The Mechanism of the Formation of Terephthalic Acid from Benzonitrile*

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It has been claimed by Henkel and Cie[1] that terephthalic acid can be obtained by the reaction of benzonitrile and potassium carbonate in either the presence or absence of a cadmium catalyst.

Although the reaction seems to proceed by way of benzoic acid, it is curious that the reaction proceeds even in the absence of a catalyst, since it has been known that benzoic acid cannot give an appreciable amount of terephthalic acid under the same conditions.

Moreover, the stoichiometry of the reaction and the cleaving bond in $C_6H_5-C\equiv N$ are still not clear. The present paper will describe the results of our mechanistic study by means of a tracer study with radioactive carbonate and also the results of a study of reaction products together with the effect of conditions on the composition of the products.

Experimental

Typical Procedure for the Preparation of Terephthalic Acid from Benzonitrile. — An intimate mixture of benzonitrile (1.0 g., 0.01 mol.), finely powdered dry potassium carbonate (2.76 g., 0.02 mol.) and cadmium iodide (0.50 g., 0.00137 mol.) was placed in a sealed tube. The tube was enveloped with glass wool and placed in an autoclave together with toluene (ca. 30 ml.) in ordor to balance the internal pressure of the tube. The reaction was carried out at 360~500°C for 2.5~7 hr. The product was extracted with petroleum

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[1] a) Henkel and Cie, DAS 1027656 (1958); Brit. Pat. 808894 (1959). b) Henkel and Cie, DAS 1051841 (1959); U. S. Pat. 2913488 (1959). c) Henkel and Cie, DAS 1053491 (1959); U. S. Pat. 2866815 (1958).

TABLE I. YIELDS OF TEREPHTHALIC ACID FROM BENZONITRILE, POTASSIUM BENZOATE OR BENZAMIDE
Reaction time, 2.5 hr. except a)

Reactant				Reaction temp. °C	Product Yield of terephthalic acid	
C_6H_5CN g.	K_2CO_3 g.	CdI_2 g.	KOCN g.		mg.	%
1.0	2.76	0.50	—	490	267.0	33.1
1.0	2.76	0.50	—	490[a]	265.6	33.0
1.0	2.76	0.50	0.81	490	173.6	21.5
1.0	1.38	—	0.81	460	63.8	8.0
$C_6H_5CO_2K$ g.						
1.6	2.76	0.50	—	490	276.4	34.3
1.6	1.38	—	0.81	490	63.5	7.9
1.6	—	—	0.81	470	83.5	10.4
$C_6H_5CONH_2$ g.						
1.21	2.76	0.50	—	490	69.6	8.6
1.21	2.76	0.50	—	490[a]	85.8	10.7

a) Reaction time, 7.0 hr.

ether (20 ml.), and the extract was analyzed to determine the benzonitrile and benzoic acid contents. The benzonitrile was identified by ultraviolet spectrography and by hydrolysis to benzoic acid; m. p. and mixture m. p. 122.5°C. Benzene was identified by ultraviolet spectrography and by nitration to *m*-dinitrobenzene; m. p. and mixture m. p. 88°C. The residual solid of the extraction was dissolved in hot water (100 ml.), filtered, acidified with hydrochloric acid, and again filtered while hot. The precipitate after drying gave terephthalic acid, which on esterification gave dimethyl terephthalate, m. p. and mixture m. p. 140°C. The filtrate was extracted with ether, the extract after the evaporation of the ether being washed with chloroform to extract benzoic acid alone, separating it from the residual isophthalic and terephthalic acids. The results are shown in Table I, together with the results of terephthalic acid formation from benzoic acid and benzamide.

The Estimation of Isophthalic and Terephthalic Acids in the Products.—Ultraviolet spectrophotometry was used. The reaction mixture was dissolved in hot water (100 ml.). The filtered solution was acidified and filtered after cooling. The precipitate after drying was analyzed for isophthalic and terephthalic acids contents by means of ultraviolet spectrophotometry by measuring the extinction at the wavelength of 284.7 mμ (for terephthalic acid) or of 280.5 mμ and 288.4 mμ (for isophthalic acid).[2] These data, shown in Table III, are of special interest in connection with the effect of potassium cyanate on the ratio of isophthalic acid to terephthalic acid in the product.

The Formation of Benzonitrile from Benzoic Acid and Potassium Cyanate. — A mixture of potassium benzoate (1.6 g., 0.01 mol.) and potassium cyanate (0.81 g., 0.01 mol.) was heated in a sealed tube at 470°C for 2.5 hr. Terephthalic acid (83.5 mg.) was obtained. The other products were analyzed by gas chromatography employing a Yanagimoto Model GCG-220 operated with a 1.3 m. column packed with Silicone D. C. 703 using helium with a flow rate of 28.4 ml./min. at 80°C for benzene (367 mg.) and of 31.25 ml./min. at 150°C for benzonitrile (13.8 mg., 1.4%). The retention times were 3.66 min. for benzene and 7.4 min. for benzonitrile. Quantitative determinations were made using the corresponding authentic sample as an internal standard.

The Formation of Terephthalic Acid from Benzamide.—A mixture of benzamide (1.21 g., 0.01 mol.), cadmium iodide and potassium carbonate was heated under the same conditions as above and worked up similarly. The results are shown in Table I.

Tracer Experiments.—Labeled carbon dioxide-^{14}C was evolved by hydrochloric acid from labeled barium carbonate obtained from the Isotope Center of Japan and absorbed in an aqueous solution of a calculated amount of potassium hydroxide. The solution was then evaporated to dryness in a vacuum, yielding labeled potassium carbonate. The method for the isolation of the product was the same as that given as a typical procedure above. The radioactivities of samples were expressed as those of the corresponding barium carbonates. All the data in Table II are averages of duplicate experiments; they have been calibrated for their background against standard barium carbonate.

Results and Discussion

The product from the cadmium salt-catalyzed reaction of benzonitrile with potassium carbonate was found to contain benzoic, isophthalic and terephthalic acids, together with benzene and potassium cyanate. Potassium was identified by converting it with aniline hydrochloride to phenylurea; m. p. and mixture m. p. 147°C.

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[2] N. Berman, C. H. Ruof and H. C. Howard, *Anal. Chem.*, 23, 1882 (1951).

It was confirmed by gas chromatography that potassium cyanate and benzoic acid can form a small quantity of benzonitrile. Therefore, the stoichiometric equation may be:

$$C_6H_5CN + K_2CO_3 \rightleftharpoons C_6H_5COOK + KOCN$$

$$2\,C_6H_5COOK \rightarrow p\text{- and } m\text{-}KOOC\text{–}C_6H_4\text{–}COOK + C_6H_6$$

Here, the first step is reversible, and the second step is a disproportionation of the benzoic acid formed which has been confirmed by a tracer study previously reported.[3]

However, it is still strange that the conversion of bonzonitrile to potassium terephthalate is possible without a cadmium catalyst. It is probable that the potassium cyanate formed behaves as a catalyst for the terephthalate synthesis, since it was observed that the added potassium cyanate possessed a slight catalytic ability to convert potassium benzoate to terephthalate (Table I).

It is apparent that potassium cyanate has the effect of increasing the ratio of isophthalic to terephthalic acid in the product (Table III). The meta : para ratio becomes exceptionally small in the presence of a cadmium catalyst (Table III).

The tracer experiments with cadmium iodide and $K_2{}^{14}CO_3$ indicated that only 1/10.72 of the original activity was incorporated in the terephthalate produced from normal benzonitrile. The extent of the incorporation was very close to the value (1/10.63) obtained in conversion of potassium benzoate to terephthalate with $K_2{}^{14}CO_3$ and CdI_2 in a sealed tube under the same conditions. Since radioactivities were detected in the recovered benzoate in the cadmium-catalyzed conversion of benzonitrile or potassium benzoate to potassium terephthalate, the labeled carbon is introduced by the exchange of the carboxylate group in the benzoate.

Table II. Tracer experiments for the conversion of benzonitrile or potassium benzoate to benzoic acid and/or terephthalic acid

Reaction time, 2.5 hr.

Reactant[a]	(g.)	Temp. °C	Product counted	Radioactivity c.p.m.
C_6H_5CN	(0.5)[b]	490	Benzoic acid	24
$C_6H_5CO_2K$	(0.8)[b]	490		5
C_6H_5CN	(0.5)	360		4
C_6H_5CN	(0.5)	425		3
$C_6H_5CO_2K$	(0.8)	425		3
$C_6H_5CO_2K$	(0.8)	490		100
C_6H_5CN	(0.5)	490		211
$C_6H_5CO_2K$	(0.8)	490	Terephthalic acid	244
$C_6H_5CO_2K$	(0.8)	490		246

a) 1.38 g. of $K_2{}^{14}CO_3$ (2616 c.p.m. as $Ba^{14}CO_3$) and 0.25 g. of CdI_2 were added to the reactants.

b) Without cadmium iodide.

Table III. The effect of potassium cyanate on the ratio of isophthalic acid to terephthalic acid

Reaction time, 2.5 hr.

Starting material $C_6H_5CO_2K$ 1.60 g.

KOCN g.	m-C_6H_4-$(CO_2K)_2$ mg.	p-C_6H_4-$(CO_2K)_2$ mg.	m/p ratio	Temp. °C
0.41	166	134	1.24	475
0.81	212	123	1.72	475
1.62	217	119	1.82	475
4.05[a]	48	183	0.26	480

a) 0.30 g. of CdI_2 was added.

In spite of the description of the pertinent Patent,[1] the yield of potassium terephthalate from benzamide at 490°C in a sealed tube under the same conditions was low; this implies that the reaction of benzonitrile to the terephtalate may not proceed via benzamide. The formation of terephthalic acid from benzamide, claimed in the patent,[1] may be the result of the formation of benzonitrile from benzamide by dehydration.

These facts suggest that the reaction of benzonitrile with potassium carbonate to form terephthalate is a conversion to potassium benzoate, followed by disproportionation. Here, the carboxylate group of benzoate may be exchanged with carbonate in the presence of a cadmium catalyst:

$$C_6H_5COOK \underset{(Cd^{2+})}{\overset{^{14}CO_3{}^{2-}}{\rightleftarrows}} C_6H_5{}^{14}COOK$$

There seems to be no chance for the introduction of a carboxyl group from outside carbonate or carbon dioxide except at the exchange in benzoate. The extent of the exchange of carboxylate groups increases with an increase in the reaction temperature, and the exchange is catalyzed by cadmium salts. It is of interest to note that the exchange is impossible without a cadmium catalyst and that this situation is different from that of phthalate, where the exchange is possible without cadmium salt.[3a]

Summary

A mixture of benzonitrile, cadmium iodide and potassium carbonate has given, when heated in a sealed tube at 360~500°C, terephthalic acid (21~33%), together with a considerable amount of isophthalic acid. The

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[3] a) Y. Ogata, M. Tsuchida and A. Muramoto, *J. Am. Chem. Soc.*, **79**, 6005 (1957); b) Y. Ogata. *Chem. & Chem. Ind. (Japan)*, **11**, 148 (1958); c) Y. Ogata, M. Hojo and M. Morikawa, *J. Org. Chem.*, **25**, 2082 (1960).

reaction was possible without a cadmium catalyst, but the yield of terephthalic acid was poorer (8.0%). The tracer study with $K_2{}^{14}CO_3$, as well as the identification of cyanate in the products, showed that the reaction proceeds by way of the conversion of benzonitrile to potassium benzoate and potassium cyanate, followed by the disproportionation of potassium benzoate to potassium terephthalate and isophthalate. Potassium cyanate seems to be a weak catalyst for the disproportionation.

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