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Solvent-assisted Carboxylation of Alkali Metal Phenoxide with Carbon Dioxide†

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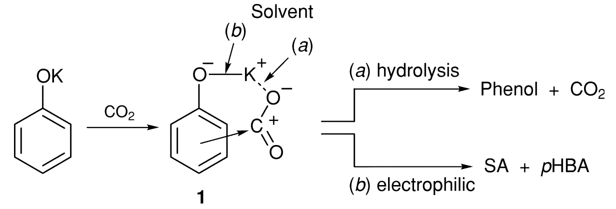
The carboxylation of alkali metal phenoxide with carbon dioxide gives not only *ortho*- but also *para*-hydroxybenzoic acids at room temperature, unlike the well-known Kolbe–Schmitt reaction.

The carboxylation of alkali metal phenoxide with carbon dioxide to hydroxybenzoic acids is well known as the Kolbe–Schmitt reaction.[1] At the initial stage of the reaction, it has been accepted for a long time that the CO_2 complex (alkali metal phenoxide$\cdot CO_2$) is formed at room temperature. Phenyl carbonate ($PhOCO_2M$, where M is K or Na) was originally proposed for the complex,[2] but the IR absorption spectra[3] showed a band at 1684 cm^{-1} which is not in agreement with those of structurally similar carbonates such as methyl phenyl carbonate (1754 cm^{-1}), and dimethyl carbonate (1748 cm^{-1}). The most plausible structure, at the present time, is structure **1**[4,5] where the π-electrons of potassium phenoxide move toward carbon dioxide and probably its oxygen atom forms a weak bonding with potassium. The complex is assumed to change into salicyclic acid (SA) upon heating above 120 °C, and further heating at 180–250 °C leads to *p*-hydroxybenzoic acid (*p*HBA) *via* dipotassium salicylate.[6] In fact, the mass of potassium (or sodium) phenoxide increased with the introduction of carbon dioxide at room temperature. When the complex was washed with chloroform to remove free phenol, the NMR spectra surprisingly showed SA and *p*HBA besides phenol. Therefore, potassium phenoxide was kept for 1 h in an autoclave after the introduction of carbon dioxide at 25–60 °C, and treatment of the resulting complex with water or with organic solvents without removing the trace amount of water that they contained at room temperature led to carboxylation. It is suggested that hydrolysis of the complex to SA and *p*HBA occurs (Table 1).

Remarkable features different from the Kolbe–Schmitt reaction are as follows: (*a*) SA is produced at much lower temperatures, (*b*) the formation of *p*HBA is not ascribable to thermal rearrangement from SA at such low temperatures, and (*c*) *p*HBA is obtained even from sodium phenoxide. Similar features to the last observation (*c*) have been reported by Hirao *et al.*[7] using aprotic polar solvents such as DMF or DMSO which enable the Kolbe–Schmitt reaction to be homogeneous at 100–180 °C. The formation of *p*HBA in a part of their reaction in solvents must essentially be the same as occurred in the present method which forms the CO_2 complex without disturbance by solvent prior to the carboxylation. Another analogous reaction, but different in type from the Kolbe–Schmitt reaction, is that using phenol carboxylase,[8] though the enzymatic reaction gives *p*HBA from only potassium but not sodium phenoxide. Therefore the present reaction, together with those reported by Hirao *et al.*,[7] is the sole method by which sodium phenoxide produces *p*HBA. The present reaction is explicable by competition between decomposition to phenol and the carboxylation as shown in Scheme 1. Solvolytic decomposition may be followed by hydrolysis with a small mount of water to form phenol and carbon dioxide or carbonates, but the ratio of the two paths seems to be affected little by solvent properties. The difference in the stabilities between the potassium and sodium phenoxides–CO_2 complex is critical to the orientation to either the *ortho*- or the *para*-position in the Kolbe–Schmitt reaction where thermal rearrangements of the CO_2 complex occur to give SA, then *p*HBA at higher temperatures, but the solvent assisted carboxylation levels off the difference, probably because of simple electrophilic rearrangements occurring around room temperature.



Scheme 1

Experimental

Potassium and sodium phenoxide were prepared by addition of 1 equiv. of the corresponding *ca.* 0.2 M alkali hydroxide solution to phenol in methanol. The solvents were evaporated using an aspirator, then a vacuum pump on an oil bath at 160 °C, to dryness. The resulting solid was ground to fine powder in a dry box. The white powder (*ca.* 2.5 g) was placed in a 200 ml autoclave, and carbon dioxide of more than 99.95% purity was quickly introduced. The reaction vessel was kept at constant temperature (25–60 °C)

Table 1 Solvent assisted carboxylation of alkali phenoxides[a]

Run	CO_2[b]	Time/h	Temp./°C	Solvent (decomp.)	Yield(%) SA	*p*HBA	Total
1	6.0 (MPa)	1	30	H_2O	8.6	5.7	14.3
2	6.0	1	60	H_2O	12.4	8.2	20.6
3	6.5	1	25	$CHCl_3$	23.8	16.1	39.9
4	6.5	1	25	CH_3OH	15.1	8.5	23.6
5	6.5	2	25	$CHCl_3$	32.3	4.6	36.9

[a]Potassium phenoxide (2.5 g, 1.65×10^{-2} mol) except Run 5 (sodium phenoxide; 2.5 g, 2.10×10^{-2} mol) was used. [b]Initial pressure.

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in a thermostat bath. After the reaction, the reaction mixture was dissolved in 50 ml of water, then was adjusted to pH 7 with dilute hydrochloric acid. The unreacted phenol was recovered with diethyl ether and the products were extracted from the solution after further acidification (pH < 1).

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