

One-Step Synthesis of Terephthalic Acid from Benzene in Water Using Cyclodextrin as Catalyst

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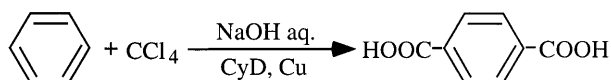
The one-pot synthesis of terephthalic acid from benzene has been achieved by treatment with tetrachloromethane, copper powder, and an aqueous sodium hydroxide solution using cyclodextrin as a catalyst at 30 °C under nitrogen in 46 mol% yield with 100% selectivity.

In recent years, there has been a great interest in the synthesis of aromatic dicarboxylic acids as versatile raw materials for high-performance polymers and liquid crystalline compounds.¹ Terephthalic acid is an essential monomer for poly(ethylene terephthalate), poly(*p*-phenylene terephthalamide), poly[(terephthalic acid)-*alt*-(*p*-phenylene diamine; 3,4'-diaminodiphenylether)], etc., and is produced in industries by liquid-phase oxidation of *p*-xylene,² or by disproportionation of potassium benzoate.³ The conventional preparation process of terephthalic acid is composed of many steps: separation of xylene from petroleum, isomerization of xylene, separation of *p*-xylene, and oxidation of *p*-xylene. In addition purification is required in each step.

One-pot synthesis, in which a target compound is synthesized by successive addition of reagents to a reaction vessel without separation or purification of intermediates in each step, is ideal for organic synthesis. This method requires high selectivity and high yield in each reaction step, since otherwise separation of the desired compound from various by-products in the final reaction mixtures should be difficult. Komiyama and Hirai reported one-pot preparation of 4-hydroxychalcone from phenol by the use of cyclodextrin (CyD).⁴

α -, β - and γ -CyD, cyclic oligosaccharides consisting of 6, 7 and 8 glucose units linked by α (1–4) bonds, have hydrophobic cavities which can solubilize hydrophobic organic compounds into water by inclusion.^{5–7} We have reported selective synthesis of terephthalic acid from benzoic acid in an aqueous sodium hydroxide solution.⁸ In this reaction benzoic acid can be easily soluble in an aqueous alkaline solution as benzoate, which can be concerned with the reaction. On the other hand, benzene will be little concerned with the reaction in an alkaline solution because of the low solubility (0.7 g dm⁻³ at 22 °C) without CyD. Here we report for the first time a selective one-step synthesis of terephthalic acid in water using CyD (Scheme 1). To the best of our knowledge, there is no report on the introduction of two carboxyl groups into benzene by one-step reaction.

Benzene (2.8 mmol), copper powder (0.8 mmol), and CyD (2.0 mmol) were mixed in 30 cm³ of 30 wt% aqueous solution of sodium hydroxide. To the mixtures 27 mmol of tetra-



Scheme 1.

chloromethane was added and the mixtures were stirred for 7 h at 30 °C under nitrogen. After the reaction, the excess tetrachloromethane was removed by evaporation under reduced pressure. The reaction mixtures were neutralized with hydrochloric acid. The product analysis on the reaction mixtures was made by high performance liquid chromatography (HPLC).⁹ The main product was isolated and confirmed to be terephthalic acid by comparison with the authentic sample (HPLC, IR, MS, ¹H-NMR). The yield and selectivity of terephthalic acid were calculated on the basis of the starting amount of benzene, and the total amount of carboxylated products, respectively.

Table 1 exhibits a catalytic effect of CyDs for carboxylation of benzene. The yield of terephthalic acid is 26 mol% in the presence of β -CyD, where the yields of both phthalic acid (*ortho*-carboxylated product) and isophthalic acid (*meta*-carboxylated product) are 0 mol%. In other words, the selectivity for the production of terephthalic acid among carboxylated products is 100%. In the absence of β -CyD, however, the reaction does not proceed at all. The solubility of benzene in water is poor as described above. Therefore, benzene itself may be little concerned with the reaction in an aqueous alkaline solution. In the presence of β -CyD, benzene can be solubilized in an aqueous alkaline solution by inclusion in the cavity of the β -CyD and concerned with the reaction.

When α -CyD or γ -CyD was used instead of β -CyD, the carboxylation did not occur at all. This may be attributed to the much smaller formation constants of benzene inclusion complexes of α - and γ -CyDs than that of β -CyD.¹⁰ In addition the poor solubility of tetrachloromethane in water might cause the present difference in the reactivity. The formation constant of the inclusion complex of tetrachloromethane with α -CyD (42 \pm 17 dm³ mol⁻¹) is smaller than that with β -CyD (150 \pm 35 dm³ mol⁻¹), determined by the volatilization rate.¹¹ The association between γ -CyD and tetrachloromethane is not observed at all.¹¹ Thus, the carboxylation of benzene with tetrachloromethane by using α -CyD or γ -CyD hardly proceeded.

Figure 1 shows the dependence of the yield of terephthalic acid on the initial mole ratio of β -CyD to benzene. The yield increases with increasing amounts of β -CyD, and has the maxi-

Table 1. Catalytic effect of cyclodextrins for production of terephthalic acid from benzene

CyD	Yield of carboxylated products / mol%	Selectivity of terephthalic acid / %
None	0	–
α -CyD	0	–
β -CyD	26	100
γ -CyD	0	–

Conditions: 30 wt% NaOH aq. 30 cm³, benzene 2.8 mmol, Cu powder 0.8 mmol, CyD 1.4 mol, CCl₄ 8.5 mmol, 30 °C.

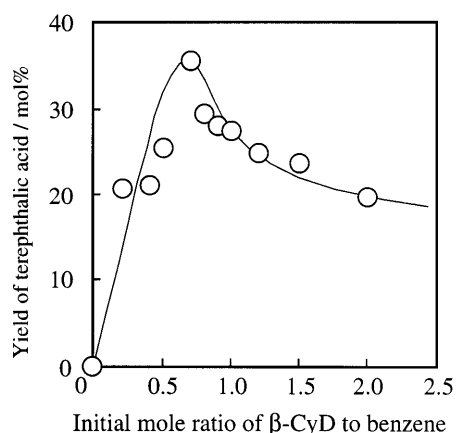


Figure 1. Plot of the yield of terephthalic acid vs. the initial mole ratio of β -CyD to benzene. Conditions: 30 wt% NaOH aq. 30 mL, benzene 2.8 mmol, Cu powder 0.8 mmol, CCl_4 8.5 mmol, 30 °C.

mal value (36 mol% with 100% selectivity) at a mole ratio of β -CyD to benzene of 0.7. The promotion of carboxylation by β -CyD is probably attributable to inclusion complex formation. The solubilities of tetrachloromethane and benzene in a concentrated aqueous alkaline solution increase by the addition of β -CyD. Decrease in the yield of terephthalic acid at the initial mole ratios of β -CyD larger than 0.7 may be associated with deactivation of trichloromethyl radical⁸ by coupling since much β -CyD can allow easy formation of trichloromethyl radical, resulting in hexachloroethane by coupling without reaction with benzene. In fact, Steudel reported the trichloromethyl radicals were rapidly converted to hexachloroethane.¹²

The relationship between the yield of terephthalic acid and the initial amount of tetrachloromethane at a mole ratio of β -CyD to benzene of 0.7 is shown in Figure 2. The yield of terephthalic acid takes the maximum (46 mol% with 100% selectivity) at a mole ratio of tetrachloromethane to benzene of 9.5. Tetrachloromethane is required in excess to get the good yield of terephthalic acid, probably because considerable parts of the active species formed from tetrachloromethane are decomposed by reaction with hydroxide in the aqueous solution. Decrease in the yield of terephthalic acid at the initial mole ratios of tetrachloromethane larger than 25 may be due to the overwhelming formation of the β -CyD–tetrachloromethane complex, which may prevent the formation of β -CyD–benzene complex.

The essential factor of the carboxylation by the use of β -CyD is considered to be the inclusion complex formation of β -CyD with benzene and tetrachloromethane in the reaction mixtures. Benzene is axially included in the cavity of β -CyD, according to the literature.¹⁰ The benzene molecule included in β -CyD may be predominantly attacked by trichloromethyl radical, as the active species. Thus, a benzoate anion is formed in the aqueous alkaline solution as an intermediate. The benzoate anion was axially included in the cavity of β -CyD with orientation which locates the 4-position of benzoate at the secondary hydroxyl side of β -CyD.¹³ The reaction of benzoate anion included in β -CyD is sterically hindered at the 2- and 3-positions of benzoate anion, and is preferentially attacked at the 4-position by trichloromethyl radical, producing terephthalic acid

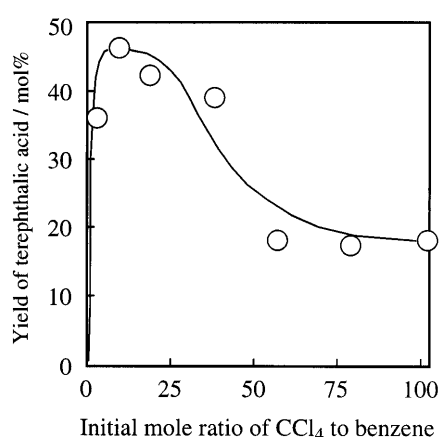


Figure 2. Plot of the yield of terephthalic acid vs. the initial mole ratio of CCl_4 to benzene. Conditions: 30 wt% NaOH aq. 30 mL, benzene 2.8 mmol, β -CyD 1.96 mmol, Cu powder 0.8 mmol, 30 °C.

with very high selectivity.

In conclusion, the introduction of two carboxyl groups into the *para*-positions of benzene has been achieved by the one-step reaction of benzene with tetrachloromethane by the action of copper powder in aqueous alkali in the presence of β -CyD at 30 °C, producing terephthalic acid in 46 mol% yield with 100% selectivity.

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