Carboxylation by Alkali Salts and Carbon Monoxide. II.[1] A Selective Preparation of p-Hydroxybenzoic Acid

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The reaction of potassium phenoxide with carbon monoxide and potassium carbonate was studied in detail. The effects of reaction variables on the yield and the selectivity were investigated. The reaction proceeds very smoothly at a temperature above the melting point of potassium formate (167°) even under low pressure of carbon monoxide to afford dipotassium *p*-hydroxybenzoate and potassium formate in very high yield. The carboxylation occurs mainly at the *para* position to the hydroxyl group. When the molar ratio of potassium carbonate to potassium phenoxide is larger than unity, tripotassium 4-hydroxyisophthalate is also formed by the subsequent but rather slow carboxylation.

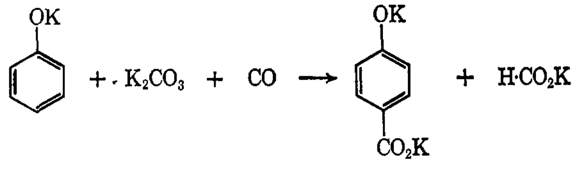
p-Hydroxybenzoic acid (or its potassium salt) has been prepared by various procedures. One of the most practical is the Kolbe–Schmitt reaction.[2,3]

On the other hand, the carboxylation of potassium benzoate by carbon monoxide and potassium carbonate to give dipotassium terephthalate was reported by Murase, *et al.*[4] Although the mechanism of the reaction is not clear, the reaction probably proceeds through the following steps: potassium carbonate reacts first with carbon monoxide to form potassium oxalate[5] as an intermediate, and then the potassium oxalate converts potassium benzoate into dipotassium terephthalate.[6]

The carboxylation reaction of potassium phenoxide with carbon monoxide and potassium carbonate was reported in the previous paper.[1] The reaction is investigated in detail in this paper.

Results and Discussion

Effects of the Reaction Variables.—The equimolar mixture of potassium phenoxide and potassium carbonate was heated under fairly high pressure of carbon monoxide at an appointed temperature for 5 hr (Figure 1). Even at 125°, the carboxylated products, though the conversions were very low, were detected. The yield and the selectivity of *p*-hydroxybenzoic acid increased slowly with temperatures up 170°. At above 170°, near the melting point of potassium formate (167°), an abrupt increase of the yield was observed. At temperatures above 210°, the yield of *p*-hydroxybenzoic acid was almost quantitative. The almost stoichiometrical absorption of carbon monoxide and the almost quantitative formation of formic acid show the reaction to be formulated as



(1)

One of the reasons of the low reaction rate at a temperature below 167° is presumably that there is no liquid phase in the reaction mixture. At temperatures above 210°, the change of carbon monoxide pressure indicated that the reaction rate depends considerably on the temperature (Figure 2).

The effect of the carbon monoxide initial pressure on the yield of *p*-hydroxybenzoic acid was examined at 240° (Figure 3). When the reaction was carried out in the absence of carbon monoxide, no carboxylated product was obtained. When carbon monoxide was present enough for the amount of potassium phenoxide (0.050 mol of carbon monoxide corresponds to a pressure of about 15 atm, at room temperature in our system), the yield of *p*-hydroxybenzoic acid was nearly quantitative irrespective of the carbon monoxide initial pressure. This shows that the reaction proceeds even under low pressure. Figure 4 indicates clearly that the reaction rate is affected by the initial pressure.

The effect of the molar ratio of potassium carbonate to potassium phenoxide was studied at 240° (Figure 5). The yield of *p*-hydroxybenzoic acid corresponded to the proportion of potassium carbonate up to the ratio of unity. When 1.5 or 2.0 times as much potassium carbonate was used, a small amount of 4-hydroxyisophthalic acid was obtained. The formation of it is by the subsequent carboxylation of dipotassium *p*-hydroxybenzoate, but the reaction rate was so slow that usually *p*-hydroxybenzoic acid can be obtained preferentially (Table I).

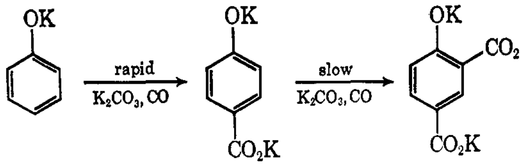


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TABLE I

CARBOXYLATION OF DIPOTASSIUM *p*-HYDROXYBENZOATE[a]

Solvent, $H{\cdot}CO_2K$, mol	Initial CO, atm	Time, hr	Yield of product,[b] %		
			4-HIPA	HTMA	*p*-HBA
0	50	5.0	0	0	97
0.050	50	5.0	14	0	84
0.050	50	24.0	43	4	50
0.050	10	5.0	0	0	97
0.050	10	24.0	3	0	95

[a] A mixture of 0.050 mol of dipotassium *p*-hydroxybenzoate and 0.050 mol of potassium carbonate was heated at 240°. [b] 4-HIPA, 4-hydroxyisophthalic acid; HTMA, hydroxytrimesic acid; *p*-HBA, *p*-hydroxybenzoic acid.

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[1] Y. Yasuhara and T. Nogi, *Chem. Ind.* (London), 229 (1967), may be considered as part I in this series.

[2] H. Kolbe, *J. Prakt. Chem.*, [2] **10**, 100 (1874).

[3] A. S. Lindsey and H. Jeskey, *Chem. Rev.*, **57**, 583 (1957).

[4] T. Murase, I. Mikami, and M. Tamura, British Patent 1,003,725 (1965); *Chem. Abstr.*, **64**, 655*b* (1966).

[5] C. Matignon and C. Faurholt, *C. R. Acad. Sci., Paris*, **179**, 273 (1923).

[6] W. Stein and H. Schütt, German Patent 1,042,568 (1958); *Chem. Abstr.*, **54**, 18444*g* (1960).

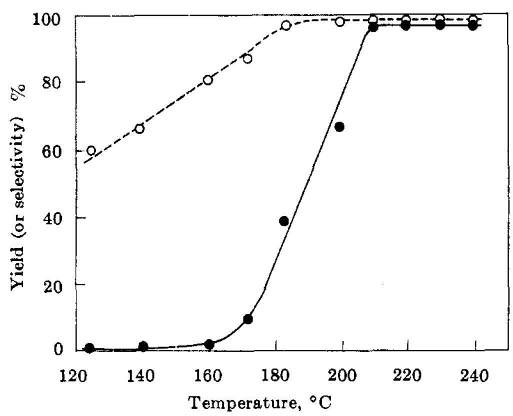

Figure 1.—Over-all yield of hydroxybenzoic acids (—●—) and selectivity of the *para* isomer (- -○- -) as a function of temperature. A mixture of 0.050 mol of PhOK and 0.050 mol of K_2CO_3 was heated under the initial pressure (80 atm) of CO at an appointed temperature for 5 hr.

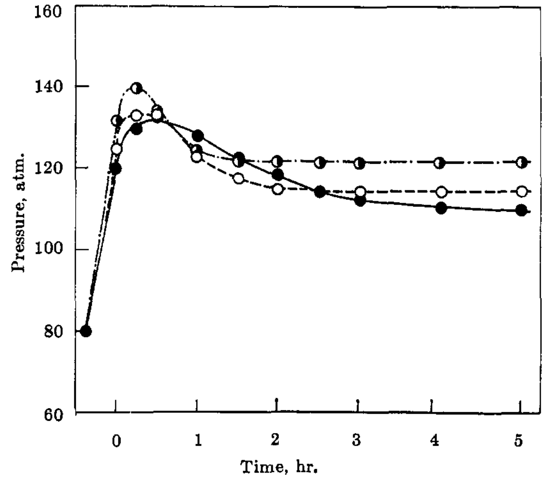

Figure 2.—Reaction velocity expressed by change of CO pressure as a function of temperature (—●—, 210°; - -○- -, 220°; - · -◑- · -, 240°). For the reaction conditions, see Figure 1.

The fact that 4-hydroxyisophthalic acid was not detected in the reaction of dipotassium *p*-hydroxybenzoate with carbon monoxide in the absence of potassium formate may be understood in terms of the absence of liquid phase in the reaction mixture.

Mechanism of the Carboxylation Reaction.—To elucidate the course of reaction 1, the behavior of dipotassium salicylate under the present reaction conditions was examined (Table II).

TABLE II

CARBOXYLATION OF DIPOTASSIUM SALICYLATE[a]

Solvent, HCO_2K, mol	Temp, °C	Time, hr	Yield of product,[d] %		
			SA	*p*-HBA	4-HIPA
0[b]	175	5.0	95	0	3
	240	0.4	4	90	2
	240	5.0	0	93	5[e]
0.025[c]	170	5.0	86	5	7
	170	20.0	57	25	16
	240	0.4	0	93	2
	240	5.0	0	92	4

[a] The reagents were 0.050 mol of dipotassium salicylate and 0.050 mol of potassium carbonate. [b] The initial pressure of CO was 80 atm. [c] The initial pressure of CO was 60 atm. [d] SA, salicylic acid; *p*-HBA, *p*-hydroxybenzoic acid; 4-HIPA, 4-hydroxyisophthalic acid. [e] Mainly hydroxytrimesic acid.

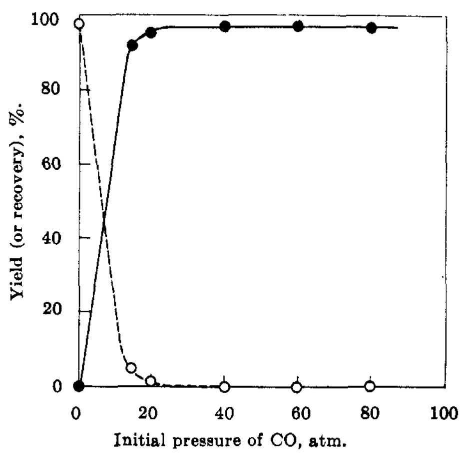

Figure 3.—Yield of *p*-hydroxybenzoic acid (—●—) and recovery of PhOH (- -○- -) as a function of initial pressure of CO. A mixture of 0.050 mol of PhOK and 0.050 mol of K_2CO_3 was heated under an appointed initial pressure of CO at 240° for 3 hr.

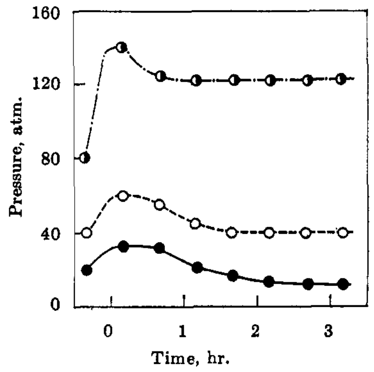

Figure 4.—Reaction velocity expressed by change of CO pressure as a function of the initial CO pressure (—●—, 20 atm; - -○- -, 40 atm; - · -◑- · -, 80 atm). For the reaction conditions, see Figure 3.

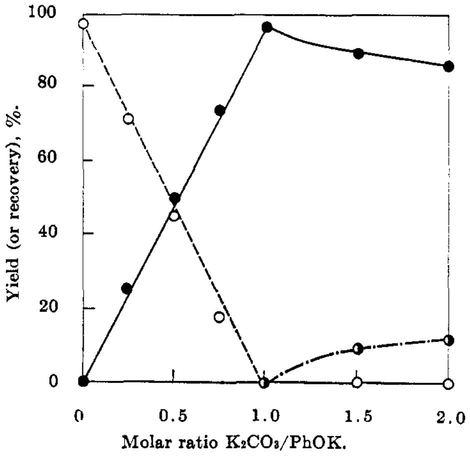

Figure 5.—Yield of *p*-hydroxybenzoic acid (—●—) and 4-hydroxyisophthalic acid (- -○- -) and recovery of PhOH (- · -◑- · -) as a function of molar ratio of K_2CO_3 to PhOK. A mixture of 0.040 mol of PhOK and an appointed amount of K_2CO_3 was heated under the initial pressure (50 atm) of CO at 240° for 5 hr.

At temperatures below 175°, the yield of *p*-hydroxybenzoic acid obtained by the rearrangement of dipotassium salicylate was much lower than that by the carboxylation of potassium phenoxide, irrespective of the presence of potassium formate. These results lead to the conclusion that most of *p*-hydroxybenzoic acid was formed by the direct *para* carboxylation, at least at temperature below 175°.

At 240°, where dipotassium salicylate rearranges rapidly to the *para* isomer in the Kolbe–Schmitt reaction,[7-9] the rapid rearrangement was also observed accompanied with small extent of the polycarboxylation. Since the rearrangement is inhibited at the same temperature in the presence of 1 mol of potassium hydroxide[10,11] (or methoxide[8,10]) in the Kolbe–Schmitt reaction, the carboxylation was examined also in the presence of potassium hydroxide. The potassium hydroxide, however, reacted smoothly with carbon monoxide to give potassium formate.[12,13] Therefore, at 240° a possibility of the initial *ortho* carboxylation was not thoroughly avoided.

The assumption that potassium oxalate is an intermediate carboxylating agent of potassium phenoxide should be abandoned, because both were recovered on heating them together at 250° for 6 hr.

Experimental Section[14]

Reagents.—Potassium phenoxide, dipotassium *p*-hydroxybenzoate, and potassium formate were prepared by neutralization of aqueous *n*-propyl alcohol or aqueous *n*-butyl alcohol solutions, followed by distillation of solvents to yield crystals, and drying the crystals at 130° *in vacuo* (N_2, 20 mm). Dipotassium salicylate was difficult to crystallize, and so was prepared by drying an aqueous methanol solution at 150° *in vacuo*. The absence of *p*-hydroxybenzoic acid which may be formed by the thermal rearrangement on drying was confirmed by extraction of the regenerated acid with chloroform.[15] High purities (97–98%) were proved by potentiometric titration (and gravimetry of the regenerated acid) in all cases. Potassium oxalate was used after drying the commercial monohydrate at 160° *in vacuo*. Potassium carbonate and carbon monoxide (Matheson Co.) were used without further purification.

Procedure.—The pulverized reagents (usually 0.050 mol of potassium phenoxide and 0.050 mol of potassium carbonate) were mixed well, and then put into a glass vessel having a coiled capillary vent together with a steel ball. The vessel, after evacuation (N_2, 2–20 mm) at 150° for 5 hr, was placed in an autoclave (*ca.* 100 ml). The autoclave was filled with carbon monoxide to an appointed pressure at room temperature. Then the autoclave was settled in an aluminum block heater regulated within $\pm 2°$ and agitated vigorously. About 20 min were required to bring the temperature of the autoclave constant.

After heating for an appointed time, the autoclave was withdrawn and the gas pressure was recorded. The pressure drop reflecting usually the extent of the carboxylation. The gas was submitted to gas chromatography [column of activated charcoal (2 m, 90°), carrier gas, He (50 ml/min)] and proved usually to consist of carbon monoxide with only a trace amount of carbon dioxide.

The glass vessel was weighed and the increase of the weight was generally equal to the amount of absorbed carbon monoxide. The crude product under the typical reaction conditions (0.050 mol of PhOK, 0.050 mol of K_2CO_3, 50 atm of CO, 240°, 5 hr) showed practically the same ir spectra and also the same titration curve as an equimolar mixture of dipotassium *p*-hydroxybenzoate and potassium formate.

Isolation and Analysis of Product.—The reaction mixture was dissolved in 50 ml of water and neutralized to pH 9.0 with 6 *N* sulfuric acid, and the regenerated phenol was extracted with ether. The solid phenol (identified by the ir spectra), obtained after evaporation of the solvent and drying, was weighed.

After acidification with 12 *N* sulfuric acid to pH 1.0, the aqueous solution was extracted again with ether. The crude *p*-hydroxybenzoic acid, obtained from the ether extract, was weighed, and its melting point and ir spectra were determined. The crude acid usually melted at 208–212°, and showed the practically identical ir spectra with that of the pure acid. After recrystallization of the crude acid from water and drying *in vacuo* (N_2, 10 mm) at 130° for 8 hr, *p*-hydroxybenzoic acid melted at 213–214° (lit.[16] mp 213–214°).

Anal. Calcd for $C_7H_6O_3$: C, 60.86; H, 4.38. Found: C, 60.92; H, 4.45.

Separation of the other acid from the crude *p*-hydroxybenzoic acid, if necessary, was carried out as follows. Salicylic acid was extracted with 160 ml of chloroform[15] from 50 ml of an aqueous suspension of the crude acid, and 4-hydroxyisophthalic acid was separated from the aqueous solution of *p*-hydroxybenzoic acid by fractional recrystallization.[17,18] Salicylic acid and 4-hydroxyisophthalic acid thus obtained were identified by the mixture melting points with authentic samples and by the ir spectra. In certain cases (for example, dipotassium *p*-hydroxybenzoate, 0.050 mol; K_2CO_3, 0.050 mol; HCO_2K, 0.050 mol; CO, 50 atm, 240°, 24 hr), hydroxytrimesic acid, mp 304–306° (crystallized from water, lit.[16] mp 306°), was isolated together with 4-hydroxyisophthalic acid.

Anal. Calcd for $C_9H_6O_7$: C, 47.80; H, 2.67. Found: C, 48.23; H, 2.81.

In some cases, formic acid was titrated potentiometrically in the following manner. The aqueous solution of the reaction product, after removal of the regenerated phenol, was acidified to pH 1.0 and extracted exhaustively with ether. The extract was titrated with 0.5 N sodium hydroxide in aqueous ethanol. The yield of formic acid was calculated from the difference between the total amount of formic acid and *p*-hydroxybenzoic acid which was determined from the end point of the titration, and the amount of *p*-hydroxybenzoic acid weighed by the above procedure. Generally the yield of formic acid was equal to that of *p*-hydroxybenzoic acid. Formic acid (bp 100–101°) was isolated from the aqueous solution, from which *p*-hydroxybenzoic acid had been removed, by exhaustive extraction with ether and fractional distillation; the ir spectra was consistent with that of an authentic sample; the **anilide**[19] had mp 46–48° (lit.[20] mp 50°).

Anal. Calcd for C_7H_7NO: C, 69.40; H, 5.83; N, 11.57. Found: C, 69.25; H, 5.89; N, 11.62.

Registry No.—Carbon monoxide, 630-08-0; potassium carbonate, 584-08-7; potassium phenoxide, 100-67-4; *p*-hydroxybenzoic acid, 99-96-7.

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(20) See ref 16, p 1456.