

The improved Kolbe–Schmitt reaction using supercritical carbon dioxide

Takayuki Iijima and Tatsuaki Yamaguchi*

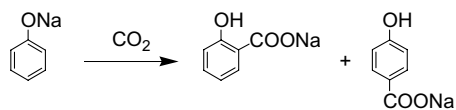
Department of Life and Environmental Sciences, Faculty of Engineering, Chiba Institute of Technology, 2-17-1 Tsudanuma, Narashino, Chiba 275-0016, Japan

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Abstract—A comparative analysis of the reactions between sodium phenoxide and CO₂ under the gaseous and supercritical conditions has demonstrated the preferential effect of supercritical conditions for promoting the reactivity of CO₂. A significant increase in product yield was obtained in supercritical CO₂ compared to reactions undertaken in gaseous CO₂.

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The conversion of carbon dioxide into industrially useful compounds has recently attracted much interest in view of the so-called ‘Green Chemistry’ and ‘Sustainable Society’ concepts. As a potential pathway for the effective utilization of carbon dioxide as a safe and cheap C1 building block in organic synthesis,^{1–3} the synthesis of hydroxybenzoic acid via coupling reactions between carbon dioxide and phenols has attracted much attention. This is because hydroxybenzoic acid can be used in many application areas as valuable feedstock and as an intermediate in the production of pharmaceuticals and fine chemicals. However, the conventional Kolbe–Schmitt reaction⁴ (Scheme 1), which is a heterogeneous reaction in the gas–solid phase, requires a high temperature and long reaction time. The yields of aromatic hydroxycarboxylic acids in polar aprotic solvents were much greater than conventional Kolbe–Schmitt reaction. The polar aprotic solvents aid in the dissolution of the metal salt, forming a homogeneous solution. This



Scheme 1. Kolbe–Schmitt reaction of sodium phenoxide.

Keywords: Supercritical carbon dioxide; Sodium phenoxide; Salicylic acid; *p*-Hydroxybenzoic acid; Kolbe–Schmitt reaction.

* Corresponding author. Tel./fax: +81 47 478 0420; e-mail: tatsuaki.yamaguchi@it-chiba.ac.jp

is because polar solvents solvate the cation–anion pair by increasing their intramolecular distances.^{5,6}

Supercritical fluid (SCF) medium has recently attracted much attention as the fourth phase for performing chemical synthesis, besides gas, liquid, and solid phases. The physical properties of SCFs can be continuously varied from those analogous to gases to those analogous to liquids by manipulating its pressure and/or temperature; hence, SCFs are expected to enhance the reaction rate and product selectivity in comparison with conventional organic solvents.^{7–9} Among SCFs, supercritical carbon dioxide is the most attractive reaction medium because of its low critical temperature (304 K) and pressure (7.3 MPa), as well as due to its nontoxic and non-flammable nature and low cost.

Here we wish to report the carboxylation of sodium phenoxide¹⁰ promoted by supercritical carbon dioxide. First, to compare supercritical CO₂[†] with gaseous CO₂, we systematically investigated the reaction under a number of pressures ranging from 3 to 17 MPa.¹¹ Figure 1 presents the effect of CO₂ pressure on the conversion of sodium phenoxide to hydroxybenzoic acid. The yield drastically changes with variations in the CO₂ pressure demonstrating the preferential effect of the supercritical conditions in promoting the reactivity of CO₂ as seen in Figure 1. The conversion of sodium

[†] CAUTION! Experiments, using compressed gases such as supercritical CO₂, are potentially hazardous and must only be carried out using appropriate equipment and safety precautions.

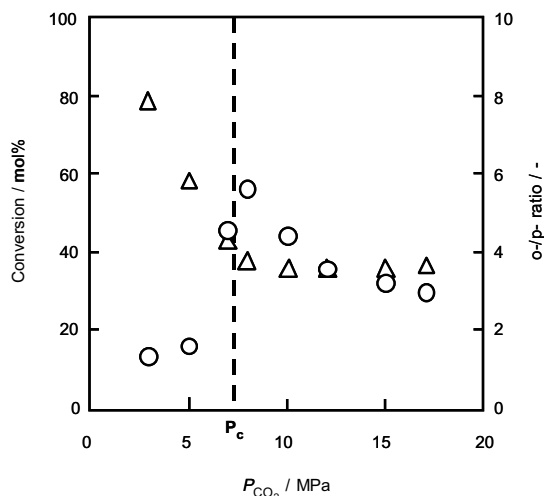


Figure 1. Effect of CO_2 pressure on the conversion of sodium phenoxide. Reaction conditions are as follows: a 50-mL stainless steel autoclave; sodium phenoxide, 10 mmol; reaction time, 1 h; reaction temperature, 393 K; (○) conversion, (△) *o/p*-ratio.

phenoxide tends to be dependent on the CO_2 pressure at lower pressures, but is remarkably lower than that under supercritical conditions. This phenomenon may be explained by a local augmentation effect;¹² the reaction rate increases because of the clustering of solvent molecules around the solute species.¹³ The apparent increase in the conversion for the reaction with CO_2 is likely due to the increased local concentration of CO_2 around the sodium phenoxide. Sodium phenoxide is dissolved in supercritical CO_2 , creating a homogeneous solution. This is done because the carboxylation of naphthoxide readily occurs through the use of a polar solvent. However, the reaction system seems to have two phases due to the low solubility of sodium phenoxide in supercritical CO_2 . The reason is that supercritical CO_2 has a low dielectric constant, with a value generally between 1.1 and 1.5. Furthermore, the conversion decreases with an increase in the CO_2 pressure above 10 MPa, because the local solvation occurs in supercritical fluids at conditions near the critical pressure. Interestingly, in the CO_2 pressure range from 8 to 17 MPa, we found that the product selectivity is almost independent providing *p*-hydroxybenzoic acid with 20% selectivity. In the low-pressure region, the reaction proceeds with the formation of a sodium phenoxide– CO_2 complex as an intermediate. On the other hand, in the high-pressure region, the reaction occurs by the dissolution of phenoxide in CO_2 . The difference in the reaction mechanism in the low- and high-pressure regions results in some change in product selectivity.

We conducted similar experiments with a variety of compositions in the supercritical region in order to determine whether the density effect is the principle cause for the rate enhancement effect. Because melting is normally initiated by the formation of a liquid in CO_2 – N_2 inclusions,¹⁴ N_2 was selected for the entrainer. The dependence of the conversion on the fluid composition of the CO_2 – N_2 system at 8 and 15 MPa is shown in Figure 2. The right ends of the plots represent the reac-

tion in a pure CO_2 solvent. The decrease in the conversion with an increased N_2 presence in the reaction fluid is very pronounced at the two reaction pressures, but the product selectivity was unaffected, as can be seen in Figure 3. There is no doubt that the presence of N_2 in the supercritical region decreases the conversion of phenoxide. Zhang and King¹⁵ reported that the density of the fluid is linearly proportional to the dissolved mixture content in the CO_2 . However, this relationship is not linear. This result suggests the density of the fluid alone does not explain the conversion drop in CO_2 – N_2 mixtures. The significant drop of in the conversion of sodium phenoxide in binary mixtures may involve a disruption of the CO_2 shell around the phenoxide.

In summary, we have reported that a step in developing an efficient and mild method for the synthesis of hydroxybenzoic acid by using supercritical CO_2 , an ideal

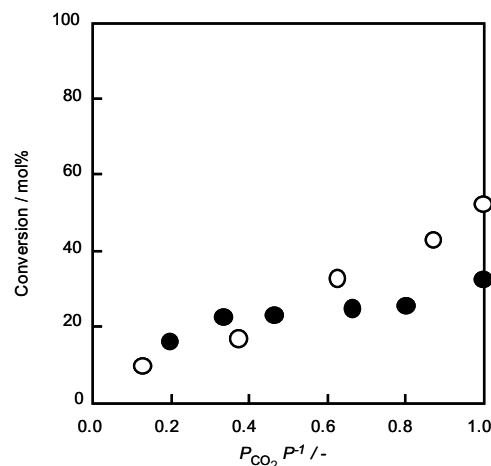


Figure 2. Sodium phenoxide conversion in CO_2 – N_2 having different N_2 content and at selected pressures. Reaction conditions are as follows: Sodium phenoxide, 10 mmol; reaction time: 1 h; reaction temperature: 393 K; (○) 8 MPa, (●) 15 MPa.

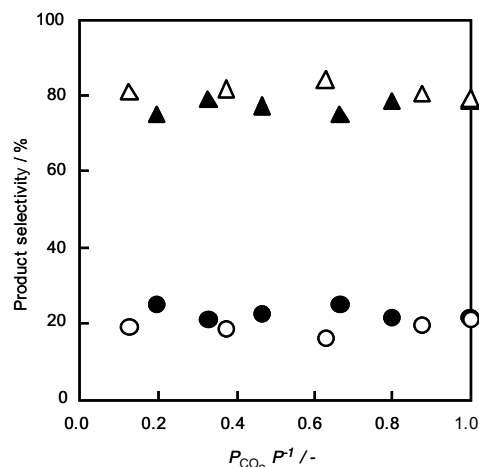


Figure 3. A plot of product selectivity from carboxylation of sodium phenoxide in CO_2 – N_2 having different N_2 content and at selected pressures. Reaction conditions are as follows: Sodium phenoxide, 10 mmol; reaction time: 1 h; reaction temperature: 393 K; (△) oHBA-8 MPa, (▲) pHBA-8 MPa, (○) oHBA-15 MPa (●) pHBA-15 MPa.

reaction medium in view of *green chemistry*, as a reactant and a reaction medium. The reaction in supercritical CO₂ proceeds dramatically as compared with the conventional Kolbe–Schmitt reaction, presumably due to the increase in the density of CO₂ around the phenoxide. The addition of nitrogen as an entrainer led to a decrease in the reaction rate through the disintegration of the CO₂ shell in the vicinity of sodium phenoxide. Further work may include trying this reaction at even higher temperatures to further enhance the reaction rate.

References and notes

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10. *Preparation of sodium phenoxide*: Phenol (9.4 g, 100 mmol) was dissolved in 100 mL of an aqueous solution of sodium hydroxide, followed by stirring at room temperature for 1 h. The resultant solution was placed in a rotary evaporator and heated at 353 K for 3 h. The resulting solid was dissolved in a large amount of ethanol and heated at 333 K for 3 h. The white solid thus obtained was further dried in vacuo at 473 K for 6 h to obtain pure sodium phenoxide.
11. *General procedure and analysis*: The reaction was performed with a supercritical CO₂ reactor system including SCF-Get, SCF-Bpg, and SCF-Sro (JASCO). The prepared sodium phenoxide was placed in a 50-mL stainless steel autoclave (SUS-316) containing a stirring bar. Liquid CO₂, cooled to 263 K, was introduced into the autoclave, which had been heated to 393 K, using a high performance liquid chromatography (HPLC) pump after flushing with nitrogen. The resultant mixture was stirred for 1 h at 393 K with the CO₂ pressure constantly maintained at the requisite pressure. The autoclave was cooled in an ice bath, and the pressurized CO₂ was gradually released. The resulting solid mixture was washed from the autoclave with deionized water. The solution was analyzed by HPLC with an ODS column (250 × 4.6 Ø mm) on a Shimadzu LC-10AD chromatograph.
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