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An Investigation of the Mechanism of the Henkel Reaction by Deuterium and Carbon-14 Isotope Techniques

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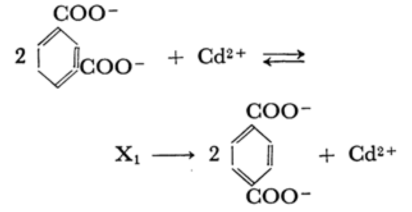
The thermal rearrangements and the disproportionation of potassium benzenecarboxylates have been investigated at 350—460°C using potassium deuterophthalate, deuterobenzoate, benzoate-1-^{14}C and benzoate-7-^{14}C. The following results were obtained: (1) Hydrogen atoms of potassium phthalate and benzoate transfer intermolecularly during the conversion. The hydrogen atoms seem to exchange many times. (2) The intermolecular transfer of hydrogen atoms also takes place between different benzenecarboxylates. (3) The hydrogen atoms transfer intermolecularly many times, irrespective of either the reaction temperature, the kinds of catalysts, and the kinds of potassium carboxylates. (4) The hydrogen exchange takes place only during the conversion. (5) Many of the carboxyl groups of potassium benzoate are replaced by carbon dioxide in the gas phase and by carbon dioxide from potassium carbonate. A possible mechanism is presented.

The catalytic conversion of potassium phthalate, benzoate, or isophthalate into potassium terephthalate is often called the Henkel reaction.1) The mechanism of this reaction has been investigated by many authors1−9) and two different mechanisms have been proposed. One of them is the bimolecular mechanism proposed by Ogata *et al.*:2b,2c)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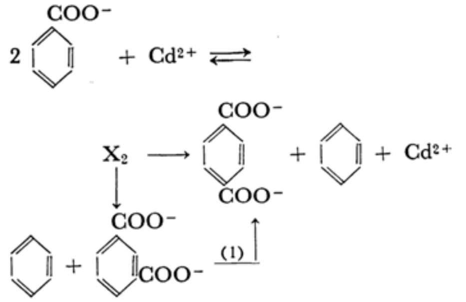
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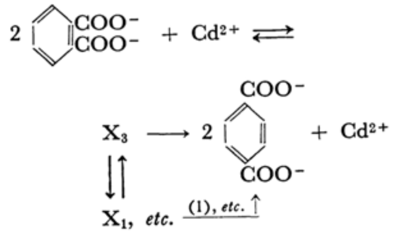
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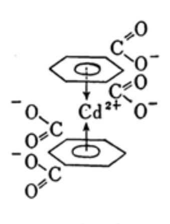
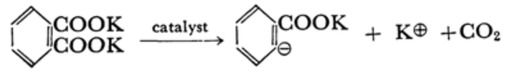
where X_1, *etc.* are complexes of the sandwich type and are assumed as intermediates:



The other mechanism is the carboxylation-decarboxylation mechanism proposed by Sorm and Ratusky4) and by Terashi *et al.*6), who assume an intermediate of the phenyl anion type:



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2) a) Y. Ogata, M. Tsuchida and A. Muramoto, *J. Am. Chem. Soc.*, **79**, 6005 (1957); Y. Ogata, M. Hojo and M. Morikawa, *J. Org. Chem.*, **25**, 2082 (1960); Y. Ogata and Y. Furuya, *Chem. & Ind.*, **1964**, 2011. b) Y. Ogata and K. Sakamoto, *ibid.*, **1964**, 749; *ibid.*, **1964**, 2012. c) Y. Ogata and K. Nakajima, *Tetrahedron*, **21**, 2393 (1965).

3) K. Ogata, Dissertation thesis.

4) F. Sorm and J. Ratusky, *Chem. & Ind.*, **1958**, 294. *ibid.*, **1962**, 40; M. Kraus, K. Kochloefl, L. Beranek, V. Bezant and F. Sorm, *ibid.*, **1961**, 1160.

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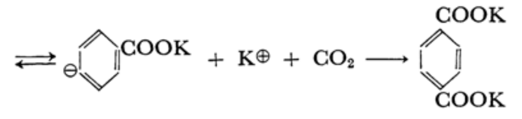
9) K. Chiba, *Kogyo Kagaku Zasshi, (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 1289, 1294 (1966).



(4)

Recently, however, Arai *et al.*[8] found that potassium phthalate, benzoate, and trimesate are produced during the conversion of potassium isophthalate, while potassium phthalate, isophthalate, and trimesate are produced during the conversion of potassium benzoate. Moreover, according to the investigation by Chiba,[9] all kinds of potassium benzenecarboxylates are produced during the conversion of potassium phthalate. These facts can not be accounted for by the above mechanisms.

In the present paper, potassium deuterophthalate, deuterobenzoate, benzoate-1-^{14}C and benzoate-7-^{14}C will be used to elucidate the transfer aspects of hydrogen atoms and carboxyl groups during the conversion and propose a new mechanism which can account for the above facts.[8,9]

Experimental

Material. Phthalic acid-3, 4, 5, 6-d_4, threee kinds of partly, but statistically uniformly, deuterated terephthalic acid-$d_{(\bar{n})}$ (n=1, 2 or 3) (n/4 fractions of ring hydrogen atoms are replaced by deuterium atoms), and partly deuterated isophthalalic acid-$d_{(\bar{n})}$ were prepared from, respectively, *o*-xylene-3, 4, 5, 6-d_4, *p*-xylene-$d_{(\bar{n})}$ and *m*-xylene-$d_{(\bar{n})}$ by oxidation with an alkaline permanganate solution. The deuteroxylenes were prepared from the corresponding undeuterated xylenes and 50 mol% deuterosulfuric acid by a method similar to that described by Grime and Ward.[10]

Terephthalic acid-2, 3, 5, 6-d_4 (Fig. 1c) and benzoic acid-2, 3, 4, 5, 6-d_5 were prepared from potassium phthalate-d_4 by the Henkel reaction.

Terephthalic acid-2-d_1 (Fig. 1b) and benzoic acid-2-d_1-, 3-d_1 and -4-d_1 were prepared from the corresponding bromoxylene and bromotoluenes by the Grignard reaction and by deuteration by deuterium oxide respectively.[11] The isotopic purities of these materials were estimated to be about 90, 75, 80 and 70 mol% respectively, either by a method to be described below or by referring to the infrared absorption data of the benzoic acid-d_1s and the toluene-d_1s obtained by Tiers *et al.*[12] and Takahasi.[11]

Deuterosulfuric acid was prepared by a method similar to that described by Ingold.[13]

Benzoic acid-1-^{14}C was obtained from the New England Nuclear Corporation, U. S. A. Benzoic acid-7-^{14}C was obtained from the Radiochemical Center, England.

Procedure. Each pair of the reactants (specified in the tables) was placed together with the catalyst in a stainless-steel autoclave (20 m*l*) and heated at a given temperature for an hour under 40—50 atmospheres pressure of carbon dioxide. The products were then dissolved in hot water and filtered. An excess of hydrochloric acid was added to the boiling filtrate, and a precipitate of terephthalic acid was filtered off. Benzoic acid was extracted with chloroform from the remaining filtrate. Phthalic acid was recovered from the last filtrate by extraction with ethyl ether. Isophthalic acid was then precipitated from the filtrate at 0°C. The infrared spectra of these acids were observed by the KBr disk method using the IR-27C infrared spectrophotometer of the Shimadzu Co., Ltd. In the experiments using radioactive carbon, activities were measured in the states of acids themselves by Radiocounter, Model 100, of the Institute of Physical and Chemical Research in Japan. The values of radioactivities were accurate within 3%.

Results

Assignment of Infrared Absorption Bands of Deuteroterephthalic acid. In the 645—735 cm^{-1} range, terephthalic acid-$d_{(\bar{2})}$ (which contains all kinds of terephthalic acid-d_n, n=0—4) shows five main absorptions, at 735, 700, 675, 653, and 645 cm^{-1} (Fig. 2a) (the absorptions at 653 and 645 cm^{-1} overlap with each other in this case). These absorptions are all assigned to the aromatic C–H or C–D deformation vibrations.[10] It has been concluded, by referring to the spectra of the samples of terephthalic acid-h_4, -d_1 and -d_4 (Fig. 1), that the absorption at 735

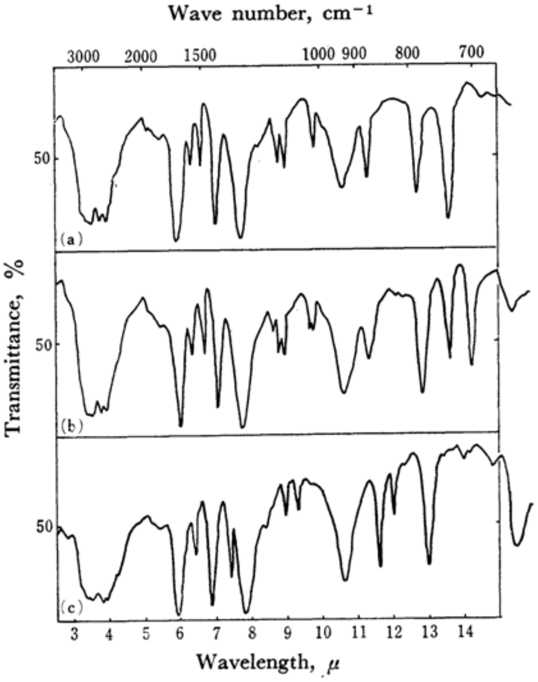


Fig. 1. Infrared absorption spectra of
(a) Terephthalic acid-h_4,
(b) Terephthalic acid-d_1,
(c) Terephthalic acid-d_4.

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[10] D. Grime and I. M. Ward, *Trans. Faraday Soc.*, **54**, 959 (1958).

[11] M. Takahasi, This Bulletin, **33**, 808 (1960).

[12] G. V. Tiers and J. H. Tiers, *J. Chem. Phys.*, **20**, 761 (1952).

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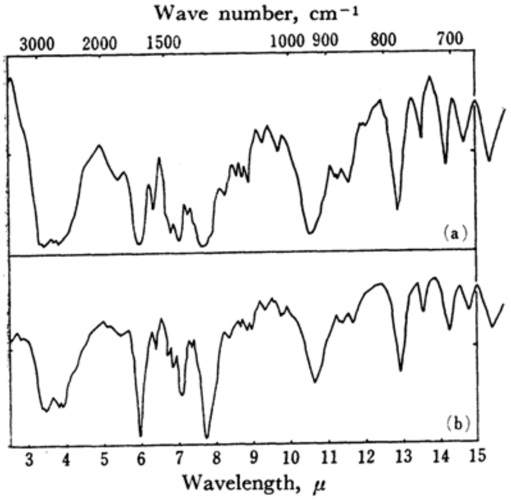

Fig. 2. Infrared absorption spectra of
(a) Terephthalic acid-$d_{(\mathrm{II})}$
(b) Terephthalic acid produced from an equimolecular mixture of potassium phthalate-h_4 and -d_4.

cm^{-1} may be assigned to -h_4 and -d_1, the absorption at 700 cm^{-1}, to -d_1, and the absorption at 645 cm^{-1}, to -d_1 and -d_4. The absorptions at 675 and 653 cm^{-1} never appear in the spectra of these three isomers (-h_4, -d_1 and -d_4); they must belong to -d_3 and/or three kinds of -d_2 isomers. It may happen that some of -d_3 and -d_2 isomers also have an absorption at 700 or 645 cm^{-1}, but the absorption at 735 cm^{-1} should belong only to -h_4 and -d_1 isomers, since this absorption band does not appear in the spectra of terephthalic acid-$d_{(\mathrm{III})}$, which is expected to involve large fractions of -d_2, -d_3, and -d_4 isomers, with only small fractions of -h_4 and -d_1 components.

Relative Absorbancies of the Absorptions at 735 cm^{-1} of Terephthalic Acid-h_4 and -d_1. To estimate the amounts of -h_4 and -d_1 components, R_n (the subscript n stands for the number of deuterium atoms of a benzene ring of the sample), the ratio of the intensity of the absorption at 735 cm^{-1} to that of the absorption at 940 cm^{-1}, was calculated. The latter absorption is assigned to the C–COOH streching vibration[14]; therefore, the intensity of this absorption is expected to be almost independent of the numbers and positions of the deuterium atoms at terephthalic acid-d_n. R_0 was estimated to be 1.60 from the spectrum of the pure -h_4 sample. R_1 was calculated as follows. Terephthalic acid-$d_{(\mathrm{II})}$ should contain 6.25 mol% of -h_4 and 25.0 mol% of -d_1 components in the equilibrated isotopic mixture. As the observed value of $R_{(\mathrm{II})}$ was 0.24, R_1 could be calculated to be 0.55. Using the R_1 value obtained here, the isotopic purity of the prepared terephthalic acid-d_1 was estimated to be about 90 mol%. The R_n values were accurate within 4%.

The Conversion of Potassium Phthalate. The infrared spectrum of terephthalic acid, which is converted from an equimolecular mixture of potassium phthalate-h_4 and -d_4 by being heated at 430°C for an hour, is shown Fig. 2b. All of the five main absorption bands, at 735, 700, 675, 653, and 645 cm^{-1}, appear in it. This result shows that not only terephthalic acid-h_4 and -d_4, but also -d_1, -d_2 and -d_3 components are produced by the conversion and confirms that the intermolecular transfer of hydrogen atoms takes place during the conversion. The observed R value of this terephthalic acid is very near to $R_{(\mathrm{II})}$. Moreover, the infrared spectrum of this terephthalic acid is almost the same as that of terephthalic acid-$d_{(\mathrm{II})}$. This implies that hydrogen and deuterium are distributed quite at random in the product, showing that the exchange takes place a number of times during the conversion. The same is true also in the case of terephthalic acid converted from the same mixed sample at different temperatures or under different pressures with a cadmium catalyst, or at 430—460°C with catalysts of different kinds (Table 1, I-1, 3, 4, 5, 6). It is found below that the hydrogen transfer takes place only during the conversion. The infrared spectrum of phthalic acid recovered from the partly-converted mixed sample is found to be identical with that of the original mixture of phthalic acid-h_4 and -d_4. A mixture of terephthalic acid-h_4 and -d_4 does not show any difference in its infrared spectrum between before and after the heat treatment. Moreover, a mixture of potassium phthalate-d_4 and terephthalate-h_4 gives only a mixture of terephthalic acid-h_4 and -d_4 after the conversion. Therefore, it may be concluded that the intermolecular transfer of hydrogen atoms takes place simultaneously with the intermolecular exhcange of carboxyl groups.

The Conversion of Potassium Benzoate. The infrared spectrum of terephthalic acid produced from an equimolecular mixture of potassium benzoate-h_5 and -d_5 with a cadmium catalyst exhibits all of the five main absorptions, and its features are very similar to those of terephthalic acid-$d_{(\mathrm{II})}$. Moreover, the observed R value is very near to $R_{(\mathrm{II})}$. Each of the infrared spectra of terephthalic acids produced from potassium benzoate-2-d_1, -3-d_1 and -4-d_1, is very much like the others and simulates that of terephthalic acid-$d_{(\mathrm{I})}$. This implies that the intermolecular transfer of hydrogen atoms takes place a number of times during the conversion. It is also found that the hydrogen exchange takes place only during the conversion (I-13) and that the same is the case in the presence of other catalysts (I-14, 15).

The Conversion of Mixed Samples of Two Different Kinds of Molecules. The five main

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[14] E. Gonzalez-Sanchez, *Spectrochim. Acta*, **12**, 17 (1958).

TABLE 1. COMPARISONS OF INFRARED ABSORPTION SPECTRA OF DEUTEROBENZENECARBOXYLIC ACIDS

	Components in samples, mmol	Catalyst	Temp., °C	Infrared spectra of species			
				Obs.	Refered	Comparison	R_{obs}
I-1	K_2P-h_4(2.0)+K_2P-d_4(2.0)	$CdCl_2$	360	PA	PA-h_4+PA-d_4	Identical	
				TA	TA-h_4+TA-d_4	Different	0.25±0.01
I-2	K_2P-h_4(0.5)+K_2P-d_4(0.5)	$CdCl_2$	430	TA	TA-h_4+TA-d_4	Different	0.25±0.01
I-3	K_2P-h_4(0.5)+K_2P-d_4(0.5)	$CdCl_2$	430	TA	TA-h_4+TA-d_4	Different	0.28±0.01
I-4	K_2P-h_4(0.5)+K_2P-d_4(0.5)	$ZnCl_2$	430	TA	TA-h_4+TA-d_4	Different	0.27±0.01
I-5	K_2P-h_4(0.5)+K_2P-d_4(0.5)	$CuCl_2$	430	TA	TA-h_4+TA-d_4	Different	0.27±0.01
I-6	K_2P-h_4(0.5)+K_2P-d_4(0.5)	$CaCl_2$	460	TA	TA-h_4+TA-d_4	Different	
I-7	K_2P-d_4(0.5)+K_2T-h_4(0.5)	$CdCl_2$	430	TA	TA-h_4+TA-d_4	Identical	
I-8	K_2T-h_4(0.25)+K_2T-d_4(0.25)	$CdCl_2$	430	TA	TA-h_4+TA-d_4	Identical	
I-9	KB-h_5(0.5)+KB-d_5(0.5)	$CdCl_2$	430	TA	TA-h_4+TA-d_4	Different	0.26±0.01
I-10	KB-2-d_1(2.0)	$CdCl_2$	430	TA	TA obtained in I-12	Identical	
I-11	KB-3-d_1(2.0)	$CdCl_2$	430	TA	TA obtained in I-12	Identical	
I-12	KB-4-d_1(2.0)	$CdCl_2$	430	TA	TA-h_4	Different	
I-13	KB-4-d_1(2.0)	$CdCl_2$	350	BA-4-d_1	BA-4-d_1	Identical	
I-14	KB-4-d_1(2.0)	$ZnCl_2$	430	TA	TA obtained in I-12	Identical	
I-15	KB-4-d_1(2.0)	$CuCl_2$	430	TA	TA obtained in I-12	Identical	
I-16	K_2P-d_4(0.5)+K_2I-h_4(0.5)	$CdCl_2$	430	TA	TA-h_4+TA-d_4	Different	0.26±0.01
I-17	K_2P-d_4(0.5)+KB-h_5(1.0)	$CdCl_2$	430	TA	TA-h_4+TA-d_4	Different	
I-18	K_2P-d_4(0.5)+K_3Tri-h_3(0.33)	$CdCl_2$	430	TA	TA-h_4+TA-d_4	Different	
I-19	K_2P-h_4(2.0)+K_2I-$d_{(2)}$(2.0)	$CdCl_2$	350	PA	PA-h_4	Identical	
I-20	K_2I-h_4(2.0)+K_2I-$d_{(2)}$(2.0)	$CdCl_2$	400	IA	IA-h_4+IA-$d_{(2)}$	Identical	
I-21	K_2P-h_4(2.0)+KB-4-d_1(2.0)	$CdCl_2$	350	PA	PA-h_4	Identical	
I-22	K_2P-h_4(2.0)+D_2O(10.0)	$CdCl_2$	430	TA	TA-h_4	Different	

Catalyst: 0.05 mol %
Initial pressure of carbon dioxide: 30 atm except for I-3 (20 atm).

K_2P:	Potassium phthalate	KB:	Potassium benzoate	K_2I:	Potassium isophthalate
K_2T:	Potassium terephthalate	K_3Tri:	Potassium trimesate	PA:	Phthalaic acid
BA:	Benzoic acid	IA:	Isophthalic acid	TA:	Terephthalic acid

absorption bands also appear in the infrared spectra of terephthalic acids produced from mixed samples of potassium phthalate-d_4 with the same equivalent of potassium benzoate-h_5, isophthalate-h_4, or trimesate-h_3. This shows that the intermolecular hydrogen transfer takes place also in these cases. However, their spectra are different from each other. The infrared spectrum of terephthalic acid from a mixture with potassium benzoate-h_5 exhibits features intermediate between those of terephthalic acid-$d_{(2)}$ and of -$d_{(1)}$. The infrared spectrum of terephthalic acid produced from a mixture with isophthalate-h_4 is very similar to that of terephthalic acid-$d_{(2)}$, and its R value is very near to $R_{(2)}$. The spectrum of terephthalic acid produced from a mixture with trimesate-h_3 is similar to that of terephthalic acid-$d_{(2)}$, with slight deviation towards that of terephthalic acid-$d_{(3)}$. It is also found in these cases that the hydrogen exchange does not take place before the conversion (I-19, 20, 21).

The Conversion of Potassium Benzoate-1-^{14}C. The radioactivities of terephthalic acids produced from the mixtures of potassium benzoate-1-^{14}C with either non-radioactive potassium benzoate (pair I) or phthalate (pair II) are listed in Table 2. It is of interest to note that the ratio of the radioactivity of terephthalic acid produced from a mixture with non-radioactive potassium benzoate to that of terephthalic acid from a mixture with potassium phthalate is not $[K^*B]_I([K^*B]_{II}+2[K_2P]_{II})/[K^*B]_{II}$, the theoretical value obtained on the assumption that the potassium benzoate and phthalate are converted independently into potassium terephthalate (case 1), but near to $[K^*B]_I/[K^*B]_{II}$, a theoretical value obtained on the assumption that the two carboxylates react with each other (case 2). Here $[K^*B]$ and $[K_2P]$ are the mole fractions of potassium benzoate-1-^{14}C and phthalate in the mixtures respectively.

The Conversion of Potassium Benzoate-7-^{14}C. Potassium benzoate-7-^{14}C is heated at 430°C in an atmosphere of carbon dioxide gas with or without potassium carbonate, and the exchange coefficient, $S=[(TA)/(BA)_{-7\text{-}^{14}C}/[(TA)/(BA)]_{-1\text{-}^{14}C}$, is calculated. Here (BA) is the radioactivity of the

TABLE 2. RADIOACTIVITIES OF TEREPHTHALIC ACIDS PRODUCED FROM POTASSIUM BENZOATE-1-^{14}C SAMPLES

	Components in samples, mmol	Temp. °C	Yield of TA, %	Radioactivity cpm	Ratio of radioactivities		
					Obs.	Theoretical	
						Case 1	Case 2
II-1	KB-1-^{14}C(20)	430	81.0	736± 5			
II-2	KB-1-^{14}C(20)+K_2P(10)	430	83.5	531±30	0.72	0.5	0.67
II-3	KB-1-^{14}C(20)+K_2P(20)	430	82.0	358± 5	0.49	0.33	0.5
II-4	KB-1-^{14}C(20)+KB(20)	430	70.0	394± 5	0.54	0.5	0.5
II-5	KB-1-^{14}C(20)+K_2P(20)	360	27.2	363± 5	0.49	0.33	0.5

Catalyst: $CdCl_2$ (0.05 mol%)
Initial pressure of carbon dioxide: 30 atm

TABLE 3. RADIOACTIVITIES OF TEREPHTHALIC ACIDS PRODUCED FROM POTASSIUM BENZOATE-7-^{14}C SAMPLES

	Samples, mmol	Radioactivities of samples, cpm	Additive compounds	Radioactivities of TA, cpm	Exchange coefficients
III-1	KB-1-^{14}C(20)	827±10	—	762±10	
III-2	KB-7-^{14}C(20)	504±10	—	816±10	1.75
III-3	KB-7-^{14}C(20)	504±10	K_2CO_3(20 wt%)	599±10	1.29
III-4	KB(20)	0	$K_2{}^*CO_3$(20 mol%)	47± 2	
III-5	K_2P(20)	0	$K_2{}^*CO_3$(20 mol%)	29± 1	

Catalyst: $CdCl_2$ (5 mol%)
Reaction temperature: 430°C
Pressure of carbon dioxide: 30 atm
Radioactivity of $K_2{}^*CO_3$: 144 cpm as $Cd{}^*CO_3$
KB: Potassium benzoate K_2P: Potassium phthalate TA: Terephthalic acid

benzoic acid specified by the subscript and (TA), the radioactivity of terephthalic acid produced from the benzoic acid specified by the subscript. The results listed in Table 3 demonstrate that about 10% of the carboxyl groups are replaced by carbon dioxide in the gas phase, and 20—30% by carbon dioxide from potassium carbonate under the conditions involved. The exchange of carbon dioxide between carboxyl groups and potassium carbonate also takes place in the case of potassium phthalate (Table 3, III-5).

The Conversion of Potassium Phthalate with Deuterium Oxide. Potassium phthalate-h_4 is placed with deuterium oxide in an autoclave and heated at 430°C. A weak absorption band appears at 700 cm^{-1} in the spectrum of terephthalic acid obtained. This shows that terephthalic acid-d_1 is produced during the conversion, and is consistent with the fact that water promotes decarboxylation and converts potassium phthalate into benzoate during the reaction.1)

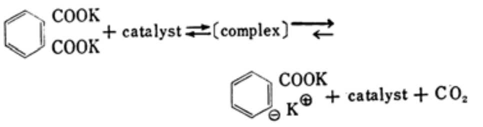
The products of the partial conversion of potassium phthalate at 360°C are dissolved in deuterium oxide in place of water. The infrared spectrum of the benzoic acid which is extracted as a by-product of the conversion is identical to that of benzoic acid-h_5. This seems to be incompatible with the suggestion7) that an active intermediate is still present even at room temperature and that loosely-bound carboxyl groups of the intermediate would be replaced by hydrogen atoms of water when the products are dissolved in water.

Discussion

It seems to be established by the present study that the hydrogen atoms of potassium phthalate, benzoate, or isophthalate transfer a number of times between molecules during the conversion into potassium terephthalate, and that they transfer simultaneously with the carboxyl groups. Therefore, the mechanism proposed by Ogata *et al.*2b) for the conversion of potassium isophthalate and benzoate (Eqs. (1) and (2)) must be discarded, because, according to (1) and (2), the number of times the hydrogen atoms exchange intermolecularly during a single conversion should not exceed unity. Therefore, the calculated R value, assuming one hydrogen exchange, is never below 0.538 and is incompatible with the observed R values (Table 1, I-9, 1-16).

The results obtained in the experiment on the conversions of a mixture of two kinds of molecules with different activities seem to suggest that the hydrogen exchange also takes place between any pair of different molecules. We can see it in the case of a mixture of potassium phthalate and benzoate. The infrared spectrum and radioactivities of terephthalic acids, which are produced from mixtures of potassium phthalates and potassium benzoates, show that the fraction of the terephthalic acid originating from potassium benzoate exceeds a value calculated by assuming that these two species are converted independently. This can not be explained unless potassium phthalate itself or the potassium carboxylates produced from potassium phthalate during the conversion interact with potassium benzoate before potassium benzoate disproportionates into potassium dicarboxylates and benzene. The infrared spectra of terephthalic acids produced from a mixture of potassium phthalate-d_4 with isophthalate-h_4 and with trimesate-h_3 show that the hydrogen and deuterium of benzene rings exchange so as to nearly reach an equilibrium during the conversions. This can more readily be explained on the assumption that the intermolecular transfer of hydrogen atoms also takes place between potassium carboxylates with different activities.15)

The following mechanism for the conversion of potassium phthalate into potassium terephthalate seems plausible:



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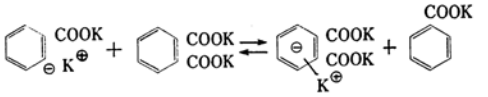
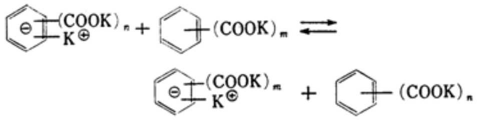
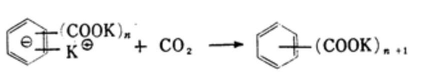


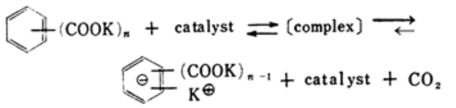
(6)



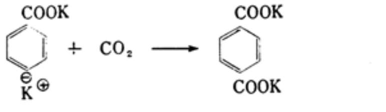
(7)



(8)

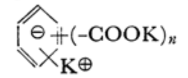


(9)

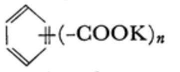


(10)

(5) is the initiation reaction and would determine the rate of the over-all reaction. (6) and (7) are the transfer reactions, which take place rapidly and almost independently of either the reaction temperature, the kinds of catalysts, or the kinds of potassium carboxylates. However, these steps are probably limited within a small domain surrounding the catalyst. (10) is the termination reaction.



is an active intermediate of the phenyl anion-type, similar to that proposed by Sorm and Ratusky.4) The presence of such an intermediate may be inferred from the following considerations: (1) The hydrogen atoms transfer intermolecularly many times irrespective of either the reaction temperature, the kinds of catalyst, or the kinds of the potassium benzenecarboxylates, while the rate of the over-all reaction depends on them.2,15) (2) A number of carboxyl groups exchange with carbon dioxide in the gaseous state or in carbonates during the conversion.2,4,5) (3) The yields of terephthalic acids decrease with a decrease in the pressure of carbon dioxide.9) (4) Transition metal cations which are effective in decarboxylation reaction16) are also effective in this reaction.15) The form of the [complex] can not be determined in detail as yet, but the sandwitch form proposed by Ogata *et al.*2) seems unlikely because cadmium and zinc cations are apt to be co-ordinated by the bases in tetrahedral directions.17)



may not be a free potassium carboxylate or a free carboxylate anion, but a carboxylate anion which is surrounded by several potassium cations accompanying various anions, as we see in a crystal,18) since the conversion takes place in the molten or solid state.

In the conversion of potassium benzoate or isophthalate, the mechanism would be almost the same except that the numbers and positions of carboxyl groups of carboxylates in (5) and (6) are different.

As has been mentioned earlier, many kinds of carboxylic acids are found as by-products in the Henkel reaction.8,9) This can also be accounted for by the present mechanism.

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