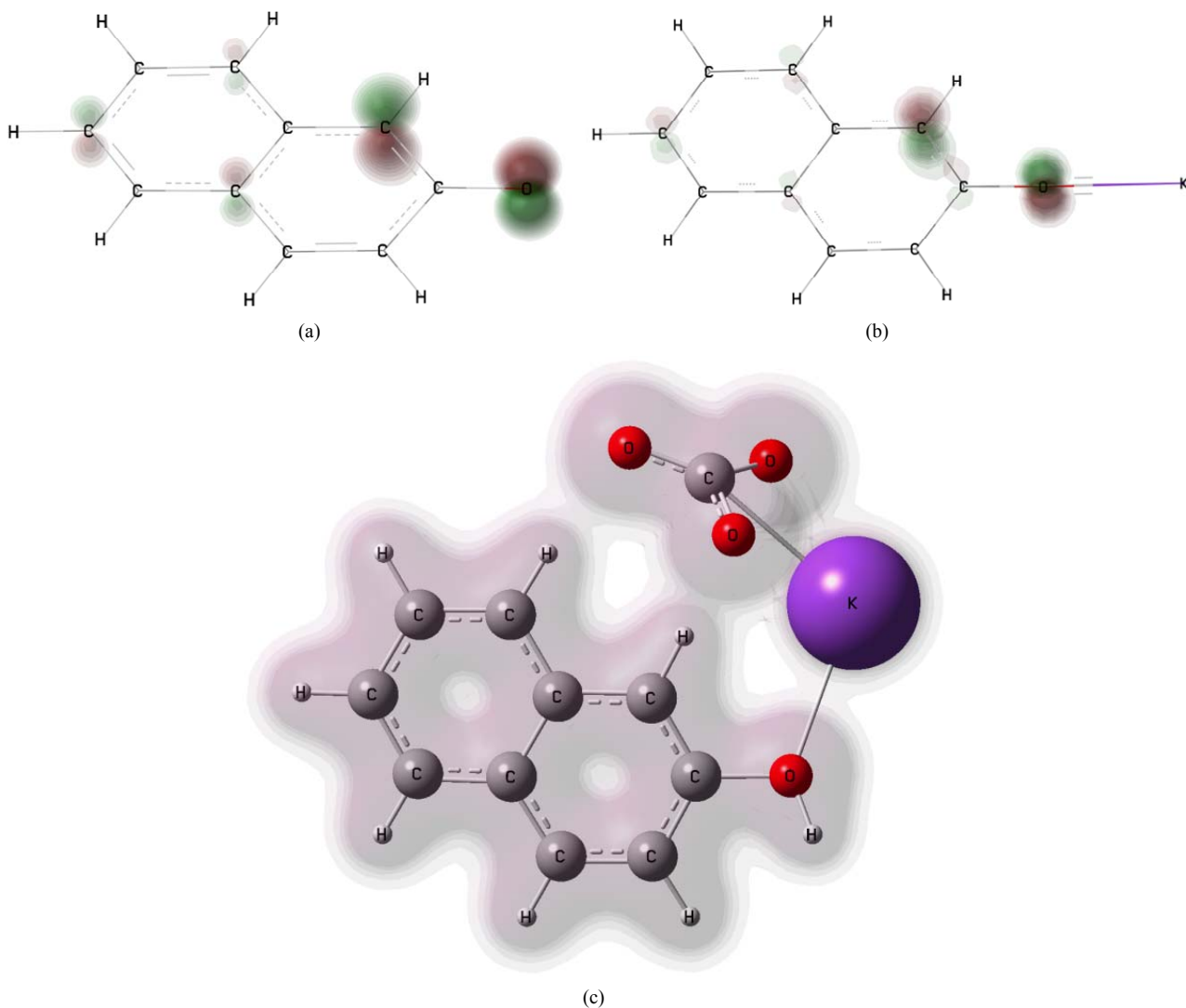


Figure 2. The results of DFT calculations. (a) 2-naphtholate (HOMO); (b) potassium 2-naphtholate (HOMO); (c) 2-naphthol- K^+ complex (total density).

The increase of the product yield and selectivity to 2-H-6-NA by the increase of the molar ratio of K_2CO_3 could be explained by the solvation (or clustering) effect by some additional K_2CO_3 to the first one, blocking the most reactive carbon position-1 of 2-naphthol.

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