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A Study of the Mechanism of the Carboxylation of Potassium Phenoxide by Means of the Carbon-14 Tracer Technique[1]

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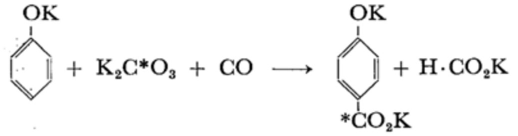
A novel synthesis of *p*-hydroxybenzoic acid from potassium phenoxide, potassium carbonate, and carbon monoxide has previously been reported.[2] The reaction mechanism has, however, not yet been established, it has not been made clear whether the carboxyl group of *p*-hydroxybenzoic acid is derived from either potassium carbonate or carbon monoxide. In the present study, potassium carbonate ^{14}C is used to throw light on the mechanism.

Results and Discussion

The radioactivities of the two products, *p*-hydroxybenzoic acid and formic acid, are listed in Table 1. The results lead to the conclusion that the carbon atom of potassium carbonate attacks the phenoxide nucleus and that carbon monoxide is converted into potassium formate:



Since this reaction proceeds almost quantitatively, and since most of the carboxyl group seems to be introduced directly into the position *para* to the hydroxyl group,[2,3] a possible mechanism of the reaction is:

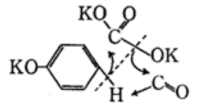


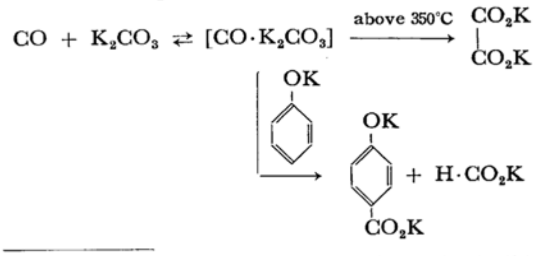
TABLE 1. RADIOACTIVITIES OF *p*-HYDROXYBENZOIC ACID AND FORMIC ACID PRODUCED FROM POTASSIUM CARBONATE-^{14}C

Sample* mg	Radioactivity dpm	Specific activity μCi/mg
p-HBA: 2.92	50.17×10^4	7.8×10^{-2}
0.50	8.71×10^4	7.9×10^{-2}
FA: 56	9.13×10^4	7.4×10^{-4}

* *p*-HBA: *p*-hydroxybenzoic acid
FA: formic acid

It is rather difficult to postulate that the termolecular complex is directly formed in such a smooth reaction. To study the mechanism of this reaction in detail, the reaction of potassium carbonate with carbon monoxide,[4] that of potassium phenoxide with carbon monoxide, and that of potassium phenoxide with potassium carbonate were each examined at 250 and 350°C. Among these six cases, only in the case of potassium carbonate with carbon monoxide at 350°C was a chemical change observed. Oxalic acid (1.2 g, 11%) was obtained from 13.8 g of potassium carbonate under an initial carbon monoxide pressure of 90 kg/cm² (at room temperature) after 6 hr. By analogy with the Kolbe-Schmitt reaction,[5] the formation of a complex of potassium phenoxide and carbon monoxide might be suggested. However, in view of the facts described above, together with the fact that phenol itself can also be carboxylated with potassium carbonate under a carbon monoxide atmosphere,[6] such a possibility may be ruled out in this case.

Thus, the following assumption is the most probable. First, potassium carbonate and carbon monoxide form a complex, which may be a precursor of dipotassium oxalate. Secondly, the complex reacts with potassium phenoxide, and dipotassium *p*-hydroxybenzoate and potassium formate are formed:



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[1] Carboxylation by Alkali Salts and Carbon Monoxide. IV. Paper III: Y. Yasuhara and T. Nogi, *Chem. & Ind. (London)*, **1969**, 77.

[2] Y. Yasuhara and T. Nogi, *Chem. & Ind. (London)*, **1967**, 229.

[3] Y. Yasuhara and T. Nogi, *J. Org. Chem.*, **33**, 4512 (1968).

[4] C. Matignon and C. Faurholt, *Compt. Rend.*, **179**, 273 (1923).

[5] J. L. Hales, J. I. Jones and A. S. Lindsey, *J. Chem. Soc.*, **1954**, 3145.

[6] T. Nogi and Y. Yasuhara, in preparation.

The results shown in Table 1 indicate also that the exchange of the carboxyl group between dipotassium *p*-hydroxybenzoate and potassium formate is very slow. This is in contrast to the Kolbe-Schmitt reaction,[7] in which an appreciable exchange of the carboxyl group between dipotassium salicylate and potassium carbonate accompanies the rearrangement, and to the Henkel process,[8] in which the exchange between dipotassium phthalate and potassium carbonate takes place through carbon dioxide in the gas phase. However, it is not obvious whether such different results come from differences, alone or in combination, in the temperatures, in the atmospheres (CO and CO_2), or in the reagents (the formate and the carbonate).

Experimental

Materials. The potassium phenoxide was prepared by neutralizing phenol with potassium hydroxide in *n*-propanol. After filtration the crystals were dried at 130°C *in vacuo* (N_2, 20 mmHg). Potassium carbonate-^{14}C was prepared by heating a mixture of 6.9 g of potassium carbonate and 9.0 m*l* of an aqueous solution containing *ca.* 1 mCi of sodium carbonate-^{14}C (the Radiochemical Centre, England) to dryness.

Procedure. A glass vessel containing potassium phenoxide (6.6 g) and potassium carbonate-^{14}C (6.9 g) was placed in a stainless-steel autoclave (*ca.* 100 m*l*) and then dried *in vacuo* (N_2, 10 mmHg) at 220°C for 5.5 hr. The autoclave was then filled with carbon monoxide at a pressure of 85 kg/cm^2 (initial, at room temp.) and heated at 240—250°C for 6.0 hr (20 min preheating). The product was dissolved into 50 m*l* of water, and then the solution was acidified to pH 9.0 with 6N sulfuric acid. The regenerated phenol was extracted with ether. After further acidification with 12N sulfuric acid to pH 1.0, the aqueous solution was extracted again with ether. From the ether extract *p*-hydroxybenzoic acid was obtained, and, after treatment with activated charcoal, recrystallization from water, and drying, 3.0 g of purified *p*-hydroxybenzoic acid (mp 211—213°C) was recovered. Formic acid (bp 100—101°C) was obtained from the aqueous solution by exhaustive extraction with ether and fractional distillation. The reactions of three pairs, potassium carbonate and carbon monoxide, potassium phenoxide and potassium carbonate, and potassium phenoxide and carbon monoxide, were carried out analogously to that described above.

The radioactivities of *p*-hydroxybenzoic acid (in dioxane) and formic acid (in toluene) were measured on a Tracerlab LSC-20A liquid scintillation counter.

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7) S. E. Hunt, J. I. Jones, A. S. Lindsey, D. C. Killoh and H. S. Turner, *J. Chem. Soc.*, **1958**, 3152.

8) S. Furuyama, This Bulletin **40** 1212 (1967).