The Mechanism of the Oxidative Decarboxylation of Benzoic Acid*

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The oxidative decarboxylation of benzoic acids with copper has been known as a method to produce phenols.[1] Although its precise mechanism is not clear, it has been suggested that the reaction involves the initial formation of cupric benzoate between two molecules of benzoic acid and cupric oxide, followed by the intramolecular attack of the carboxyl oxygen at the ortho-position of the other benzene ring, producing, via the equilibrium formation of a six-membered cyclic intermediate, phenyl benzoate, which is presumed to be the precursor of phenol.[2] In this case the oxygen atom of the phenol formed is expected to come from the carboxyl group. Meanwhile, if salicylic acid is formed by the pyrolysis of basic cupric benzoate,[3] the oxygen atom of the resulting phenol is likely to come from the water used. Another possibility is that the oxygen atom in the resulting phenol originates in the air. Thus, we have undertaken the pyrolysis of ^{18}O-labeled benzoic acid and traced the origin of the oxygen atom in the resulting phenol.

Experimental

Benzoic Acid Labeled with ^{18}O.—A mixture of 3.5 g. of benzoyl chloride and 2 ml. of $H_2{}^{18}O$ was refluxed until no hydrogen chloride gas evolved. After the mixture had then cooled, colorless crystalline

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[*] Phenols and Phenolic Esters. Paper X.

[1] W. W. Kaeding, R. O. Lindblom and R. G. Temple, *Ind. End. Chem.*, **53**, 805 (1961).

[2] W. G. Toland, *J. Am. Chem. Soc.*, **83**, 2507 (1961).

[3] W. W. Kaeding and A. T. Schulgin, *J. Org. Chem.*, **27**, 3551 (1962).

precipitates were filtered, washed with a small amount of water, and then recrystallized from water. The yield was 2.6 g. (84.9%); m. p. 123°C.

The Decarboxylation of ^{18}O-Labeled Benzoic Acid.—The apparatus used for the reaction is shown in Fig. 1. In a generator an air-steam mixture was prepared by bubbling air into hot water. The air-steam mixture was thus generated at the rate of 0.5—0.6 l./hr., the temperature of the water being kept at 80—90°C. As a reaction vessel, it is convenient to use a three-necked flask equipped with an air-steam-mixture-inlet tube, a thermometer, and a reflux condenser packed with glass beads and heated by an electric furnace, the temperature being kept at 130—140°C. The upper end of the reflux condenser was connected to a receiver. Phenol, water and other volatile products were collected in a receiver, and the carbon dioxide generated was entrapped by passing it through a barium hydroxide solution. A typical run for decarboxylation was as follows. In a reaction vessel, a mixture of 2.0 g. of ^{18}O-labeled benzoic acid, 40 mg. of cupric oxide and 68 mg. of magnesium oxide was charged and heated to 230—240°C by stirring it with a magnetic stirrer. The air-steam mixture was then introduced. After treatment for 5 hr., an excess of bromine water was added to the receiver flask. By this method, 1.5 g. of tribromophenol was obtained, in a 29% yield, when mixed with an authentic sample, its melting point did not drop. A brownish residue in a reaction vessel was washed with water and ether. Crude benzoic acid (0.95 g.) was thus recovered, while phenyl benzoate was obtained as a by-product. The overall yield was 53%.

^{18}O-Analysis.—^{18}O analyses of phenol, the recovered benzoic acid and carbon dioxide were carried out as usual by changing each sample into carbon dioxide gas, which was then subjected to mass spectrometry.

The Reaction of Phenol with Water.—Control experiments were carried out in order to test the oxygen exchange between phenol and $H_2{}^{18}O$ under the same reaction conditions. After phenol had been recovered as its 2, 4, 6-tribromide, the ^{18}O-content of the phenol was analyzed by the same procedure. The ^{18}O-concentration was found to be 0.20 atom%, which is that of the natural abundance of ^{18}O. The results showed no ^{18}O exchange between phenol and water.

Discussion

The analytical data on the ^{18}O content of the resulting phenols and benzoic acids, both those initially-employed and those recovered, are summarized in Table I.

Most of the ^{18}O initially-labeled in the carboxyl group was found in the phenol produced, except when the reaction was carried out with the extensive introduction of a steam. However, in every run, a small decrease in the ^{18}O content of the products was observed, especially in the recovered benzoic acid. This is presumably because of an oxygen exchange between ^{18}O-labeled benzoic acid and water during the reaction. These observations are clearly in accord with the mechanism involving the formation of phenol via the cyclic intermediate. As is shown by the run 3 in Table I, the intervention of another possible reaction, i e., that of the basic salt of benzoic acid, is conceivable in this case, since the basic salt is presumably formed quite readily in the presence of an excess of water. Accordingly, it seems that only a minor portion of the reaction proceeds through a path involving the basic salt, while the major part of the reaction proceeds through an ordinary process with cupric salt of benzoic acid, with the ^{18}O concentration gradually reduced during the reaction.

TABLE I. ^{18}O CONTENTS OF BENZOIC ACID AND PHENOL IN THE DECARBOXYLATION OF ^{18}O-LABELED BENZOIC ACID (^{18}O-atom%)

Run	Benzoic acid		CO_2	Phenol
	Initial	Recovered		
1[a)]	1.05	0.93	0.81	1.02
2[a)]	1.25	0.99	—	1.01
3[b)]	0.87	0.46	0.33	0.42

a) The reaction was carried out at 230—240°C for 5 hr.

b) A large excess of steam was passed through the vessel, and the reaction was performed at 230—240°C for 10 hr.

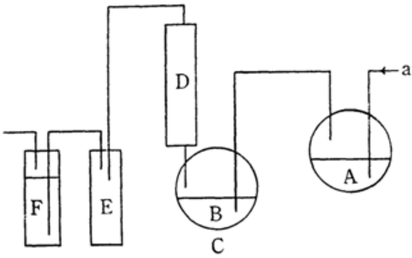

Fig. 1. Apparatus.

A Hot water
B Reacter
C Hotting stirrer
D Reflux condenser
E Product receiver
F CO_2 trap