

# Regioselective carboxylation of aromatic compounds using cyclodextrin as mediator

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Dedicated to Professor Teiji Tsuruta on the occasion of his 88th birthday (Beiju).

## Abstract

The direct introduction of a carboxylic group into an aromatic carboxylic acid has been considered difficult theoretically. Recently, the regioselective syntheses of terephthalic acid, 4,4'-biphenyldicarboxylic acid and 2,6-naphthalene-dicarboxylic acid have been achieved by the carboxylation of benzoic acid, 4-biphenylcarboxylic acid and 2-naphthalenecarboxylic acid, respectively, with carbon tetrachloride and copper powder in aqueous alkali, using  $\beta$ -cyclodextrin ( $\beta$ -CyD) as mediator under mild conditions. The one-pot syntheses of terephthalic acid, 4,4'-biphenyldicarboxylic acid and 2,6-naphthalene-dicarboxylic acid have been attained by the carboxylation of benzene, biphenyl and naphthalene, respectively, with carbon tetrachloride and copper powder in aqueous alkali, using  $\beta$ -CyD as mediator. The essential factor of the carboxylation by the use of  $\beta$ -CyD is the inclusion complex formations of  $\beta$ -CyD with aromatic hydrocarbon,  $\beta$ -CyD with aromatic monocarboxylate and  $\beta$ -CyD with carbon tetrachloride, respectively, in the reaction mixture. The conformations of CyD–aromatic monocarboxylate inclusion complexes in aqueous alkali have been determined by the nuclear magnetic resonance spectroscopy using <sup>1</sup>H homonuclear Overhauser enhancement on the rotating frame. The high selectivity is ascribed to the conformation of the  $\beta$ -CyD–aromatic monocarboxylate inclusion complex. The reaction mechanism is discussed on the basis of inclusion complex formation.

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## 1. Introduction

Aromatic dicarboxylic acids are a key monomer for the syntheses of high performance polymers

and liquid-crystalline compounds [1]. Terephthalic acid is widely used as an essential monomer, not only for conventional polyesters, namely poly(ethylene terephthalate) and poly(*p*-phenylene terephthalamide), but also for high performance polymers such as poly[(terephthalic acid)-*alt*-(*p*-phenylene diamine; 3,4'-diaminodiphenylether)], poly(*p*-phenylene

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benzobisthiazol), etc. 4,4'-Biphenyldicarboxylic acid is an effective monomer for poly[(ethylene glycol)-*alt*-(4,4'-biphenyldicarboxylic acid; terephthalic acid)] [2], which has mechanical and thermal properties superior to those of poly(ethylene terephthalate). 2,6-Naphthalene-dicarboxylic acid is a versatile intermediate for the syntheses of high performance polymers and liquid-crystalline compounds. For instance, poly(ethylene 2,6-naphthalene-dicarboxylate) surpasses poly(ethylene terephthalate) in mechanical properties, thermostability and gas-barrier ability of films [3,4].

Terephthalic acid, 4,4'-biphenyldicarboxylic acid and 2,6-naphthalene-dicarboxylic acid are conventionally synthesized by the oxidation of the corresponding dialkyl aromatic compounds, that is, *p*-xylene [5], 4,4'-dimethylbiphenyl [6] and 2,6-dimethylnaphthalene [7], respectively. However, the production of these dimethyl isomers from the petro- and a coal-chemical industry is limited, and the alkylation of aromatic compound is not selective enough to yield the regiospecific dimethyl isomers. Therefore, the effective process is required for the syntheses of aromatic dicarboxylic acid.

$\alpha$ -,  $\beta$ - and  $\gamma$ -Cyclodextrins ( $\alpha$ -CyD,  $\beta$ -CyD and  $\gamma$ -CyD) are cyclic oligomers of 6, 7 and 8 glucose units, respectively, linked by  $\alpha(1-4)$  bonds with a central cavity, as shown in Fig. 1. The external diameter at the secondary hydroxyl side of CyD is larger than that at the primary hydroxyl side of CyD. The cavity diameters of  $\alpha$ -CyD,  $\beta$ -CyD and  $\gamma$ -CyD are 4.7–5.2 Å, 6.0–6.4 Å and 7.9–8.0 Å, respectively. While the outside of CyD molecule is hydrophilic, the cavity inside is a hydrophobic medium such as diethyl ether, and various hydrophobic substances in aqueous med-

ium can be included therein as the guest, when they are spatially fitted in the cavity [8,9]. The inclusion complex formation in solution is a dynamic process of the equilibrium between the inclusion state and the free state of the substrate. The time scale of the exchange of these states is faster than that of NMR spectroscopy.

The carboxyl group of benzoic acid has a deactivating effect on the electrophilic substitution reaction of the aromatic ring. It has been considered difficult to introduce directly the carboxylic group into the aromatic carboxylic acid. Recently, the selective carboxylations of the aromatic carboxylic acids, that is, benzoic acid, 4-biphenylcarboxylic acid and 2-naphthalenecarboxylic acid with carbon tetrachloride and copper powder have been found to occur in aqueous alkali by the use of  $\beta$ -CyD as mediator [10,11]. We have also succeeded in the one-pot syntheses of terephthalic acid, 4,4'-biphenyldicarboxylic acid and 2,6-naphthalene-dicarboxylic acid from benzene, biphenyl and naphthalene, respectively, with carbon tetrachloride and copper powder in aqueous alkali using  $\beta$ -CyD as mediator. For elucidation of the mechanism of the regioselective carboxylation of aromatic compounds using CyD as mediator, the conformations of CyD inclusion complexes formed with benzoic acid, 4-biphenylcarboxylic acid and 2-naphthalenecarboxylic acid, respectively in aqueous alkali have been determined by the  $^1\text{H}$  NMR spectrometry. In this review, the positional selectivity of the carboxylation is discussed on the basis of the conformation of the inclusion complex.

## 2. Regioselective carboxylation of benzoic acid using cyclodextrin as mediator

The carboxyl group of aromatic monocarboxylic acid has a deactivating effect on the electrophilic substitution reaction of the aromatic ring and exerts a *meta* orientation [12]. Consequently, the direct introduction of carboxylic group into benzoic acid has never been attempted, especially to yield terephthalic acid. The present authors have succeeded in the selective synthesis of terephthalic acid by the carboxylation of benzoic acid with carbon tetrachloride and copper powder in aqueous alkali in the presence  $\beta$ -CyD under mild conditions, as shown in Scheme 1a [13].

In our previous papers [13,14], the optimum amounts of  $\beta$ -CyD, carbon tetrachloride and copper powder, respectively, were investigated on the car-

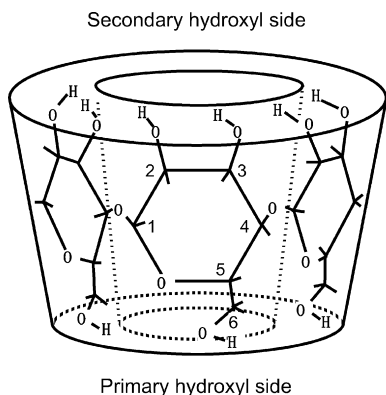


Fig. 1. Structure and positional numbers of protons in  $\beta$ -cyclodextrin ( $\beta$ -CyD).

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