



Efficient regioselective carboxylation of phenol to salicylic acid with supercritical CO₂ in the presence of aluminium bromide

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ABSTRACT

Salicylic acid is obtained in good to excellent yield by carboxylation of phenol with a carbon dioxide in the presence of Lewis acid catalysts at moderate temperatures (293–353 K). Among the catalysts investigated, aluminium bromide (AlBr₃) was found to be the most active. To optimize the reaction conditions and study the reaction mechanism, the experimental variables including the various Lewis acids, temperature, carbon dioxide pressure, amount of AlBr₃, chlorotrimethylsilane additive, etc. were studied. Under the optimized conditions, nearly complete carboxylation of phenol to salicylic acid was observed with 10 mmol of AlBr₃ added to an autoclave. On the basis of experimental findings, the most feasible reaction mechanism proposed involves the formation of an organoaluminium-like compound.

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1. Introduction

Carbon dioxide as a greenhouse gas contributes significantly to global warming [1]; the amount of greenhouse gases is continuously increasing with the growth of industrial processes and energy-related activities. The Kyoto Protocol adopted in December 1997 intends to restrict the emission of greenhouse gases [2].

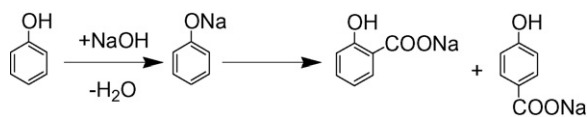
The chemical fixation of carbon dioxide is a viable approach to mitigate the excessive carbon dioxide preferably by transformation to valuable products [3–5]. Although several methods are known for the chemical conversion of carbon dioxide, they are generally very energy demanding, limiting the practicality of their use. Therefore, the development of green processes based on the chemical fixation of CO₂ has attracted considerable attention in the field of industrial chemistry from the viewpoint of environmental protection [6]. One of the most versatile processes for carbon–carbon bond formation is the synthesis of aromatic hydroxycarboxylic acids such as salicylic acid, *p*-hydroxybenzoic acid, *p*-aminosalicylic acid, and 3- and 6-hydroxy-2-naphthoic acid via the coupling of CO₂ with phenols. These aromatic hydroxycarboxylic acids have been widely used for various purposes, for example, as valuable raw materials and intermediates in the production of pharmaceutical and fine chemicals.

Aromatic hydroxycarboxylic acids have long been synthesized via the Kolbe–Schmitt reaction (Scheme 1) [7–10], an industrial synthetic process that utilizes CO₂ as a reactant. This reaction consists of two steps: (1) the production and purification of alkali metal phenoxides and (2) carboxylation. In step 1, the alkali metal phenoxides are generally prepared from alkali metal hydroxides and phenol. A mixture of alkali metal hydroxides, phenol, and deionized water is evaporated at 353 K, and the precipitate is further dried in vacuo at 453 K. However, the major disadvantages of this process are its high-energy consumption and production costs that stem from the requirement for the purification of the alkali metal phenoxide. In other words, this two-step manipulation is one of the main drawbacks of this process.

The other synthetic method (Scheme 2) [11,12] is via the attack of a trichloromethyl cation (generated by a copper catalyst from carbon tetrachloride) of a phenoxide anion, followed by the hydrolyses of the C–Cl bonds in an intermediate ternary molecular complex with concentrated sodium hydroxide because it is fairly difficult to replace an aromatic hydrogen with a carboxyl function.

To eliminate the production and purification step of alkali metal phenoxides in the two-step manufacturing process, the most desirable route for the synthesis of aromatic hydroxycarboxylic acids would be the direct reaction of phenols and carbon dioxide; this could be regarded as the third access to aromatic hydroxycarboxylic acid from CO₂. In our previous study, several types of basic metal oxides, such as γ -aluminas, zirconia, ceria, and alkali metal and alkaline earth metal salts, have been used in this process [13,14]. Among the base catalysts examined, potassium carbonate was the

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most effective, and its carboxylation was 99% selective for salicylic acid; however, the reaction took over 10 h to reach completion. Accordingly, the keys to performing a direct carboxylation reaction of phenol are the selection of active catalysts, and the tuning of reaction parameters to proceed the reaction. Despite all attempts, no satisfactory conditions were found for the direct carboxylation of phenol with supercritical carbon dioxide (scCO₂) to hydroxybenzoic acids, and this remained a long-standing challenge.

The purpose of this article is to demonstrate that the direct synthesis of salicylic acid can be performed in scCO₂ with the aid of a Lewis acid catalyst. The effects of catalyst usage and reaction conditions, such as reaction time, reaction temperature and CO₂ pressure, on the reaction were then investigated in detail. Based on the experimental observations, a possible reaction mechanism is proposed.

2. Experimental

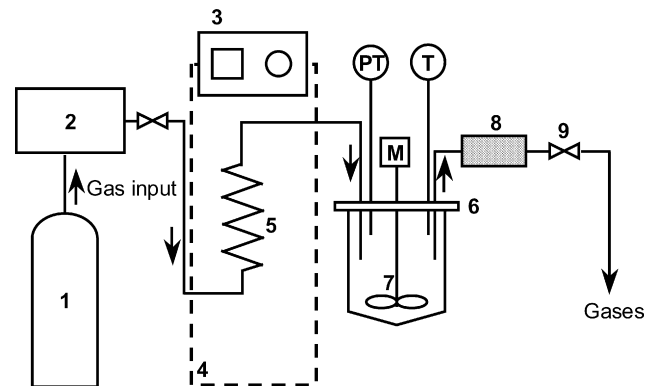
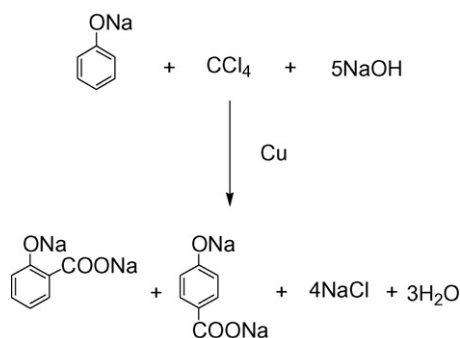
2.1. Materials

Anhydrous AlBr₃, AlCl₃, FeCl₃, SnCl₂, ZnCl₂, ZnBr₂, CuCl₂, and H₂SO₄ (Wako Pure Chemical, 99.5%) as well as phenol (Wako Pure Chemical, 99.5%) were used as supplied. CO₂ with a purity of 99.9% was used without further purification.

2.2. General procedures and analyses

CAUTION: Experiments using compressed gases such as scCO₂ are potentially hazardous and must only be conducted by using appropriate equipment and taking safety precautions.

The direct catalyzed reaction was performed with a scCO₂ reactor system comprising an SCF-Get, SCF-Bpg, and SCF-Sro (JASCO). All equipments were assembled as outlined in Scheme 3. Phenol (10.0 mmol) and AlBr₃ (2.0 mmol) were placed in a 50-mL stainless steel autoclave (SUS-316) with a stirring bar. Liquid CO₂ cooled to 263 K was then introduced into the autoclave, which had been heated to the requisite temperature and flushed with nitrogen, using an HPLC pump. The resultant mixture was stirred for 5 h at the requisite temperature 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, and an inner standard was added into the solution. The solution was



Scheme 3. A schematic illustration of experimental apparatus for the synthesis of hydroxybenzoic acid isomer in supercritical CO₂. (1) CO₂ reservoir; (2) computer-controlled metering syringe pumps; (3) bath-heater; (4) thermostat; (5) preheating unit; (6) reactor; (7) stainless steel stirring bar; (8) filter; (9) back pressure regulator; T: thermocouple; PT: pressure transducer.

analyzed by HPLC with a column (ODS column 250 mm × 4.6 mmØ) on a Shimadzu LC-10AD chromatograph.

2.3. Solubility measurement

A saturation column was first packed with a solid compound of interest and placed in a constant-temperature bath. Liquid CO₂ at the ambient temperature was charged into an HPLC pump and compressed to the desired pressure. The pump was used to continuously deliver the solvent at flow rates ranging from 0.1 to 10 standard cm³/min and at a constant pressure of up to 30 MPa. After reaching a thermal equilibrium with the constant-temperature bath, the solvent was fed into a stainless steel high-pressure equilibrium cell. The entrainment of the solute was prevented by inserting glass wool plugs at the top of the packed column. Once the saturated solution exited the equilibrium cell, it was flashed to atmospheric pressure across a heated metering valve, and the heavy component was collected in a cold trap held at ice temperature. The amount collected was determined by weighing and by HPLC with an ODS column, and the corresponding volume of CO₂ was measured with a wet-test meter. The equilibrium pressure was measured at the exit of the equilibrium cell. Fluctuations in the pressure due to the HPLC pump were less than ±25 psi over the entire pressure range. The temperature was measured within 1 K with a calibrated copper-constantan thermocouple referenced to an ice bath.

3. Results and discussion

3.1. Selection of catalysts

First, the direct synthesis of salicylic acid from phenol and scCO₂ was performed at 353 K and 8 MPa in the presence of several types of Lewis acids such as AlBr₃, AlCl₃, FeCl₃, SnCl₂, ZnCl₂, ZnBr₂, and CuCl₂, as catalysts. Some typical experimental results from catalyst screening are tabulated in Table 1. Under the reaction conditions used here, no *p*-hydroxybenzoic acid could be detected, and salicylic acid was the only isolable product in all cases. Without a catalyst, the coupling of scCO₂ with phenol afforded no product; while in the presence of catalytic amounts of Lewis acid halides, such as entries 4–10 in Table 1, a carboxylated product was obtained in good yield, and their carboxylation was 100% selective for salicylic acid. Although not shown in Table 1, the reaction was also performed with protic acids such as H₂SO₄ and CH₃COOH. However, these compounds showed no activity for the reaction. The acidic metal oxides Al₂O₃, SiO₂ and ZrO–SO₄²⁻ (Table 1, entries

Table 1
Catalytic activities of various Lewis and protic acid catalysts for the direct carboxylation of phenol to salicylic acid in supercritical carbon dioxide

Entry	Catalyst	Conversion (mol%)	oHBA yield (mol%)	pHBA yield (mol%)
1	Al ₂ O ₃	0	0	0
2	SiO ₂	0	0	0
3	ZrO ₂ -SO ₄ ²⁻	0	0	0
4	FeCl ₃	6.5	6.5	0
5	CuCl ₂	1.8	1.8	0
6	SnCl ₂	1.6	1.6	0
7	ZnCl ₂	5.2	5.2	0
8	ZnBr ₂	12.9	12.9	0
9	AlCl ₃	2.7	2.7	0
10	AlBr ₃	55.9	55.9	0

Reaction conditions are as follows: phenol, 10 mmol; catalyst usage, 2.0 mmol; reaction time, 1 h; reaction temperature, 353 K; CO₂ pressure, 8 MPa.

1–3), which are weak inorganic acids, were not effective catalysts for the direct synthesis of salicylic acid. As for the Lewis acid, AlBr₃, which combines the highest Lewis acidity and good solubility in nonpolar solvents [14], showed the best performance among the Lewis acids examined (Table 1, entry 10). With AlBr₃ as the catalyst, salicylic acid yield reached 55.9%. On the other hand, other Lewis acid halides, which were less strong in Lewis acidity than AlBr₃, demonstrated relatively less activity toward the carboxylation reaction. This is similar to the pioneering work of Olah and coworkers for the carboxylation of benzene with an activated carbon dioxide–Al₂Cl₆/Al system [15], where aluminium halides were able to promote the effective carboxylation reaction; however, the other Lewis acids were inactive. Because AlBr₃ itself is also inactive in its hydrated forms (AlBr₃·H₂O to AlBr₃·6H₂O), it became clear that the optimum range of acid catalysts for the reaction is very narrow. After screening many Lewis acid halides, we pursued the carboxylation of phenol by AlBr₃ in detail.

3.2. Effects of reaction time on the reaction behavior

To learn more about the carboxylation reaction and to find the optimized conditions, we extended the study to experimental variables such as reaction time, reaction temperature, CO₂ pressure, and catalyst usage. First, the effect of reaction time was studied. Fig. 1 shows the changes in the yield of salicylic acid with reaction

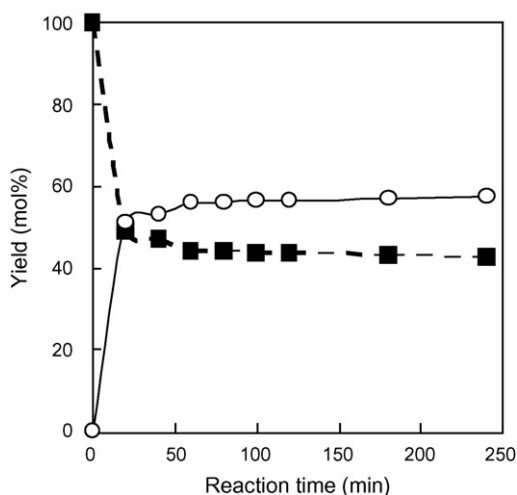


Fig. 1. Time dependence of product yield of AlBr₃ catalyzed carboxylation of phenol at 353 K and 8 MPa. Reaction conditions are as follows: Phenol, 10 mmol; AlBr₃ quantity, 2.0 mmol; reaction temperature, 353 K; CO₂ pressure, 8 MPa; (■) phenol; (○) salicylic acid.

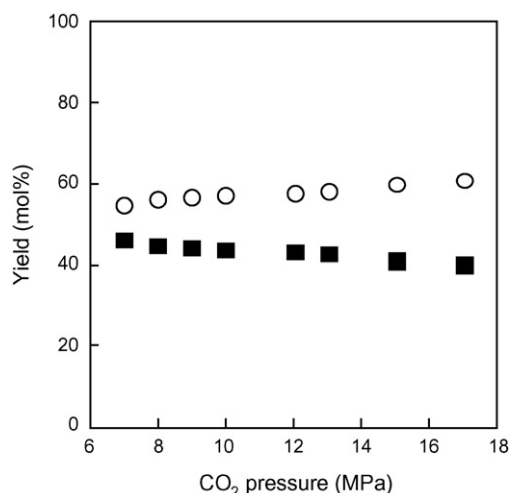


Fig. 2. Illustrating the effect of CO₂ pressure on the carboxylation of phenol over AlBr₃ at 353 K by varying the CO₂ pressure from 7 to 17 MPa. Reaction conditions are as follows: phenol, 10 mmol; AlBr₃ quantity, 2.0 mmol; reaction temperature, 353 K; reaction time, 1 h; (■) phenol; (○) salicylic acid.

time over AlBr₃ catalyst. The reactions were performed in the presence of AlBr₃ (2.0 mmol) at 353 K under a CO₂ pressure of 8 MPa, and were monitored in the range of 20–240 min at regular intervals. The results indicated that the carboxylation reaction proceeded rapidly within the first 20 min. It is amazing to note that within 60 min, the salicylic acid yield reached a maximum of 55.9 mol%, which is comparable to the result for the reaction time of 240 min, suggesting a deactivation of the carboxylation activity. Notably, the selectivity remained 100% for the entire course of the reaction. This suggests that a reaction time of 1 h is appropriate for the direct synthesis of salicylic acid from phenol and scCO₂.

3.3. Effects of CO₂ pressure on the reaction behavior

Generally, the solubilizing power of a substance increases with an increase in its density [16]. Therefore, if the poor solubility of phenol in scCO₂ retards the reaction, an increase in the CO₂ density should enhance the reaction rate.

We systematically investigated a number of reaction pressures ranging from 7 to 17 MPa, while the reaction temperature was maintained constant 353 K in order to increase the CO₂ density. The effect of the CO₂ pressure on the yields of salicylic acid for the AlBr₃ catalyst is illustrated in Fig. 2. It has been reported that, when CO₂ is used as a solvent or a reactant, the reaction rates are maximal near the critical pressure of CO₂ [8,17,18]. In the other words, excessively high CO₂ pressures may retard the interaction between a substrate and a catalyst [19]. As is obvious from Fig. 2, however, increasing the CO₂ density through an increase in the CO₂ pressure gradually increases the activities of the AlBr₃ catalyst, demonstrating the preferential effect of supercritical conditions for promoting the reactivity of CO₂. The increase in the CO₂ pressure and density could increase the solubility of phenol, and may cause a high concentration of phenol in the vicinity of the catalyst, thus resulting in a high yield.

The solubilities of phenol and salicylic acid in scCO₂ have been measured over a pressure range of 8–30 MPa at 323 K to assist in the study of the carboxylation reaction. The experimental solubility data for phenol and salicylic acid in scCO₂ as a function of pressure at 323 K are plotted in Fig. 3. The solubility isotherms in Fig. 5 for phenol and salicylic acid continue to increase at elevated pressures. However, the solubility of phenol in CO₂ is two orders of magnitude higher than the binary system solubility of salicylic acid

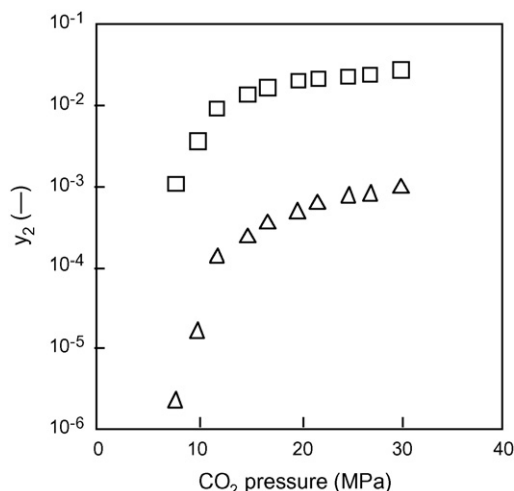


Fig. 3. Solubility isotherms of phenol (□) and salicylic acid (Δ) as a function of pressure.

over the same range of pressures. This is consistent with the literatures reports of these compounds [20,21]. The key advantage of this method is that the high solubility of phenol in scCO_2 enhances the concentration of phenol in the vicinity of the catalyst.

3.4. Effects of reaction temperature on the reaction behavior

We performed similar experiments in the range of 273–373 K in order to investigate the catalytic activity at different temperatures. Fig. 4 shows the effect of raising the reaction apparatus temperature whilst the CO_2 pressure was maintained constant at 8 MPa. A relatively high temperature was found to be favorable for an efficient reaction. Unlike the K_2CO_3 -catalyzed carboxylation of phenol to hydroxybenzoic acids, where the reaction occurs at temperatures approaching 473 K, the salicylic acid yield increased steadily from 0 to approximately 70% with a reaction temperature up to 373 K. However, a further increase in the reaction temperature to 393 K led to a considerably slower reaction, possibly due to the decomposition of salicylic acid at the higher temperature. Olah et al. performed the carboxylation of benzene with an AlCl_3 catalyst [15]. They showed that no benzoic acid could be observed above 383 K.

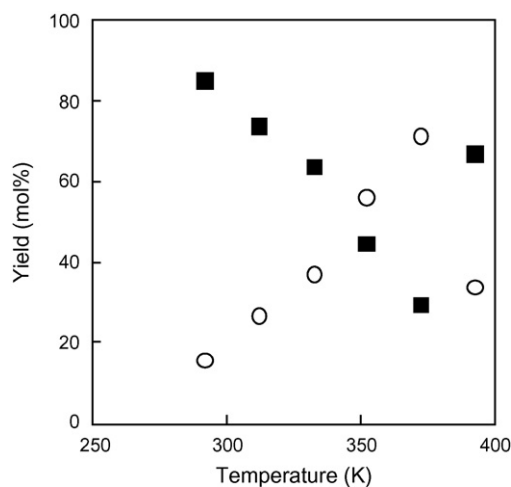


Fig. 4. A plot of yield of salicylic acid from the carboxylation of phenol at 8 MPa increasing the temperature from 293 to 393 K over AlBr_3 catalyst. Reaction conditions are as follows: phenol, 10 mmol; AlBr_3 quantity, 2.0 mmol; reaction time, 1 h; CO_2 pressure, 8 MPa; (■) phenol; (○) salicylic acid.

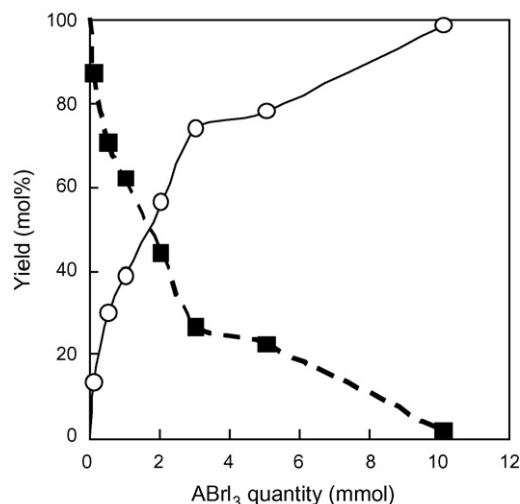


Fig. 5. Reaction rate— AlBr_3 quantity profiles for the direct carboxylation of phenol in scCO_2 . Reaction conditions are as follows: phenol, 10 mmol; reaction temperature, 353 K; reaction time, 1 h; CO_2 pressure, 8 MPa; (■) phenol; (○) salicylic acid.

Benzoic acid yield became significant at 363 K and was formed exclusively at 363 K. Dunn et al. reported that the decarboxylation of salicylic acid to phenol was proceeded in the temperature range of 363–503 K [22]. Therefore, 373 K could be the optimal temperature for this reaction.

3.5. Effects of AlBr_3 quantity on the reaction behavior

Suzuki et al. found that a certain amount of carboxylated products obtained could be dependent on the catalyst usage [14]. Thus, the influence of the amount of AlBr_3 catalyst on their carboxylation reaction was studied over the previously optimized reaction temperature and CO_2 pressure. The effects of the AlBr_3 quantity added to the autoclave for the formation of salicylic acid are presented in Fig. 5. Nearly complete carboxylation of phenol to salicylic acid was observed with 10 mmol of AlBr_3 added to the autoclave. Although the salicylic acid formation significantly increased with an increase in the AlBr_3 quantity, the amount of salicylic acid produced did not linearly increase with the amount of AlBr_3 . Another observation was that the yields calculated on the basis of the reactant: $\text{AlBr}_3 = 1:1$ ratio exceed the theoretical 100 mol%. Therefore, these observations strongly suggest that AlBr_3 is considered to be a catalyst in this system rather than a reagent in this system.

3.6. Possible reaction mechanism for the salicylic acid synthesis from phenol and CO_2 with AlBr_3

Nemoto et al. reported that the Lewis acid-mediated carboxylation of aromatic compounds with CO_2 is promoted by the addition of large excess of the chlorotrimethylsilane (TMSCl) to yield aryl-carboxylic acids [23]. Under the optimized reaction conditions, we conducted the carboxylation of phenol over the 2 mmol of AlBr_3 with TMSCl additives, in order to probe the ability of TMSCl additive for this reaction and to obtain further insight into the nature of the reaction. The obtained results are collectively presented in Table 2. The efforts to increase the yields toward salicylic acid formation using a large excess of TMSCl additives, however, failed. These results may be explained by a steric hindrance—the interaction of phenol and AlBr_3 catalyst is inhibited by a trimethylsilylated hydroxyl group. Trimethylsilylation was a frequently used protection method in several chemical conversions and synthesis of natural products due to the enhanced chemical and thermal stabil-

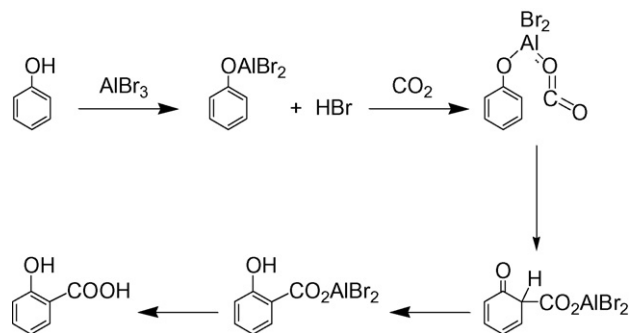
Table 2
Effect of TMSCl additives on the yield of carboxylation of phenol with CO₂ in the presence of AlBr₃ catalyst

Entry	TMSCl (mmol)	Conversion (mol%)	<i>o</i> HBA yield (mol%)	<i>p</i> HBA yield (mol%)
1	0	55.9	55.9	0
2	1	1.4	1.4	0
3	2	1.6	1.6	0
4	3	1.6	1.6	0
5	5	3.9	3.9	0
6	10	5.5	5.5	0

Reaction conditions are as follows: phenol, 10 mmol; AlBr₃ quantity, 2.0 mmol; reaction time, 1 h; reaction temperature, 353 K; CO₂ pressure, 8 MPa.

ity. Because phenols are readily transformed into the corresponding silyl ethers, which are prepared by the dehydrogenative silylation of hydroxyl groups, in excellent yields [24], these observations were expected. However, the yield could be improved by increasing the amount of TMSCl (Table 2, entries 2–6). This is due to generate arylsilanes, which is in-situ silylation of the resultant phenol at the ortho position, under the Lewis acidic conditions, followed by the carboxylation at the ipso carbon of the silyl moiety. The addition of a large excess of the silylating reagent shifts the equilibrium to the right to promote the second reaction, giving the arylsilanes in higher yield.

Although the complicated characterizations are necessary to draw a detailed reaction mechanism for the salicylic acid synthesis under the current conditions, a rough reaction pathway is suggested in Scheme 4. The reaction as exemplified with phenol is initiated by the acid system providing the salt **1**, which is depicted as the phenoxyaluminium dibromide. Generally, the presence of a phenolic group kinetically favors *ortho*-alkylation and *ortho*-acylation. For example, Naeimi et al. performed several exploratory reactions that only produced *ortho*-acylated products [25]. The intermediate **1** pictured in Scheme 4 is similar to that proposed by Casiragi et al. [26] and accommodates the regioselective *ortho*-carboxylation of phenol. In their original paper [26], Casiragi and coworkers already proposed the possibility of the formation of phenoxyaluminium chloride. The aluminium salt is a requirement for further reaction; no reaction occurred when a solu-



Scheme 4. Possible reaction mechanism for salicylic acid synthesis from phenol and CO₂ with Lewis acid catalysts.

tion of phenol was heated under a CO₂ pressure of 8 MPa. The intermediate **1** reacted with CO₂ through the cyclohexadienone structure **2** furnishing the aluminium salt of salicylate **3**. Consequently, on the basis of the presently available data, the formation of an organoaluminium-like compound appears to be the preferred pathway.

4. Conclusions

In the present study, the direct carboxylation of phenol with carbon dioxide proceeded smoothly in the presence of various Lewis acids, especially AlBr₃, at moderate temperatures under supercritical conditions. This method is a new, mild, efficient, easy, and clean method for the preparation of salicylic acid in excellent yields with a high regioselectivity in the substitution of a carboxyl group in an ortho situation. To evaluate the mechanistic aspects of the reaction and to find the optimized conditions, the effect of several experimental variables was also studied, including a reaction using a large excess of TMSCl additives. These reactions have some advantages in comparison with other methods, such as; short reaction time, high yield and regioselectivity of the product, and mild reaction conditions. In accordance with the experimental results, the formation of the phenoxyaluminium dibromide and its reaction with carbon dioxide is proposed as the most viable pathway for the studied carboxylations.

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