

Reactions of Salts of Deuterated Benzene-carboxylic Acids *

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SUMMARY

The course of transcarboxylation reactions of potassium salts of deuterated benzenecarboxylic acids was investigated. During the reaction rapid random exchange of hydrogen atoms of the benzene ring for deuterium takes place. The probable mechanism of this exchange, which involves the liberation of protons from the benzene ring and the formation of carbanions, is proposed. The mechanism of the deuterium for hydrogen exchange is in agreement with the intermolecular ionic mechanism of the transcarboxylation reaction itself since the formation of carbanions via liberation of protons is a part of this reaction.

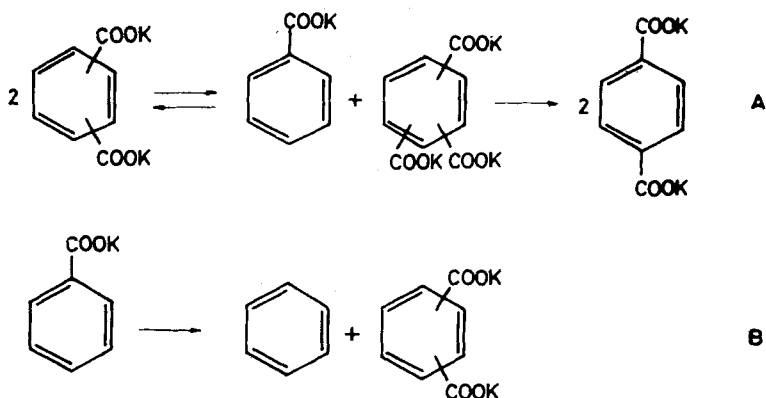
INTRODUCTION

The thermic transformations of salts of aromatic carboxylic acids, especially of benzenecarboxylic acids have acquired recently great industrial importance. These reactions were studied first by Raecke ⁽¹⁾ and later by a number of authors ⁽²⁻¹⁴⁾. Some of them postulated the mechanism of the reaction to be an intramolecular rearrangement ⁽⁶⁻⁸⁾ while others proposed an intermolecular mechanism ^(3, 4, 9-13).

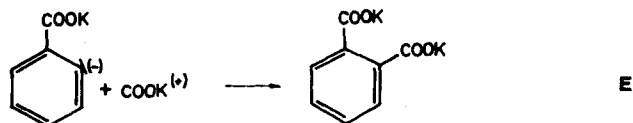
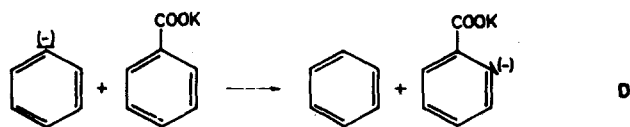
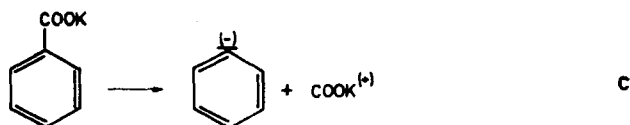
We have also studied the mechanism of these reactions and we have been able to show that the mechanism of transcarboxylation of salts of aromatic carboxylic acids involves intermolecular ionic transport of the carboxylate

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group from one aromatic ring of the salt to the other in cycles repeated many times⁽⁹⁻¹¹⁾. Thus, e.g. in the simplest case of alkaline salts of benzenecarboxylic acids, the salts of all isomeric benzenedicarboxylic acids, benzenetricarboxylic acids, and of benzoic acid are formed as intermediates during the reaction following a defined time dependence (equation A, B).



We have also shown⁽⁹⁻¹¹⁾ that these transcarboxylation reactions proceed by a mechanism of ionic decarboxylation-recarboxylation with the formation of carbanions as precursors of newly-formed salts of carboxylic acids. These carbanions arise in two different manners, (a) by liberation of a carboxylate cation (e.g. according to equation C in the case of potassium benzoate), and



(b) by the action the formed carbanion which—being an extremely strong base—tears off a proton from another molecule of salt and combines with it. By the removal of the proton the molecule of salt becomes a new carbanion (equation D) which combines with the carboxylate cation and affords the salt of a new acid (equation E).

Hence, the transcarboxylation of salts of carboxylic acids consists essentially of the following reactions: decarboxylation-recarboxylation (equations C, E) and liberation-addition of protons (equation D). It is probable that these reactions will proceed in parallel at different rates.

EXPERIMENTAL

STARTING MATERIAL.

D₂O was a 99.7 % product of C. Roth, Karlsruhe.

POTASSIUM PHTHALATE-d₄.

The compound was prepared from G. R. potassium phthalate by exchange reaction with D₂O. A modification of the method of Brown and Garnett ⁽¹⁶⁾ was employed, involving a simplified preparation of the catalyst, Pt-black from PtO₂. For the reduction of PtO₂ (0.3 g), hydrogen in D₂O (4 ml) was used instead of deuterium. After the hydrogenation had been discontinued, D₂O mixed with H₂O formed during the reaction was removed by suction and the catalyst was washed quickly with two 2-ml portions of D₂O. The catalyst together with 3.0 g of potassium phthalate and 40 ml of D₂O (ratio H : D = 1 : 80.6) was placed in a glass tube of 20 mm internal diameter which was tapered at the upper end. Hydrogen was removed from the catalyst by evacuating the tube at 20° C and 10 mm Hg for 15 minutes. The tube was sealed off while being evacuated and the ampule was heated without stirring 27 hours at 130° C. After the reaction had been discontinued, the catalyst was filtered off. To the solution a small amount of active charcoal was added, the solution was again filtered, and D₂O was evaporated. The product was dried and potassium phthalate-d₄ (3.0 g) containing 97.9 % of deuterium was isolated. The extent of the exchange was 99.1 %. The results of mass spectrographic analysis of the methyl ester of the product are given in Table I. The product without any additional purification was analyzed in the form of its methyl ester by gas chromatography ⁽¹⁵⁾ and was found to contain 99.6 % of dimethylphthalate and 0.4 % of methylbenzoate. This example shows that (1) D₂O can be used without any protection against atmospheric moisture provided the operation is carried out quickly, and (2) the catalyst, Pt-black, can be prepared from PtO₂ using hydrogen instead of deuterium without any decrease in deuterium content of the final product.

POTASSIUM BENZOATE- d_5 .

The compound was prepared by the procedure used for the preparation of potassium phthalate- d_4 by heating 4.8 g of G. R. potassium benzoate, 40 ml of D_2O (ratio H : D = 1 : 26.1), and Pt-black (0.5 g) at 130° C without stirring 29 hours. The product was treated as described for the preceding compound. Potassium benzoate- d_5 containing 95.6 % of D was obtained. The extent of hydrogen for deuterium exchange was 99 %. The melting point of free benzoic acid was 120° C. The analysis of the methyl ester of the product by gas chromatography showed the purity of methyl benzoate to be 100 %. The results of mass spectrographic analysis of the methyl ester of the product are given in Table I.

POTASSIUM TEREPHTHALATE- d_4 .*Method A.*

Potassium benzoate- d_5 (95.6 % of D, 3.2 g) and CdI_2 (0.16 g) were heated at 425° C for 15 minutes in the atmosphere of CO_2 . After the end of the reaction and treatment of the product, 0.75 g of benzene- d_6 (95.03 % of D) and 1.5 g

TABLE 1. Composition of Starting Compounds ^a.

No.	Compound	Mass Spectrum %					
		d_0	d_1	d_2	d_3	d_4	d_5
1.	BK- d_5 (95.6 % D)	0	0	0	1.6	18.7	79.7
2.	TK ₂ - d_4 (95.85 % D)	0	0	1.7	15.6	83.3	—
2a.	TK ₂ - d_4 (97.7 % D)	0	0	0	8.4	91.4	—
3.	FK ₂ - d_4 (97.9 % D)	0	0	0	8.4	91.6	—
4.	B- d_6 ^b (91.5 % D)	0	0	0	1.1	8.4	33.4
5.	B- d_6 (95.03 % D)	0	0	0	0	3.1	23.6
6.	BK- <i>o</i> - d_1	3.74	92.0	4.0	0	0	0

^a Abbreviations : BK : potassium benzoate, FK₂ : potassium phthalate, IK₂ : potassium isophthalate, TK₂ : potassium terephthalate, B : benzene, MB : methylbenzoate, DMT : dimethylterephthalate, DMI : dimethylisophthalate, DMF : dimethylphthalate, DMB : dimethyl esters of a mixture of isomeric benzenedicarboxylic acids, TMTs : trimethyltrimesinate, TMTI : trimethyltrimellitate, TMHe : trimethylhemimellitate.

^b Commercial preparation.

TABLE II. Composition of Deuterated Reaction Products after the Transcarboxylation Reaction (*).

Experiment No.	Starting Compound ^a	Reaction Time min	Products	Mass Spectrum %						
				d_0	d_1	d_2	d_3	d_4	d_5	d_6
1.	BK + BK- d_5	0.5	B MB DMB	21.50 17.80	16.25 25.30	12.00 24.80	non recorded 13.90 21.09	18.85 11.10	17.58 —	— —
2.	BK + BK- d_5	1	B MB DMB	15.46 14.0	17.50 31.0	17.10 30.6	non recorded 17.70 14.9	19.62 9.5	12.68 —	— —
3.	BK + BK- d_5	2	B MB DMB	8.63 14.5	20.00 32.5	25.2 30.5	non recorded 23.5 15.5	16.7 6.9	5.7 —	— —
4.	BK + BK- d_5	4	B MB DMB	7.35 5.4 12.5	16.6 19.3 35.9	22.4 30.4 34.5	23.3 27.4 14.0	17.4 14.7 3.0	10.5 3.0 —	2.4 — —
5.	BK + BK- d_5	5	B MB DMB	8.6 8.81 14.1	20.7 25.7 35.0	29.0 31.5 33.95	23.6 20.8 14.45	11.8 12.55 2.45	3.85 0.54 —	0.4 — —
6.	BK + BK- d_5	8	B MB DMB	7.7 8.4 13.9	21.5 26.3 34.9	30.2 32.0 34.1	24.5 20.3 13.8	12.05 12.3 3.2	3.7 0.8 —	0.4 — —
7 ^b .	BK + BK- d_5	2	B MB DMB	44.40 42.95	2.89 4.45	0 3.75	non recorded 1.40 11.67	12.62 37.15	38.69 —	— —
8 ^b .	BK + BK- d_5	3	B MB DMB	43.44 48.15	6.78 11.66	0.97 4.13	non recorded 2.67 11.08	13.97 34.83	32.15 —	— —

9 ^a .	BK+BK- <i>d</i> ₆	10	B MB DMB	26.2 36.7 47.1	13.1 11.45 12.6	2.9 2.15 3.9	1.7 4.28 12.1	8.7 17.28 35.1	24.3 28.0 —	23.1 — —
10 ^a .	TK ₂ +TK ₂ - <i>d</i> ₄	3	DMT	51.5	0	1.3	8.3	39.0	—	—
11 ^c .	IK ₂ +TK ₂ - <i>d</i> ₄	3	DMT+DMB	32.0	13.0	2.95	8.5	43.4	—	—
12 ^d .	FK ₂ +TK ₂ - <i>d</i> ₄	2	MB DMT+DMB	58.7 33.9	29.6 13.65	7.87 3.2	1.3 7.9	0.4 41.25	1.42 —	—
13.	BK+TK ₂ - <i>d</i> ₄	3	B MB DMB	88.9 92.8 48.5	11.1 7.2 4.4	0 0 0.85	0 0 5.8	0 0 40.7	0 0 —	0 0 —
14 ^d .	FK ₂ +BK- <i>d</i> ₆	3	B MB DMB	4.1 5.2 10.6	7.9 13.3 32.8	13.5 22.9 27.1	21.0 27.0 21.1	23.9 21.6 8.1	21.0 9.8 —	8.6 — —
15.	BK+B- <i>d</i> ₆	5	B MB DMB	33.50 95.0 97.85	0.96 5.0 2.15	0 0 0	1.04 0 0	6.60 0 0	22.8 0 —	35.2 — —
16 ^a .	BK+B- <i>d</i> ₆	6	B MB DMB	7.2 99.4	0.15 0.6	0 0	1.05 0	7.3 0	31.4 0	52.6 —
17.	BK- <i>d</i> ₅	15	B DMT	0 0	0 0	0 1.7	0 15.6	3.1 83.3	23.6 —	73.3 —
18.	BK- <i>o-d</i> ₁	5	B MB DMB	24.95 35.0 37.5	45.4 42.0 41.5	23.99 18.5 17.99	5.98 4.5 3.4	0 0 0	0 0 —	0 — —

^a The ratio of the starting compounds was equimolar and CdI₂ (5 % in terms of the weight of starting compounds) served as a catalyst. The reaction temperature was 425-435° C. The abbreviations are given in legend to Table I.

^b Reaction without catalyst. ^c Reaction temperature 435-450° C. ^d Reaction temperature 370-400° C.

of terephthalic acid (95.85 % of D) was obtained. The analysis of the methyl ester (m. p. 140° C) of the product by gas chromatography showed a purity of 99.5 %. The results of analysis of the product by mass spectrography are given in Table I.

Method B.

Potassium phthalate-d₄ (97.9 % of D, 240 mg) and 12 mg of CdI₂ were heated at 400° C for 8 minutes in the atmosphere of CO₂. After the end of the reaction and treatment of the reaction mixture 150 mg of terephthalic acid-d₄ (97.7 % of D) was obtained. Analysis of the dimethyl ester (m. p. 140° C) of the product showed a purity of 100 %. The results of mass spectrographic analysis of the product are given in Table I.

POTASSIUM BENZOATE-O-d₁.

Phthalic anhydride (1.5 g) was heated with 3 ml of D₂O at 390° C for 3 hours. After the reaction had been completed, 1.15 g of benzoic-o-d₁ acid melting at 121° C was isolated from the reaction mixture. Gas chromatographic analysis of the methyl ester showed the product to be 100 % pure. The results of mass spectrographic analysis of the product are given in Table I.

TECHNIQUE OF TRANSCARBOXYLATION AND ANALYSIS OF THE REACTION MIXTURE.

The reaction was carried out by heating the perfectly mixed reaction mixture, containing an equimolar ratio of deuterated and nondeuterated salt (0.5-1 mmole) in glass ampules in a manner which has been described by us earlier⁽⁹⁾. The reaction temperature varied between 375 and 450° C according to the character of the reacting components. The reaction atmosphere was dry carbon dioxide. Since we did not examine the possible reaction between the gaseous reaction atmosphere and the solid reaction mixture, we did not use the reaction components applied to a thin layer of a support. The conversion of the acids arising from the reaction to their methyl esters was carried out in the manner described by us earlier⁽⁹⁾. The obtained mixture of methyl esters was analyzed by gas chromatography at two different temperatures^(9, 15) using the combined procedure and an apparatus of Czechoslovak origin (Chrom 2). The mass spectrographic analyses of the reaction mixtures were performed on MX-1303 mass spectrograph (Acad. Sci. USSR).

The results of these experiments are summarized in Tables I-III. The starting products used for the reactions are given in Table I. The data on the composition of deuterated products isolated from the reaction mixture according to their mass spectrum are listed in Table II. In Table III essentially the same experiments as in Table II are recorded with respect to the composi-

TABLE III. Composition of Reaction Mixture of Salts of Benzenecarboxylic Acids ^a.

Experiment No.	Starting Compound	Reaction Time min.	Products mol. %						
			MB	DMT	DMI	DMF	TMTs	TMTI	TMIHe
1.	BK + BK- <i>d</i> ₆	0.5	94.70	0.17	0.63	4.50	—	—	—
2.	BK + BK- <i>d</i> ₆	1	92.00	1.34	2.33	4.35	—	—	—
3.	BK + BK- <i>d</i> ₆	2	85.40	3.98	4.38	5.90	0.10	0.20	0.06
4.	BK + BK- <i>d</i> ₆	4	65.00	10.30	12.96	9.70	0.68	1.24	0.09
5.	BK + BK- <i>d</i> ₆	5	31.80	11.70	29.60	20.80	2.20	3.50	0.50
6.	BK + BK- <i>d</i> ₆	8	16.10	71.60	6.30	3.25	1.20	1.25	0.06
7 ^b .	BK + BK- <i>d</i> ₆	2	98.30	0.12	0.42	1.15	—	—	—
8 ^b .	BK + BK- <i>d</i> ₆	3	94.50	0.94	1.90	2.60	—	traces	0.20
9 ^b .	BK + BK- <i>d</i> ₆	10	90.10	1.40	3.48	4.22	0.04	0.27	0
10 ^c .	TK ₃ + TK ₃ - <i>d</i> ₄	3	0	100.0	0	0	0	0	0
11 ^c .	IK ₃ + TK ₃ - <i>d</i> ₄	3	3.0	75.0	15.0	3.0	1.0	1.5	0.5
12 ^c .	FK ₃ + TK ₃ - <i>d</i> ₄	2	5.0	75.0	10.0	5.0	1.5	2.5	0.5
13.	BK + TK ₃ - <i>d</i> ₄	3	1.18	98.82	0	0	0	0	0
14 ^d .	FK ₃ + BK- <i>d</i> ₅	3	6.0	78.0	4.0	6.0	2.0	3.0	1.0
15.	BK + B- <i>d</i> ₆	5	20.16	53.13	12.37	8.70	1.9	3.1	0.6
16 ^b .	BK + B- <i>d</i> ₆	6	94.30	0.8	1.87	3.18	—	traces	—
17.	BK- <i>d</i> ₅	15	0.5	99.5	0	0	0	0	0
18.	BK- <i>o-d</i> ₁	5	25.0	45.0	16.0	9.0	2.0	3.0	0.5

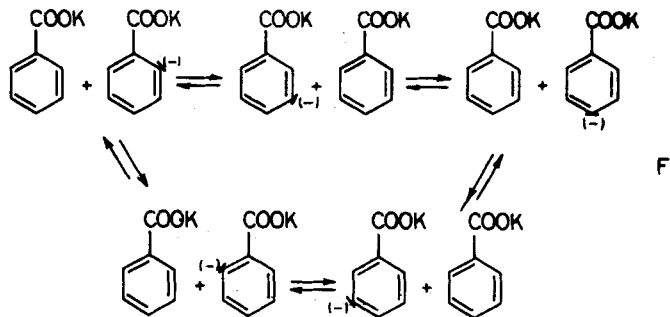
^a The abbreviations are given in legend to Table I. The reaction conditions for all experiments are the same as those of the experiments recorded in Table II.

tion of the reaction mixtures in molar per cent, as determined by the analysis of methyl esters of the products by gas chromatography. In order to make Table III simple and clear, the percentage of benzene formed during the transcarboxylation of potassium benzoate, which is a rate of the degree which the reaction had achieved, is not recorded. Hence, the composition describes only the solid components of the reaction mixture, i.e. the salts of benzene carboxylic acids. Benzene was not listed in Table III since its quantity in the reaction mixture during the initial stages of the reaction is low and its isolation can be carried out only with a great experimental error. The isolation of benzene is not necessary for following the course of the reaction itself.

RESULTS AND DISCUSSION

In an effort to elucidate the mechanism of the transcarboxylation reaction, we investigated the exchange of hydrogen atoms of the benzene ring for deuterium during thermal transcarboxylation of mixtures of deuterium-labelled and unlabelled salts of benzenecarboxylic acids. We found that this exchange does not take place at a certain site of the benzene ring but that it is of random character. Thus, e.g. in the case of potassium benzoate labelled with deuterium at the ortho position, the starting benzoate containing deuterium distributed statistically in the ring was isolated during the initial stage of the reaction. The same holds true for benzene which had been formed during the reaction (Table II, III, experiment No. 18). It should be stressed here that the formation of benzene during the transcarboxylation of benzoate is an irreversible reaction (B) and that deuterated benzene itself does not practically exchange deuterium atoms for hydrogen atoms of nondeuterated salts of benzenecarboxylic acids under the conditions of the transcarboxylation reaction (Table II, III, experiment No. 15, 16). Another piece of evidence indicative of the random exchange of hydrogens for deuterium atoms during the initial stage of the transcarboxylation reaction is the finding of the original benzoate with deuterium distributed statistically in its molecule (Table II, III, experiment No. 1-7) at the very beginning of the reaction in the reaction mixture consisting of equimolar quantities of benzoate and benzoate- d_5 . The same statistical distribution of deuterium was found also in small amounts of reaction products and intermediates, i.e. in benzene and benzenedicarboxylates which had been isolated during the initial stages of the transcarboxylation reaction (Table II, III, experiment No. 1-7). The exchange of deuterium for protium during the transcarboxylation of salts of other benzenecarboxylic acids follows a similar course (Table II, III, experiment No. 14). The situation is different when the transcarboxylation reaction does not take place at all or proceeds very slowly. In these cases the exchange of deuterium for hydrogen does not occur or is very slow. Thus, e.g. when potassium benzoate is allowed to react with benzoate- d_5 in the absence of catalyst (under otherwise identical

reaction conditions), there is practically no exchange of deuterium for hydrogen (Table II, III, experiment No. 7-9). The same can be observed when potassium terephthalate is heated with terephthalate- d_4 at the reaction temperature in the presence of catalyst (Table II, III, experiment No. 10). If, however, the transcarboxylation reaction of a salt of any benzenecarboxylic acid not labelled with deuterium is allowed to proceed in the presence of deuterated terephthalate and if the reaction mixture melts at least partly, the exchange of deuterium for protium takes place to a higher or lower degree (Table II, III, experiments No. 11-13).



From the results presented here the probable mechanism of the transcarboxylation reaction can be deduced as follows. The carbanions, which are formed primarily either by decarboxylation or by liberation of a proton accompanied by scission of a C-H-bond and which are very strong bases, readily react with the intact molecules of the salts. They tear off protons from these molecules thus converting them into new carbanions. The carbanions themselves react with the torn-off protons and regenerate salts of benzenecarboxylic acids. Thus, e.g. the carbanion formed during the transcarboxylation of potassium benzoate (according to equation D) tears off protons from the remaining molecules of benzoate and converts them into new carbanions with a free electron pair in another position at the benzene ring. The carbanion itself regenerates benzoate (equation F) by the reaction with the proton. This leads to multiple cycles of formation of carbanion with a free electron pair in different positions at the benzene ring. This carbanion then reacts with carboxylate cations which arise more slowly by decarboxylation (e.g. according to equation E). For this reason the rapidly formed and rapidly disappearing "dynamic" carbanion appears to be relatively stable (equation F) when compared with the origin of intermediary products of transcarboxylation, i.e. with salts of the remaining carboxylic acids (cf. e.g. equation A, B). The experimental data do not permit us to determine unambiguously whether the carbanions are primarily formed by scission of a C-H-bond or of the C-C-bond between the ring and the carboxylate group, since the scission of the C-C-bond of carboxylate groups of cadmium salts of carboxylic acids (i.e. of

the catalyst) is extremely easy. The proposed mechanism explains best the experimental observation that already in the initial stage of the reaction in the equimolar mixture of deuterium-labelled and unlabelled starting products the deuterium atoms of the aromatic ring are replaced at random by hydrogen atoms.

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