

melting point¹⁷ and the original infrared spectrum. Apparently, the two materials are the isomeric lactol and keto-acid.¹⁸ The formation of the lactol and the ready interconversion of the two isomers means the two groups are *cis*. The lactol was obtained in an overall yield of 35%.

Evaporation of the carbon tetrachloride from the first crystallization left a dark red, sticky material that could not

(17) If some of the material with single melting point (keto-acid) is present and/or the melting point is taken too slowly, the first melting point may be missed or not clearly observed.

be induced to crystallize. Its infrared spectrum was poorly defined with broad bands suggesting a mixture. It may have contained various oxides formed by Darzens-like condensations.⁹ It was not examined further.

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(18) The keto-acid has a single carbonyl peak in its infrared spectrum, but this is not unexpected. The carbonyl band of a benzoyl group and of a cyclopropanecarboxylic acid both would show up at about 5.95 μ and quite possibly would not or could not be resolved with the instrument used.

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Further Studies on the Preparation of Terephthalic Acid from Phthalic or Benzoic Acid

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Received May 16, 1960

The mechanism of the formation of potassium terephthalate from potassium phthalate or benzoate using cadmium or other metallic salts has been studied kinetically by C¹⁴-tracer techniques. The carbon of the carboxyl group and/or the carbonates were labeled. Contrary to the Sorm-Ratusky's postulation (Scheme 2), the results obtained support our previously proposed mechanism that the reaction of phthalate is an intramolecular rearrangement and that of benzoate is a disproportionation.

B. Raecke¹ found that potassium phthalate or benzoate is convertible to potassium terephthalate by heating it with cadmium salts at 400–450°. These processes have an industrial importance for the preparation of terephthalic acid, one of the starting materials of polyester fiber.

In our previous paper,² the effects of various catalysts on these reactions were reported and probable mechanisms were suggested; *i.e.*, intramolecular rearrangement for phthalate and disproportion for benzoate.

Afterward, Sorm and Ratusky³ reported on this reaction using phthalic and benzoic anhydrides with potassium carbonate-C¹⁴ and they postulated a mechanism involving decarboxylation-carboxylation for both reactions on the basis of a statistical isotopic exchange.

The present study was undertaken to clarify these obscurities. For this purpose, the reaction of potassium phthalate or benzoate using cadmium salt catalysts was carried out, in which the carboxyl group, cadmium carbonate or potassium carbonate, was labeled. The reactions were followed kinetically by means of radioactivity and the results were compared with those derived theoretically from these mechanisms.

EXPERIMENTAL

Materials. Barium carbonate-C¹⁴ was obtained from Isotope Center in Japan and diluted by normal barium carbonate to an activity of 8 μ c./g. (6360 cpm. at infinite thickness). Potassium carbonate-C¹⁴ and cadmium carbonate-C¹⁴ were prepared from carbon dioxide-C¹⁴ produced from barium carbonate-C¹⁴ in a vacuum line. Benzoic-carboxy-C¹⁴ acid was prepared by the reaction of the appropriate Grignard reagent with carbon dioxide-C¹⁴ at 10⁻⁵–10⁻⁶ mm. pressure and in glass-joint apparatus according to the Linstead procedure.⁴ The activities of the acid were measured as the acid itself and also as barium carbonate after decarboxylation,⁵ the specific activities being 4207 and 2720 cpm., respectively. Phthalic-carboxy-C¹⁴ acid was prepared by the permanganate oxidation of *o*-toluic-carboxy-C¹⁴ acid, prepared by the carbonation of *o*-tolylmagnesium bromide with carbon dioxide-C¹⁴.⁶ The specific activities of the product were 6200 and 2470 cpm. as acid and barium carbonate, respectively.

Tracer experiments. The previous procedure and apparatus² were used for these experiments. In the measurements of specific activity, each carbonate was converted to barium carbonate by absorbing the carbon dioxide produced by hydrochloric acid in an aqueous solution of barium acetate-potassium hydroxide. Each acid was recrystallized repeatedly until constant activity was obtained. All data are averages of duplicate experiments and they are calibrated for their background against standard barium carbonate. The activity was expressed as that of the corresponding barium carbonate even when the substance counted was the organic acid itself. Typical specific activities of the terephthalic acid obtained from labeled phthalic or benzoic acid were

(1) German Patent 936,036 and for the review see B. Raecke, *Angew. Chem.*, **70**, 1 (1958), and ref. 7.

(2) Y. Ogata, M. Tsuchida, and A. Muramoto, *J. Am. Chem. Soc.*, **79**, 6005 (1957).

(3) F. Sorm and J. Ratusky, *Chem. & Ind. (London)*, 294 (1958).

(4) R. P. Linstead, "A Course in Modern Techniques of Organic Chemistry," Butterworth Publishing Co., London, 1955, p. 77.

(5) Cf. W. G. Dauben, J. C. Reid, P. E. Yankwich, and M. Calvin, *J. Am. Chem. Soc.*, **72**, 121 (1950).

(6) W. H. Stevens and D. A. Holland, *Science*, **112**, 718 (1950).

3430 and 1240 cpm. as acid and barium carbonate, respectively.

Check of the precision of data. It was necessary to examine the precision of the tracer experiments, because the reactions were carried out at high temperature in open and heterogeneous systems. The data were satisfactory for our semi-quantitative consideration. The ratios of the activity of the terephthalic acid to that of unchanged phthalic acid in some typical runs with varying initial activity of phthalic acid (135–1235 cpm.) were 1.27, 1.21, 1.16, 1.32, and 1.30 (av. 1.25) under the same conditions.

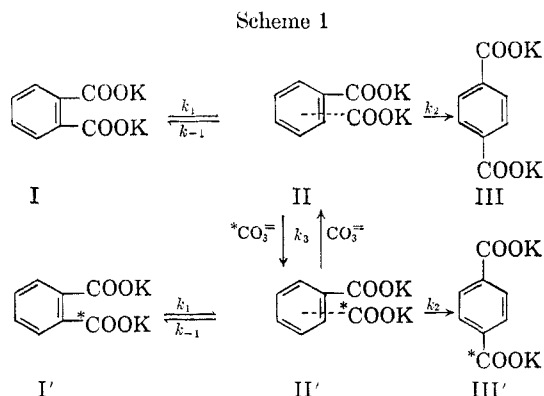
Although potassium carbonate does not decompose at the reaction temperature, cadmium carbonate is known to decompose completely at above 375°. Hence the possibility existed that carbon dioxide might escape from the system. To check this possibility, the ratio of activity of the terephthalic acid to the initial activity of carbonate was measured. The ratios were 1.3 with potassium carbonate-C¹⁴, and 1.2 with cadmium carbonate-C¹⁴. Moreover, the conservation of activity in the entire reaction system was tested with labeled phthalic acid or labeled potassium carbonate and the results showed the conservation of 98–99% of the original activity after completion of the reaction. In other words, neither cadmium carbonate nor potassium carbonate decomposes under these conditions and the isotopic exchange occurs probably by way of dissociated carbonate ion rather than carbon dioxide.

To check the presence of an appreciable amount of the isotopic effect in this reaction, the reaction of labeled potassium phthalate in the absence of carbonate was carried out and then the activities of the terephthalic acid were compared with that of recovered phthalic acid at earlier stages, using the same labeled phthalic acid. If there were an appreciable isotopic effect, the activity of terephthalic acid would be lower. However, these activities for recovered phthalic acid and terephthalic acid were of the same order, 2385 and 2340 cpm., respectively.

With the reaction of potassium benzoate, similar check experiments were done, which proved that the total activity of the system was retained during the reaction and there was no appreciable isotopic effect. Therefore, this effect was neglected in the present discussion.

RESULTS AND DISCUSSION

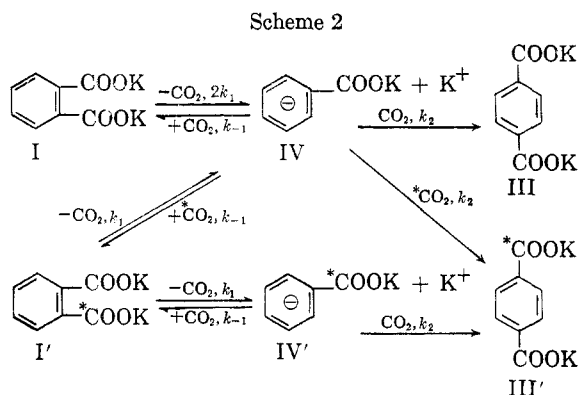
Mechanism of the reaction of potassium phthalate. As mentioned previously, there are two hypothetical mechanisms for this reaction. One of them is an intramolecular rearrangement which accompanies a simultaneous isotopic exchange between the activated complex (II) and labeled carbonate ion derived from added carbonate (Scheme 1).^{7,8}



(7) Y. Ogata, *Chemistry and Chemical Industry (Japan)*, 11, 148 (1958).

A modification of Scheme 1 in which the exchange occurs before the rearrangement without a common unstable intermediate between the rearrangement and exchange might be conceivable. This will be discussed later.

The other mechanism involves decarboxylation-carboxylation.



A modification of Scheme 2 in which slow exchange reaction occurs between carbon dioxide produced and carbonate ion can be abandoned together with Scheme 2, as described later.

If the concentration of the intermediate is so low that a steady state method can be applied, the following equations are obtained. Typical treatments are shown in the Appendix.

The specific activities of the phthalate, terephthalate, and carbonate are expressed, respectively, as⁹

$$r_p \propto \frac{[I']}{2[I]}, r_t \propto \frac{[III']}{2[III]}, r_c \propto \frac{[CO_2^*]}{[CO_2]}$$

where brackets show the concentrations. From Scheme 1:

$$\frac{dr_t}{dt} = \frac{k_1 k_2}{k_{-1} + k_2} \frac{[I]}{[III]} \left\{ \frac{r_p}{1 + \alpha[CO_3]} + \frac{\alpha[CO_3]}{1 + \alpha[CO_3]} \cdot \frac{r_c}{2} - r_t \right\} \quad (1)$$

$$\frac{dr_p}{dt} = \frac{k_1 k_{-1}}{k_{-1} + k_2} \left\{ \frac{\alpha[CO_3]}{1 + \alpha[CO_3]} \right\} \left\{ \frac{1}{2} r_c - r_p \right\} \quad (2)$$

$$\frac{dr_c}{dt} = \frac{2k_1 k_3}{k_{-1} + k_2} \left\{ \frac{[I]}{1 + \alpha[CO_3]} \right\} \left\{ r_p - \frac{r_c}{2} \right\} \quad (3)$$

where k 's are rate constants of the subscripted steps and

$$\alpha = \frac{k_3}{k_{-1} + k_2}$$

(8) S. E. Hunt, J. I. Jones, A. S. Lindsey, D. C. Killoh, and H. S. Turner, *J. Chem. Soc.*, 3152 (1958); J. I. Jones, A. S. Lindsey, and H. S. Turner, *Chem. & Ind. (London)*, 659 (1958).

(9) The activities were estimated by decomposing the phthalate to carbonate. The phthalate evolves two molecules of carbon dioxide and hence the estimated value is one half of the ratio of concentrations of labeled and normal phthalate.

When the isotopic equilibrium is established¹⁰

$$\frac{dr_t}{dt} = 0, \text{ hence } [I] = 0 \text{ and/or } r_t =$$

$$\frac{1}{1 + \alpha[\text{CO}_2]} r_p + \frac{\alpha[\text{CO}_2]r_c}{2(1 + \alpha[\text{CO}_2])} \quad (4)$$

$$\frac{dr_p}{dt} = 0, r_p = r_c/2 \quad (5)$$

$$\frac{dr_c}{dt} = 0, [I] = 0 \text{ and/or } r_p = r_c/2 \quad (6)$$

If $r_c/2 \gg r_p$, as in the case shown below, the differential equations can be solved. Thus equation 3 is transformed to equation 7, where concentrations are expressed in terms of mole fractions, subscript 0 means initial state, and Cd is cadmium iodide catalyst.

$$\ln(r_c/r_{c0}) = -\frac{k_3}{k_2} \times \frac{[\text{III}]}{[\text{I}]_0 + [\text{Cd}]_0 + (1 + \alpha)[\text{CO}_2]_0} \quad (7)$$

Since the total activity of the system is constant during the reaction, the following relation is obtained.

$$r_{c0}[\text{CO}_2]_0 + 2r_{p0}[\text{I}]_0 = 2r_t[\text{III}] + 2r_p[\text{I}] + r_c[\text{CO}_2]_0 \quad (8)$$

If the conversion is nearly quantitative, or $[I] = 0$, the system can be discussed in terms of r_t or r_c .

$$r_{c0}[\text{CO}_2]_0 + 2r_{p0}[\text{I}]_0 = 2r_t[\text{I}]_0 + r_c[\text{CO}_2]_0 \quad (9)$$

Similarly, the following equations can be derived from Scheme 2.

$$\frac{dr_t}{dt} = \frac{k_1 k_2}{k_{-1} + k_{-2}} \frac{[\text{I}]}{[\text{III}]} (r_p/2 + r_c/2 - r_t) \quad (10)$$

$$\frac{dr_p}{dt} = \frac{k_1 k_{-1}}{k_{-1} + k_2} (r_c - r_p) \quad (11)$$

$$\frac{dr_c}{dt} = \frac{k_1 [\text{I}]}{[\text{CO}_2]} (r_p - r_c) \quad (12)$$

and in the equilibrium

$$\frac{dr_t}{dt} = 0, \text{ hence } [I] = 0 \text{ and/or } r_t = r_c/2 + r_p/2 \quad (13)$$

$$\frac{dr_p}{dt} = 0, r_c = r_p \quad (14)$$

$$\frac{dr_c}{dt} = 0, [I] = 0 \text{ and/or } r_p = r_c \quad (15)$$

If $r_c \gg r_p$, the following equation is obtained

$$\ln(r_c/r_{c0}) = -\frac{k_{-1} + k_2}{k_2} \frac{[\text{III}]}{[\text{CO}_2]} \quad (16)$$

These two mechanisms, Schemes 1 and 2, may be distinguished at equilibrium as follows. The difference between intra- and intermolecular reactions is expressed as shown in Equations 17 and 18. From equation 5 or 6 together with introduction of equation 5 or 6 into equation 4, the Scheme 1 should give

$$r_t = r_p = r_c/2 \quad (17)$$

(10) The isotopic equilibrium is established by two factors; one is the completion of reaction, $[I] = 0$, and the other is the true equilibrium, $r_p = r_c/2$ etc.

and from equations 13, 14, and 15, Scheme 2 should give

$$r_t = r_p = r_c \quad (18)$$

Since equation 17 was satisfied with labeled potassium phthalate, the reaction should be intramolecular (Fig. 1). With labeled potassium carbonate the equilibrium cannot be attained even at the end of the reaction (Fig. 2). But it is of interest

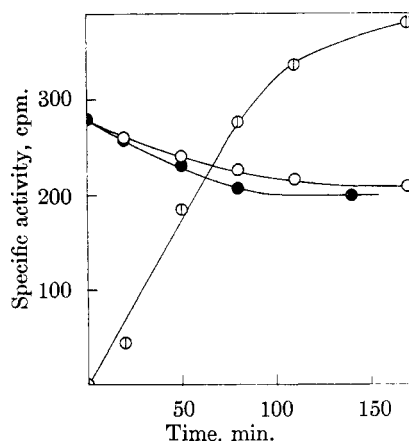


Fig. 1. Plots for the verification of Equation 17 with labeled potassium phthalate (1.0×10^{-2} mole), potassium carbonate (0.3×10^{-2} mole), and cadmium iodide (0.1×10^{-2} mole) at 400°

○ r_t , specific activity of terephthalic acid
● r_p , specific activity of phthalic acid
⊙ r_c , specific activity of potassium carbonate

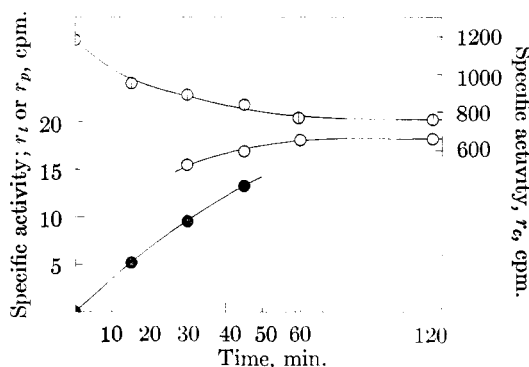


Fig. 2. Plots for the verification of $r_c \gg r_p$ with the reaction mixture of potassium phthalate (1.0×10^{-2} mole), cadmium iodide (0.1×10^{-2} mole), and potassium carbonate- C^{14} (0.3×10^{-2} mole) at 400°

○ r_t , specific activity of terephthalic acid
● r_p , specific activity of phthalic acid
⊙ r_c , specific activity of potassium carbonate

to note that Sorm and Ratusky reported that the reaction is intermolecular, since the relation was

$$r_t = r_c/2 = r_{c0}/4 \quad (19)$$

obtained with labeled potassium carbonate. However, according to their hypothesis the intermediate, $^{-O_2CC_6H_4^{-}}$, should be stable. Since this intermediate seems to be quite unstable, their suggestion is questionable. Equation 19 is in accord

with equation 17 and thus supports our intramolecular mechanism.

The intramolecular nature of the reaction may further be confirmed in the following way. If $r_c/2 \gg r_p$ (see equation 7), a plot of $1/\ln(r_c/r_{c0})$ vs. $[CO_3]$ should be linear with a definite value of the intercept, while in the intermolecular mechanism the line should pass zero at $[CO_3] = 0$. From equation 7

$$1/\ln(r_{c0}/r_c) = \frac{k_2}{k_3} ([I]_0 + [Cd]_0 + [CO_3]_0)/[III] \quad (20)$$

In fact, the condition $r_c/2 \gg r_p$ was satisfied with the labeled carbonate (Fig. 2), where the yields of (III) were practically constant with varying $[CO_3]$. Results shown in Fig. 3 are in accord with equation 20.

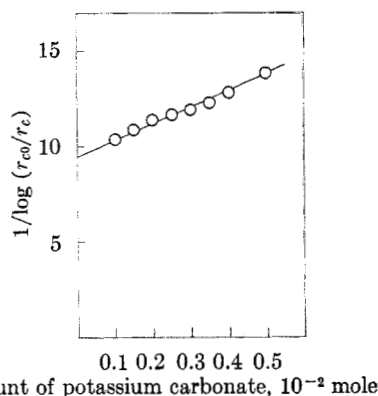
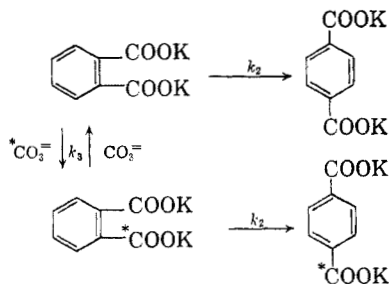


Fig. 3. Plots for the verification of Equation 20 with potassium phthalate (1.0×10^{-2} mole) and cadmium iodide (0.1×10^{-2} mole) at 420° for two hours

Finally, the modification of Scheme 1 which involves no common intermediate between rearrangement and exchange requires the following

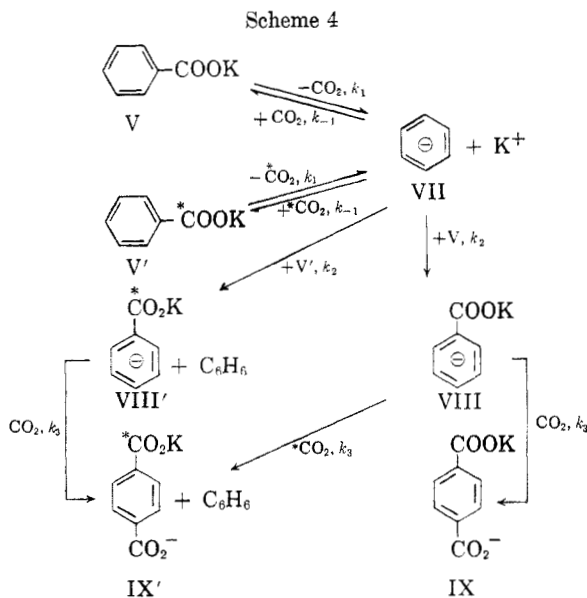
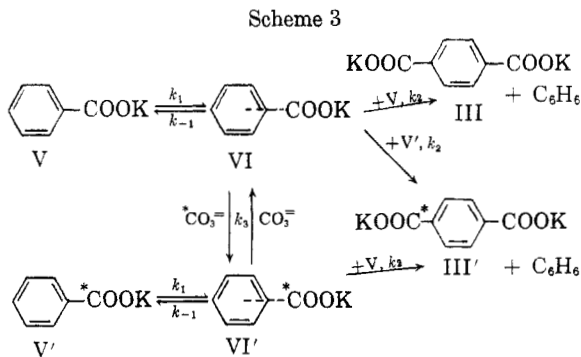


relation according to the similar deduction.

$$\frac{dr_t}{dt} = k_2 \frac{[I]}{[III]} (r_p - r_t) \quad (21)$$

This equation means $dr_t/dt < 0$ at $r_p < r_t$. But as shown in Fig. 1, this requirement is not satisfied.

Mechanism of the reaction of potassium benzoate. Two mechanisms may be possible for the reaction, i.e., a disproportionation, Scheme 3, and an elimination-substitution, Scheme 4, which is essentially the same as proposed by Sorm and Ratusky.



Rate equations can be derived from these schemes just as in the case of potassium phthalate. From Scheme 3

$$\frac{dr_t}{dt} = \frac{k_1 k_2}{(k_{-1} + k_2[V])} \frac{[V]^2}{[III]} \times \left\{ \frac{2k_{-1} + 2k_2[V] + k_3[CO_3]}{2(k_{-1} + k_2[V] + k_3[CO_3])} \right\} r_B + \frac{k_3[CO_3]}{2(k_{-1} + k_2[V] + k_3[CO_3])} (r_c - r_t) \quad (22)$$

$$\frac{dr_B}{dt} = \frac{k_1 k_{-1} k_3 [CO_3]}{(k_{-1} + k_2[V]) (k_{-1} + k_2[V] + k_3[CO_3])} \times (r_c - r_B) \quad (23)$$

$$\frac{dr_c}{dt} = \frac{k_1 k_3 [V]}{k_{-1} + k_2[V] + k_3[CO_3]} (r_B - r_c) \quad (24)$$

where

$$r_t \propto \frac{[III']}{2[III]}, r_B \propto \frac{[V']}{[V]}, r_c \propto \frac{[CO_3]}{[CO_3]}$$

and in equilibrium

$$r_t = r_B = r_c \quad (25)$$

If

$$r_B \ll r_c$$

$$\ln(r_c/r_{c0}) = - \int_0^{[III]} \frac{k_1 k_3 [V]}{k_{-1} + k_3[CO_3] + k_2[V]} d[III] \quad (26)$$

Analogously, from Scheme 4

$$\frac{dr_i}{dt} = \frac{k_1 k_2}{k_{-1}[\text{CO}_2] + k_2[\text{V}]} \frac{[\text{V}]^2}{[\text{IX}]} (r_c/2 + r_B/2 - r_i) \quad (27)$$

$$\frac{dr_B}{dt} = \frac{k_1 k_{-1}}{k_{-1}[\text{CO}_2] + k_2[\text{V}]} [\text{CO}_2](r_c - r_B) \quad (28)$$

$$\frac{dr_c}{dt} = \frac{k_1[\text{V}]}{[\text{CO}_2]} (r_B - r_c) \quad (29)$$

where

$$r_i \propto \frac{[\text{IX}']}{2[\text{IX}]}, r_B \propto \frac{[\text{V}']}{[\text{V}]}, r_c \propto \frac{[\text{CO}_2]'}{[\text{CO}_2]}$$

and in equilibrium,

$$r_i = r_B = r_c \quad (30)$$

From equation 29, if $r_B \ll r_c$

$$\ln(r_c/r_{c0}) = -\frac{k_1}{[\text{CO}_2]} \int_0^{[\text{IX}]} [\text{V}] d[\text{IX}] \quad (31)$$

Therefore, the two mechanisms cannot be distinguished on the basis of isotopic equilibrium, since both of them require the same relations, 25 and 30, which is satisfied by our results (Fig. 4). But they

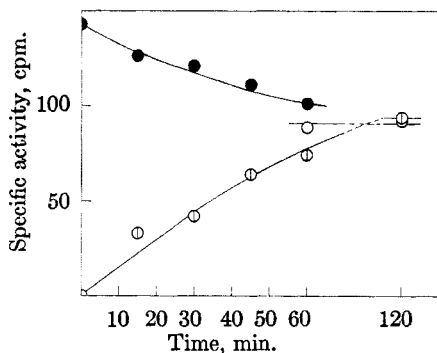


Fig. 4. Plots for the verification of Equation 25 with a mixture of labeled potassium benzoate (1.0×10^{-2} mole), potassium carbonate (0.39×10^{-2} mole) and (0.12×10^{-2} mole) at 420°

- r_i , specific activity of terephthalic acid
- r_B , specific activity of benzoic acid
- ⊙ r_c , specific activity of potassium carbonate

can be distinguished by observing the dependence of the specific activities on the amount of the added carbonate.

In Scheme 3, the specific activity depends on the following equation derived from equation 26, where constants a , b , and b' are independent of $[\text{CO}_2]$.

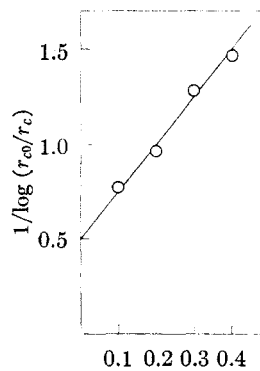
$$1/\ln(r_{c0}/r_c) = a + b[\text{CO}_2] \quad (32)$$

On the other hand, in Scheme 4, equation 31 gives

$$1/\ln(r_{c0}/r_c) = b'[\text{CO}_2] \quad (33)$$

The results, as shown in Fig. 5, correspond to equation 32 and hence the disproportionation mechanism is preferable.

The effect of catalyst. It was found that the activity of the terephthalic acid depends largely on both the concentration and nature of catalyst before the



Amount of potassium carbonate, 10^{-2} mole

Fig. 5. Plots for the verification of Equation 32 with a mixture of potassium benzoate (1.0×10^{-2} mole) and cadmium iodide (0.24×10^{-2} mole) at 440° for two hours

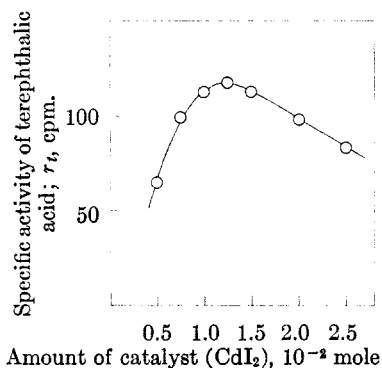


Fig. 6. Dependence of specific activity of terephthalic acid on the amount of catalyst with a mixture of potassium phthalate (1.0×10^{-2} mole) and potassium carbonate (0.2×10^{-2} mole) at 420° for three hours

equilibrium is established. These results can be explained by Scheme 1. When labeled carbonate is used, the dependence of activity of terephthalic acid (r_i) on the catalyst concentration is shown in Fig. 6, the curve having a maximum. The decrease of r_i at higher concentration of catalyst may be ascribed to the faster rate of rearrangement compared with the rate of exchange. It means that catalysts have their principal influence on k_2 in Scheme 1. On the other hand, the increase of r_i at lower concentration may depend on the lower conversion. Since the exchange depends on $k_1 k_3$, and k_3 is independent of the catalyst, it is rational that k_1 depends also on the catalyst. As shown in Table I, the catalyst cation has an influence on r_i , i.e., k_2 at 50–60% conversion, but the anion has little influence.

The following facts imply that the first process (k_1) seems to be ionization. (1) The initial rapid isotopic exchange occurs with catalysts of low melting point and even with potassium carbonate alone (Fig. 7). (2) The activity of catalyst is related to the melting point of the catalyst. (3) The reaction occurs in the basic semiliquid system as implied by electric conductivity measurement.

TABLE I

THE EFFECTS OF VARIOUS CATALYSTS ON r 's IN CPM AND ON THE CONVERSION PERCENTAGE AT 420°^a

A. With labeled phthalate				
Catalyst	r_t	Conversion (%)		
CdI ₂	448	59		
CdCl ₂	418	51		
ZnCl ₂	292	46		
B. With labeled carbonate				
Catalyst	r_t	r_p	r_c	Conversion (%)
CdI ₂	56.1	41.4	408	62
ZnCl ₂	69.0	41.4	280	59

^a Moles of reactants: phthalate (1.0×10^{-2}), carbonate (0.3×10^{-2} for A and 0.2×10^{-2} for B), catalyst (0.1×10^{-2}). Reaction time: 1 hr. (CdI₂), 2.5 hr. (ZnCl₂).

Appendix. As a typical example, Equations 1, 2, and 3 can be derived from Scheme 1 as follows:

$$\frac{d[I]}{dt} = k_{-1}[II] - k_1[I] \quad (a)$$

$$\frac{d[I']}{dt} = k_{-1}[II'] - k_1[I'] \quad (b)$$

$$\frac{d[II]}{dt} = k_1[I] + k_3[CO_3][II'] - (k_{-1} + k_2 + k_3[\overset{*}{CO}_3])[II] \cong k_1[I] - (k_{-1} + k_2)[II] \quad (c)$$

$$\frac{d[II']}{dt} = k_1[I'] + k_3[CO_3][II] - (k_{-1} + k_2 + k_3[CO_3])[II'] \quad (d)$$

$$\frac{d[III]}{dt} = k_2[II] \quad (e)$$

$$\frac{d[III']}{dt} = k_2[II'] \quad (f)$$

$$\frac{-d[CO_3]}{dt} = \frac{d[\overset{*}{CO}_3]}{dt} = k_3[CO_3][II'] - k_3[\overset{*}{CO}_3][II] \quad (g)$$

The terms for the structure having two isotopic carbons are neglected. When the steady-state method is applied, Equations c and d are transformed to h and i, respectively:

$$\frac{d[II]}{dt} = 0, [II] = \frac{k_1[I]}{k_{-1} + k_2} \quad (h)$$

$$\frac{d[II']}{dt} = 0, [II'] = \frac{k_1[I'] + k_3[\overset{*}{CO}_3][II]}{k_{-1} + k_2 + k_3[CO_3]} \quad (i)$$

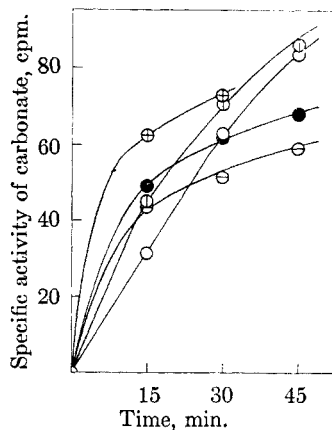


Fig. 7. Initial change of specific activity of potassium carbonate in a mixture of potassium carbonate (0.2×10^{-2} mole), catalyst (0.1×10^{-2} mole) and labeled potassium phthalate (1.0×10^{-2} mole) at 400°

Catalysts: \oplus ZnCl₂, \bullet ZnI₂, \circ CdI₂, \circ CdCl₂, \ominus no catalyst

The specific activities are expressed as

$$r_t = \frac{[III']}{2[III]}, r_p = \frac{[I']}{2[I]}, r_c = \frac{[\overset{*}{CO}_3]}{[CO_3]}$$

The introduction of the values derived from Equations a-i into time differentials of r 's gives:

$$\frac{dr_t}{dt} = \frac{d}{dt} \left(\frac{[III']}{2[III]} \right) = \frac{k_2[III][II'] - k_2[III'][II]}{2[III]^2} = \frac{k_1 k_2}{k_{-1} + k_2} \cdot \frac{[I]}{[III]} \left(\frac{1}{1 + \alpha[CO_3]} \cdot r_p + \frac{\alpha[CO_3]}{1 + \alpha[CO_3]} \cdot \frac{r_c}{2} - r_t \right) \quad (1)$$

$$\frac{dr_p}{dt} = \frac{d}{dt} \left(\frac{[I']}{2[I]} \right) = \frac{k_1[II]}{2[I]} \left(\frac{[II']}{[II]} - \frac{[I']}{[I]} \right) = \frac{k_1 k_{-1}}{k_{-1} + k_2} \left(\frac{\alpha[CO_3]}{1 + \alpha[CO_3]} \right) (r_c/2 - r_p) \quad (2)$$

$$\frac{dr_c}{dt} = \frac{d}{dt} \left(\frac{[\overset{*}{CO}_3]}{[CO_3]} \right) = k_3[II] \left(\frac{[II']}{[II]} - \frac{[\overset{*}{CO}_3]}{[CO_3]} \right) = \frac{2k_1 k_3}{k_{-1} + k_2} [I] \left(\frac{1}{1 + \alpha[CO_3]} \right) \left(r_p - \frac{r_c}{2} \right) \quad (3)$$

where

$$\alpha = k_3/(k_{-1} + k_2)$$

Acknowledgments. The authors wish to thank Professors R. Oda, R. Goto, and S. Yoshizawa for their aid in performing these experiments.

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