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KINETICS AND MECHANISM OF THE REARRANGEMENT OF POTASSIUM PHTHALATE[1]

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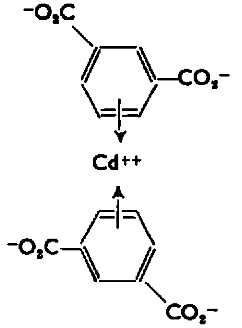
Abstract—The cadmium salt-catalysed rearrangement of potassium phthalate to terephthalate has been studied kinetically by following the concentration of potassium phthalate together with potassium benzoate, trimellitate, isophthalate and terephthalate by means of a combination of UV spectrophotometry and gravimetry. The rate of disappearance of phthalate satisfied the rate equation: $v = k_1$ [Phthalate] + $k_2^0[\mathrm{CdI_2}][\mathrm{Phthalate}]^2$, where k_1 increased with $[\mathrm{CdI_2}]$ in the range of concentration (0–0·1847 M) and then decreased linearly with increasing $[\mathrm{CdI_2}]$. A mechanism consisted of simultaneous reaction, i.e., decarboxylation and disproportionation of phthalate was proposed on the basis of these data together with the information obtained from other products, i.e., benzoate, trimellitate and isophthalate. The latter reaction seems to involve sandwich-type activated complexes.

THE cadmium salt-catalysed rearrangement of potassium phthalate to terephthalate is known as the Henkel process.[2] In previous kinetic studies, the authors have reported on the rearrangement of potassium isophthalate[3] and disproportionation of potassium benzoate.[4] The reaction of isophthalate satisfies the rate law: $v = [\mathrm{CdI_2}]$ $[\mathrm{isophthalate}]^2$, while the disproportionation of benzoate fits the equation: $v = k[\mathrm{CdI_2}][\mathrm{benzoate}]$. The rate equation for isophthalate implies the rate-determining formation of a sandwich-type activated complex (I),



I

and the equation for benzoate is explicable by the rate-determining formation of 1:1 complex followed by the rapid formation of 1:2 complex corresponding to (I).

The present paper deals with the results of the kinetic studies on the rearrangement of potassium phthalate to terephthalate. The reaction is rather complicated by the

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[2] B. Raecke, to Henkel Co., D. B. P., 936,036 (1955); B. Raecke, *Angew. Chem.* 70, 1 (1958).

[3] Y. Ogata and K. Sakamoto, *Chem. & Ind.* 749 (1964).

[4] Y. Ogata and K. Sakamoto, *Chem. & Ind.* 2012 (1964).

simultaneous formation of potassium benzoate, trimellitate and isophthalate. The rate was followed mainly by the decrease of the concentration of phthalate, and checked by the increase of the concentration of benzoate, trimellitate, isophthalate and terephthalate.

RESULTS AND DISCUSSION

The rate of a decrease of the concentration of potassium phthalate was first- and second-order with respect to the concentration of phthalate, $(a - x)$, at time t, where a is the initial concentration of phthalate.

$$v = \frac{dx}{dt} = k_1(a - x) + k_2(a - x)^2 \qquad (1)$$

$$\int_a^{a-x} \frac{dx}{(a - x)k_1 + k_2(a - x)^2} = \int_0^t dt$$

$$\frac{1}{k_2}\int_a^{a-x} \frac{k_2}{k_1}\left(\frac{1}{a - x} - \frac{1}{a - x + \frac{k_1}{k_2}}\right) dx = t$$

$$k_1 = \frac{1}{t}\left\{\ln\left(\frac{a - x + \frac{k_1}{k_2}}{a - x}\right) - \ln\left(\frac{a + \frac{k_1}{k_2}}{a}\right)\right\} \qquad (2)$$

The value of k_1 may be calculated by applying various values of (k_1/k_2) to Eqn. 2 in trial and error until the constancy of k_1 is satisfactory. The value of k_2 is obtained from the values of these (k_1/k_2) and k_1. These constants were calculated from the conversion of phthalic acid as listed in Table 1.

TABLE 1. RATE CONSTANTS FOR A TYPICAL RUN OF THE POTASSIUM PHTHALATE CONVERSION WITH INITIAL CONCENTRATIONS OF POTASSIUM PHTHALATE (1·397 M) AND CADMIUM IODIDE (0·369 M) IN POTASSIUM CYANATE AT 365 ± 2°

$k_1'/k_2' = 0{\cdot}21$

Time (min)	Conversion (%)	k_1' (min^{-1})
10·00	55·4	0·0131
19·67	34·1	0·0147
30·0	23·4	0·0150
40·0	19·93	0·0132
50·0	15·92	0·0130
60·0	11·84	0·0138
		Av. 0·0138

Therefore,

$$k_2' = \frac{k_1'}{0{\cdot}21} = 6{\cdot}57 \times 10^{-2}\ \text{min}^{-1}$$

$$k_1 = \frac{k_1'}{60{\cdot}0} = 2{\cdot}30 \times 10^{-3}\ \text{sec}^{-1}$$

$$k_2 = \frac{k_2'}{1{\cdot}397 \times 60{\cdot}0} = 7{\cdot}79 \times 10^{-4}\ \text{M}^{-1}\ \text{sec}^{-1}$$

TABLE 2. THE EFFECT OF CADMIUM IODIDE CONCENTRATION ON THE RATE CONSTANTS (k_1 AND k_2) AND RATIOS (k_1/k_2) FOR THE CONVERSION OF POTASSIUM PHTHALATE IN POTASSIUM CYANATE AT 365 ± 2°

[CdI$_2$] (M)	Initial concentration potassium phthalate (M)	$k_1 \times 10^4$ (sec^{-1})	$k_2 \times 10^4$ (M^{-1} sec^{-1})	k_1/k_2 (M)
—	1·397	0	0	...
0·0923	1·397	0·635	1·52	0·0418
0·1847	1·397	3·35	1·60	2·09
0·369	1·397	2·30	7·79	0·296
0·369	2·095	2·80	6·31	0·444
0·554	1·397	2·43	11·52	0·211
0·739*	1·397	1·66	29·8	0·557

* This rate was too rapid to obtain reliable data.

The effect of catalyst concentration. The rate constants k_1 and k_2 varied by the change of catalyst concentration as shown in Table 2 and illustrated in Fig. 1. As apparent in the Table and Fig., the first-order constant k_1 has a maximum at [CdI$_2$] of 0·1847 M, i.e., [CdI$_2$]/[Phthalate] = 1/10, and an increase of [CdI$_2$] more than 0·1847 M results in a linear decrease of the k_1 value, while the second-order constant k_2 shows a linear increase with increasing [CdI$_2$], i.e., $v = k_2^0[\text{CdI}_2][\text{Phthalate}]^2$, where $k_2^0 = k_2/[\text{CdI}_2]$. The value of k_2^0 is calculated from a tangent of the line in Fig. 1-b to be $2{\cdot}11 \times 10^{-3}$ M^{-2} sec^{-1}. These value of k_1, k_2 and k_2^0 are significantly higher than the corresponding values of isophthalate[3] ($k_2^0 = 4{\cdot}52 \times 10^{-5}$ M^{-2} sec^{-1}) and benzoate[4] ($k_0^0 = 1{\cdot}26 \times 10^{-4}$ M^{-1} sec^{-1}).

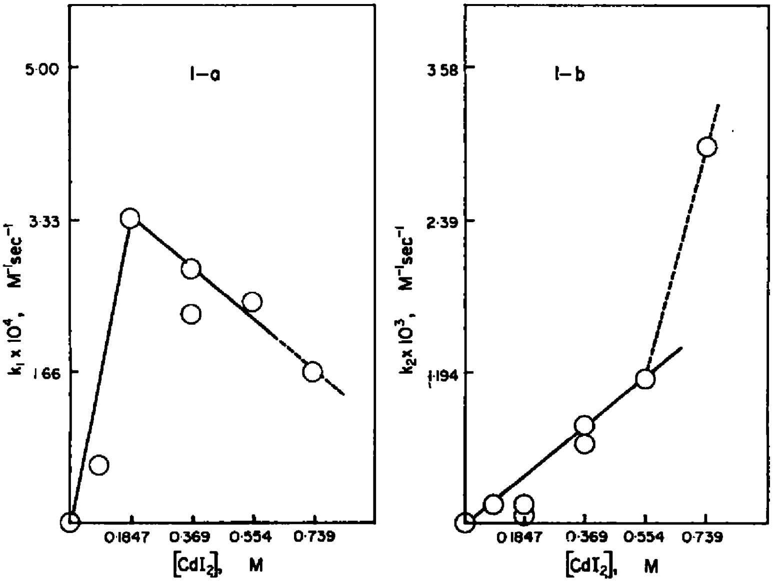
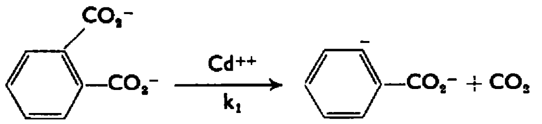


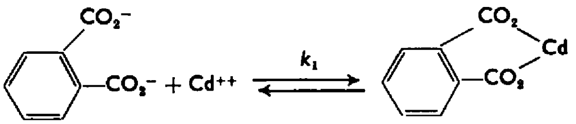
FIG. 1

The rate of formation of all products. All reaction products were analysed quantitatively by means of the methods described in experimental part. Fig. 2 shows the conversion vs. reaction time for a typical run. Figs. 3–5 shows the conversion curves for the products at the various concentrations of catalyst. As obvious from Figs. 2 and 3, the concentration of phthalate decreased rapidly at early stages of the reaction, e.g., the conversion reaches to 90% in ca. 30 min, if the high concentration of catalyst (0·739 M) was employed; the evolution of carbon dioxide was detected at the start (10–30 min) and the decarboxylation was catalysed by cadmium catalyst. A remarkable increase of the content of benzoic acid was obtained at early stages, but the conversion to benzoic acid did not surpass 50% and the content decreases as the reaction proceeded after the maximum. The similar conversion curve having a maximum was observed for the trimellitic acid formation, but in this case the conversion did not surpass 20%. The ratio of the formation of isophthalate vs. terephthalate 2–3 : 1. It is of interest to note that the rates of the formation of isophthalate and terephthalate were much slower compared with the rate of disappearance of phthalate, which seems to mean that a considerable part of the reaction may go by way of the reaction of benzoate with trimellitate or the disproportionation of benzoate.

Reaction mechanism. The data are expressed as a simultaneous reaction of first-order (decarboxylation, Eq. 3) and second-order (disproportionation, Eqs. 5-8) with respect to potassium phthalate; the summarized results suggest the following mechanism for the conversion.



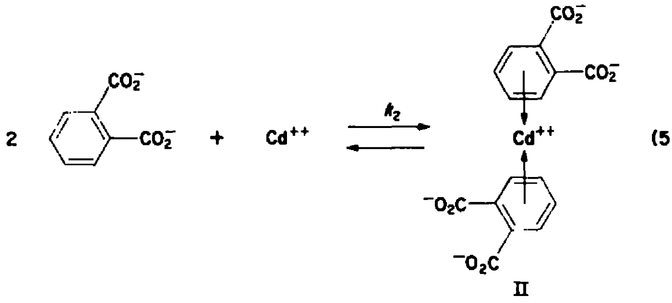
(3)

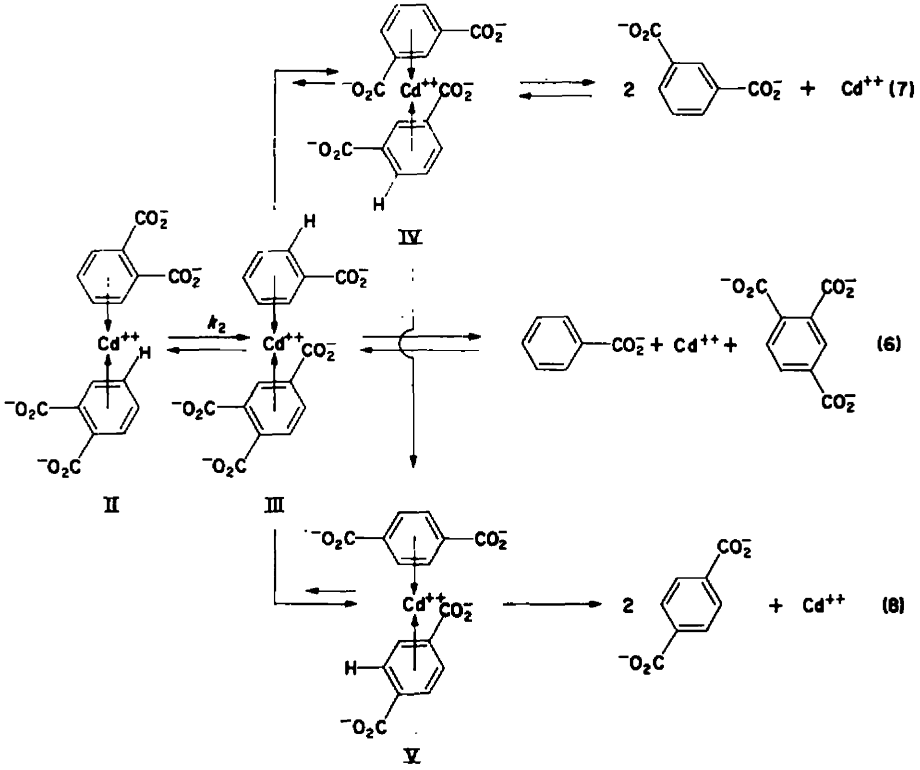


(4)

No decarboxylation occurs without CdI_2. The addition of a small amount of cadmium catalyst (1/10 mole per mole of phthalate) accelerates the decarboxylation of phthalate (Eq. 3) and increases the value of k_1, while the larger amount of it tends to retard the decarboxylation by the stabilization with the salt formation shown in Eq. 4. See Fig. 1a.

There may be several courses for terephthalate formation from phthalate. The formations of benzoate and trimellitale is predominant at early stages (Eqs. 3 and 6), but the yield of benzoic acid does not surpass 50%, and the conversion curves giving benzoate and trimellitate have similar forms with maxima at the same time; hence it seems to be favourable to go by way of the complex III which can form benzoate and trimellitate rather than complex IV or V leading directly to isophthalate or terephthalate, respectively, i.e., one hydrogen atom is changed with the nearest carboxylate group on another ring in the first stage to give complex III and then one more exchange occurs to increase the stability of complex III. Two molecules of phthalate should orient to make up the least crowded configuration, i.e., complex II, hence the exchange of an hydrogen atom with a carboxylate group always gives complex III which leads





to benzoate and trimellitate; the electrostatic and steric repulsions between *ortho* carboxylate groups may accelerate the reaction. The molar ratio of isophthalate vs. terephthalate at early stages was ca. 2:1. This phenomenon may be explained by considering the probability of exchange and the number of possible configurations of complex II; i.e., as shown in Fig. 6, in the possible configurations A and B, A has the probability of 1/2 to form isophthalate, whereas B has the probability of (1/4) + (1/4) to produce isophthalate and the probability of (1/4) + (1/4) to produce terephthalate. In summation, the ratio of the probability to form isophthalate vs. terephthalate is 2:1 (Figs. 2 and 5). Similarly, the ratio of isophthalate vs. terephthalate was 2:1 in the case of disproportionation of benzoate.[4] Since complex IV is more stabilized than III

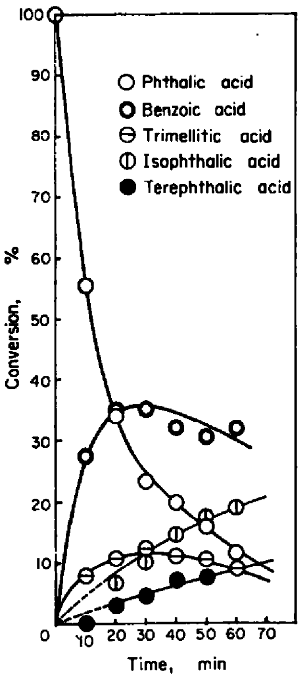


FIG. 2

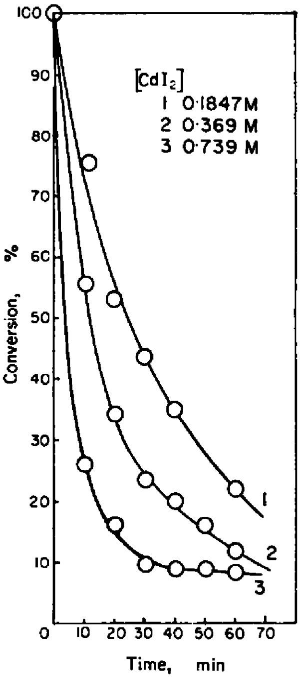


FIG. 3

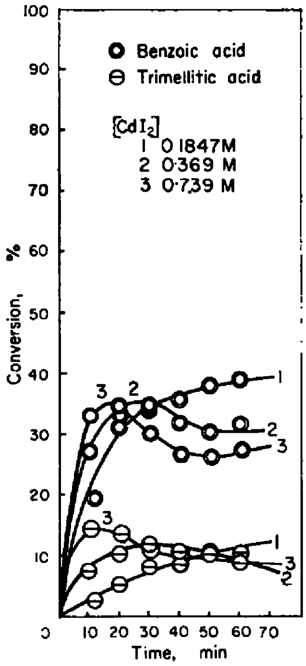


FIG. 4

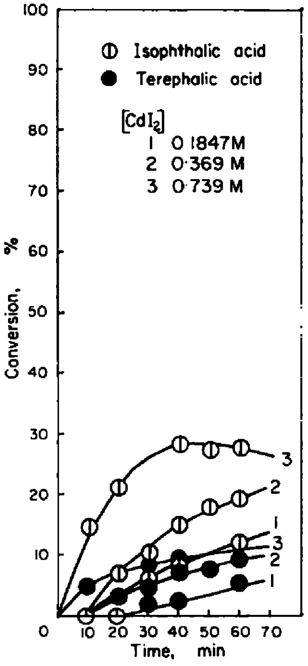


FIG. 5

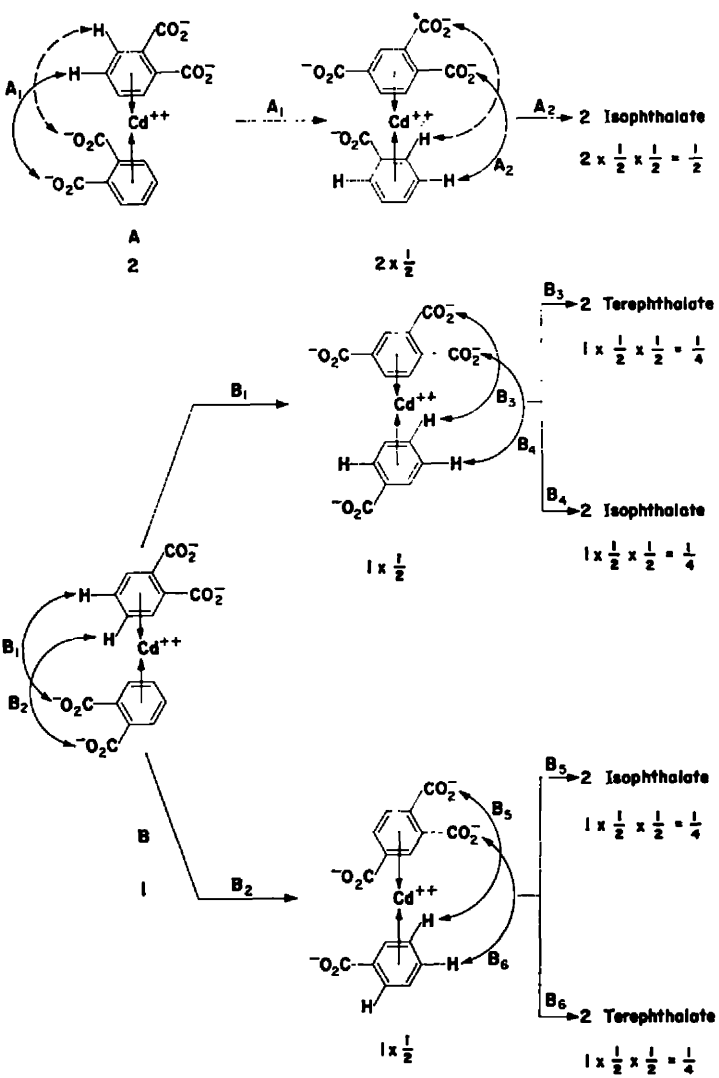


FIG. 6

in view of the less repulsion between carboxylate groups, the rearrangement of isophthalate to terephthalate ($k_2^0 = 4{\cdot}52 \times 10^{-5}$ M^{-2} sec^{-1})^3 is slower than the formation (Eq. 6) of trimellitate and benzoate described above ($k_2^0 = 2{\cdot}11 \times 10^{-3}$ M^{-2} sec^{-1}).

Symmetrical complex IV seems to be the most stabilized one and, further, formed terephthalate is removed out of the system; therefore, the conversion leads eventually to terephthalic acid.

EXPERIMENTAL

Materials. Commercial phthalic anhydride, m.p. 131°, was neutralized by KOH aq, evaporated to dryness and dried at 50° in a vacuum-drier. Cd salts and KCNO were of commercial guaranteed grade, which were used after drying.

Kinetic procedure. A mixture of known amounts of potassium phthalate, catalyst and KCNO (solvent) was introduced to 6 test tubes with rubber stoppers having constricted glass tubes. The tubes were dipped in a melted Pb-bath. The contents of tubes formed homogeneous solutions at 1–2 min after dipping; the bath temp was adjusted to 365 ± 2°. Each tube was taken out at known intervals of time and the content analysed as follows.

Analysis of reaction products. The reaction mixture was dissolved in hot water (130 ml) and, after filtering off the catalyst and other impurities, the filtrate was added with conc. HCl (20 ml) to precipitate isophthalic and terephthalic acids after standing for ca. 12 hr under ice-cooling.

The precipitate was filtered off by a glass funnel and analysed by UV spectrophotometry to determine the contents of isophthalic and terephthalic acids as reported previously by using λ_{max} 280·5 mμ and 285 mμ, respectively.[8] The filtrate was transferred to a separatory funnel to extract benzoic acid with three 20 ml portions of $CHCl_3$. The evaporation of $CHCl_3$, extract gave the wt of formed benzoic acid. The residual aqueous layer contained phthalic and trimellitic acids together with inorganic materials. The aqueous solution was transferred to a measuring flask, diluted to 250 ml with distilled water, and then 2 ml of the diluted solution was again diluted to 50 ml. The solution obtained was analysed by UV spectrophotometry to estimate the content of phthalic and trimellitic acids by means of the following simultaneous Eqs.

$$W_p = 1{\cdot}203\ (A_{276} - 0{\cdot}810\ A_{290})$$

$$W_{tr} = 0{\cdot}407\ (2{\cdot}83\ A_{290} - A_{276})$$

Here, W_p and W_{tr} is the wt (g) of phthalic and trimellitic acids, respectively, and A is the absorbance at the subscripted wave length.

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