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Selective synthesis of 2,6-naphthalenedicarboxylic acid by use of cyclodextrin as catalyst

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Abstract

The selective synthesis of 2,6-naphthalenedicarboxylic acid from 2-naphthalenecarboxylic acid with carbon tetrachloride, copper powder, and aqueous alkali was achieved by using of β-cyclodextrin (β-CyD) as a catalyst at 60°C under nitrogen, producing 2,6-naphthalenedicarboxylic acid in 67 mol% yield with 84% selectivity. The one-pot preparation of 2,6-naphthalenedicarboxylic acid from naphthalene was attained at 84°C by using of β-CyD, producing 2,6-naphthalenedicarboxylic acid in 65 mol% yield with 79% selectivity. When α-CyD or γ-CyD was used instead of β-CyD on the carboxylation of 2-naphthalenecarboxylic acid and naphthalene, respectively, the reaction hardly proceeded. The conformation of β-CyD–2-naphthalenecarboxylate inclusion complex in aqueous alkaline solution was determined by the nuclear magnetic resonance spectroscopy using ^{1}H homonuclear Overhauser enhancement on the rotating frame. The 2-naphthalenecarboxylate anion was axially included in the cavity of β-CyD with an orientation which directed the 5-, 6-, and 7-positions of 2-naphthalene-carboxylate anion to the secondary hydroxyl side of β-CyD. It was concluded that the high selectivity of the carboxylation of 2-naphthalenecarboxylic acid was ascribed to the conformation of the β-CyD–2-naphthalenecarboxylate inclusion complex. The selective carboxylation of naphthalene was attributed to the formations of the β-CyD–naphthalene and β-CyD–2-naphthalenecarboxylate inclusion complexes. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

2,6-Naphthalenedicarboxylic acid (2,6-NDA) is an effective monomer for poly(ethylene 2,6-naphthalenedicarboxylate), which has mechani-cal and thermal properties superior to those of poly(ethylene terephthalate) [1,2]. 2,6-NDA is also a versatile intermediate for liquid crystalline compounds [3]. The synthesis of 2,6-NDA is conventionally carried out by oxidation of 2,6-dialkylnaphthalene [4,5]. However, the production of 2,6-dialkylnaphthalene from petro- and coal-chemical industries is limited. 2,6-NDA

β-CyD

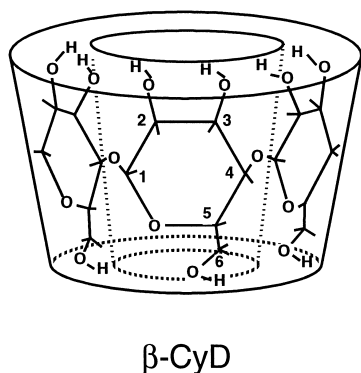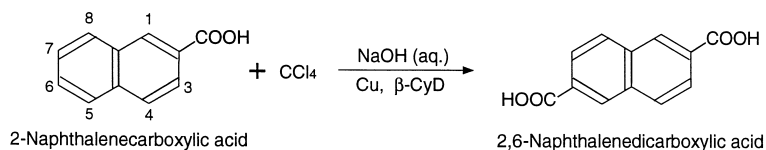Fig. 1. Structure and positional numbers of protons in β-CyD.

Scheme 1. We also report the one-pot synthesis of 2,6-NDA from naphthalene, carbon tetrachloride and copper powder in aqueous alkali by the use of β-CyD as catalyst, as shown in Scheme 2. The positional selectivity of the carboxylation is discussed on the basis of the conformation of the β-CyD–2-naphthalenecarboxylate (2-NC) inclusion complex by the rotating frame Overhauser enhancement spectroscopy (ROESY) [11–14]. The mechanisms of the selective carboxylations of 2-NCA and naphthalene, respectively, are proposed.

was recently produced by oxidation of 2-methyl-6-acylnaphthalene [6,7].

α-, β- and γ-cyclodextrins (α-CyD, β-CyD and γ-CyD) are cyclic oligosaccharides consisting of 6, 7 and 8 glucose units linked by α (1−4) bonds with a central cavity, as shown in Fig. 1. CyDs are a functional oligomer as a model of enzyme and as a polymer–catalyst [8,9]. Recently, the synthesis of terephthalic acid from benzoic acid with carbon tetrachloride and copper powder was found to occur in aqueous sodium hydroxide solution by the use of CyD as catalyst [10]. On the other hand, one-pot preparation, in which desired compounds are synthesized by successive addition of reagents to a reaction vessel without separation of intermediates in each step, is an ideal form of organic synthesis.

The present paper reports detailed results of the selective synthesis of 2,6-NDA from 2-naphthalenecarboxylic acid (2-NCA) with carbon tetrachloride and copper powder in aqueous sodium hydroxide solution under mild conditions by using β-CyD as catalyst, as shown in

2. Experimental

2.1. Materials

β-Cyclodextrin (β-CyD) was obtained from Tokyo Chemical Industry and recrystallized from aqueous solution. α- and γ-CyD were purchased from Nacalai Tesque and recrystallized from aqueous solution. Copper powder was used of organic synthesis grade (the average diameter of particles 1 μm) from Aldrich Chemical. 2-NCA and naphthalene were purchased from Nacalai Tesque and recrystallized from aqueous solution. All other chemicals were purified by the usual ways.

2.2. Carboxylation of 2-NCA

A total of 3 mmol of 2-NCA, 0.3 mmol of copper powder, and 3.0 mmol of β-CyD were added to 30 ml of 30 wt.% aqueous sodium hydroxide solution. The reaction was started with the addition of 16 mmol of carbon tetrachloride and continued for 7 h at 60°C under

2-Naphthalenecarboxylic acid   2,6-Naphthalenedicarboxylic acid
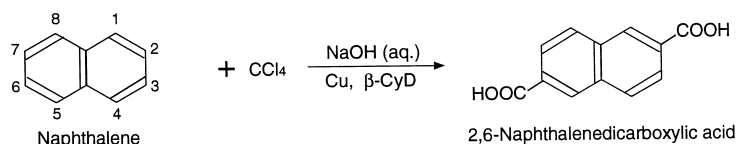
Scheme 1.

Scheme 2.

nitrogen. Then, residual carbon tetrachloride was removed by evaporation under reduced pressure. The cooled reaction mixture was neutralized with hydrochloric acid. The pH value of the mixture was adjusted to 10 with an aqueous sodium hydroxide solution, followed by filtration of the mixture through a sintered glass disk. The filtrate was analyzed by high performance liquid chromatography (HPLC) using absorbance at 258 nm. The products were identified by comparison with authentic samples (HPLC, MS). The main product was isolated and confirmed to be 2,6-NDA by ^{1}H NMR and IR, referring to the literature [15]. The yields of products were based on the starting amount of 2-NCA. The selectivity of 2,6-NDA was based on the total amount of carboxylated products.

2.3. Carboxylation of naphthalene

A total of 3 mmol of naphthalene, 0.8 mmol of copper powder, and 3.0 mmol of β-CyD were added to 30 ml of 30 wt.% aqueous sodium hydroxide solution. The reaction was started with the addition of 16 mmol of carbon tetrachloride and continued for 7 h at 84°C under nitrogen. The isolations and identifications of products were similar to those on the carboxylation of 2-NCA.

2.4. Measurements

High performance liquid chromatograms were taken with a Tosoh SC-8010 chromatograph using the absorbance at 258 nm: a strong anion exchange column (TSKgel SAX), 40°C; eluent, an aqueous solution of 0.5 M sodium nitrate and

0.05 M boric acid buffer (pH 9.7) with acetonitrile (10 vol.%).

^{1}H NMR spectra were recorded at 400 MHz on a JNM-GX400 FT-NMR spectrometer at 27°C. The samples for ^{1}H NMR spectra of a solution of β-CyD (0.1 mol l^{-1}) and a solution containing β-CyD (0.1 mol l^{-1}) and 2-NC (0.1 mol l^{-1}) were prepared in 1 wt.% NaOD/D$_2$O using 2-NCA as 2-NC. A two-dimensional ROESY (2D-ROESY) spectrum was acquired in a sweep width of 2500 Hz. A spin-lock field was used during the mixing period of 1000 ms and 500 ms in order to minimize magnetization transfer through scalar couplings. Free induction decays which accumulated 128 times at each mixing time were stored in a matrix of 1024 × 128. The data matrix was expanded to 1024 × 512 by zero-filling for F_1-axis and multiplied by the sinebell window function prior to the double Fourier transform. Chemical shifts are given in parts per million (ppm) downfield from that of tetramethylsilane in chloroform-d_1 using internal capillary.

3. Results and discussion

3.1. Carboxylation of 2-NCA

Fig. 2 exhibits the relationship between yields of NDAs and the initial mole ratio of β-CyD to 2-NCA. The yield of 2,6-NDA increases with β-CyD, and has a maximal value (61 mol% with 85% selectivity) at a mole ratio of β-CyD to 2-NCA of 2.0. The yields of 2,7-NDA and 1,6-NDA also take maximal values at a mole ratio of β-CyD to 2-NCA of 2.0, where those of 2,7-NDA and 1,6-NDA are 8.7 mol% and
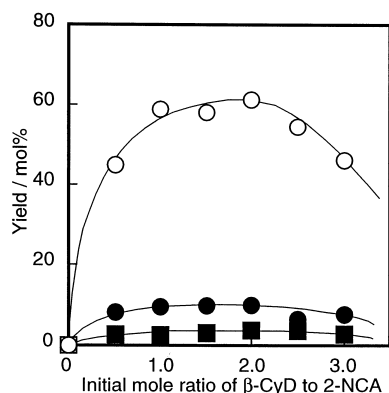
Fig. 2. Relationship between yields of NDAs and initial mole ratio of β-CyD to 2-NCA : (○) 2,6-NDA, (●) 2,7-NDA, (■) 1,6-NDA. Conditions: 30 ml of 30 wt.% NaOH aq, 3.0 mmol of 2-NCA, 0.3 mmol of copper powder, 16 mmol of carbon tetrachloride, 60°C, 7 h.

2.1 mol%, respectively. In the absence of β-CyD, however, the carboxylation did not occur. The formation of the 1:1 inclusion complex between β-CyD and 2-NCA was observed by the circular dichroism spectroscopic study by Harata and Uedaira [16]. The promotion of carboxylation by β-CyD is probably attributable to the increase in the solubilities of carbon tetrachloride and 2-NCA in aqueous alkali by the formations of the β-CyD–carbon tetrachloride complex and β-CyD–2-NCA complex, respectively. A decrease in the yield of 2,6-NDA at the initial mole ratios of β-CyD larger than 2.0 (see Fig. 2) may be associated with the deactivation of the active species formed from carbon tetrachloride too much to react with the 2-NCA in the inclusion complex. In the previous communication [17], we reported preliminarily the relationship between the yield of 2,6-NDA and the initial mole ratio of β-CyD to 2-NCA under the following conditions: the initial mole ratio of copper powder (the average diameter of particles 125 μm) to 2-NCA of 0.3 and that of carbon tetrachloride to 2-NCA of 2.8. At an initial mole ratio of β-CyD to 2-NCA of 1.0, the yield of 2,6-NDA reached a maximum (39 mol% with 78% selectivity). Shortly afterward, we examined the optimum amount of β-CyD, carbon tetrachloride and copper powder, respec-

tively, on the carboxylation of 2-NCA by the use of β-CyD as catalyst (see Fig. 2). Then, we found that the yield and selectivity of 2,6-NDA attained to 61 mol% and 85%, respectively.

When α-CyD was used instead of β-CyD, the reaction did not proceed by the size limitation of α-CyD as described below. When γ-CyD was used in place of β-CyD, the main product was 2,7-NDA in 0.7 mol% yield, where the yields of 2,6-NDA and 1,6-NDA were 0.5 mol%, and 0.2 mol%, respectively. From the positional selectivity of the reaction, the conformation of γ-CyD–2-NCA inclusion complex may be different from that of β-CyD–2-NCA inclusion complex.

The intermittent addition of carbon tetrachloride was attempted. The reaction was started with the addition of 0.6 mmol of carbon tetrachloride to the aqueous sodium hydroxide solution containing 3.0 mmol of 2-NCA, 6.0 mmol of β-CyD and 0.3 mmol of copper powder, and was continued for 8 h by adding 0.6 mmol of carbon tetrachloride to the reaction mixture every 15 min. The resulting yields of 2,6-NDA, 2,7-NDA, and 1,6-NDA were 67 mol%, 10 mol%, and 2.4 mol%, respectively, where the selectivity of 2,6-NDA was 84%. The essential factor of the carboxylation by the use of β-CyD was the inclusion complex formations of β-CyD with 2-NCA and β-CyD with carbon tetrachloride in the reaction mixture. The intermittent addition method was effective to control the formation rate of the active species formed from carbon tetrachloride in the cavity of β-CyD. Consequently, the selective carboxylation of 2-NCA with carbon tetrachloride and copper powder in aqueous alkali has been achieved by using β-CyD as catalyst, producing 2,6-NDA in 67 mol% yield with 84% selectivity.

3.2. Carboxylation of naphthalene

Table 1 exhibits the effect of the reaction temperature on yields of NDAs and NCA at the reaction time 7 h. The yields of 2,6-NDA increase slightly with temperature from 60 to

Table 1
Effect of the reaction temperature on carboxylation of naphthalene[a]

Reaction temperature (°C)	Yield (mol%)		
	2,6-NDA[b]	2,7-NDA	2-NCA[c]
60	6.7	1.0	2.3
74	6.9	0.7	5.1
78	7.1	0.7	5.3
82	20	5.9	5.3
84	21	6.0	5.6
86	18	4.6	6.7
88	18	5.3	6.9

[a]Conditions: 30 ml of 30 wt.% NaOHaq, 3.0 mmol of naphthalene, 3.0 mmol of β-CyD, 0.8 mmol of copper powder, 16 mmol of carbon tetrachloride, 7 h.
[b]NDA: naphthalenedicarboxylic acid.
[c]NCA: naphthalenecarboxylic acid.

78°C and increase eminently from 78 to 82°C. The yield of 2,6-NDA has a maximal value (21 mol% with 64% selectivity) at 84°C, where the yields of 2,7-NDA and 2-NCA are 6.0 mol% and 5.6 mol%, respectively. Carboxylation did not proceed in the absence of β-CyD. As described above, we found that 2-NCA was converted to 2,6-NDA in 67 mol% yield with 84% selectivity by the use of β-CyD as catalyst at 60°C. On the carboxylation of naphthalene at 60°C, however, the yield of 2,6-NDA was not so high. The remarkable increase in the yield of 2,6-NDA at a reaction temperature higher than 80°C (see Table 1) may be ascribed to the formation of the β-CyD–naphthalene inclusion complex. The inclusion complex formation is probably accelerated by melting of naphthalene at a reaction temperature higher than the melting point of naphthalene (80.3°C). When α-CyD was used instead of β-CyD, the reaction did not occur. When γ-CyD was used in place of β-CyD, the yields of 2,6-NDA, 2-NCA, and 1-NCA were 0.0 mol%, 0.5 mol%, and 1.1 mol%, respectively. From the positional selectivity of the reaction, the conformation of γ-CyD–naphthalene inclusion complex may be different from that of β-CyD–naphthalene inclusion complex in the same way of the reaction of 2-NCA. The promotion of carboxylation by β-CyD is proba-

bly attributable to the cavity size of β-CyD to form β-CyD–naphthalene and β-CyD–carbon tetrachloride inclusion complexes.

The yield of 2,6-NDA reached a maximal value (25 mol%) at a mole ratio of carbon tetrachloride to naphthalene of 6.0 and took a maximum (25 mol%) at a mole ratio of copper powder to naphthalene of 0.27, according to the previous communication [18]. Table 2 shows the most efficient use of carbon tetrachloride, copper powder, and β-CyD by the intermittent addition method under these conditions. The reaction is started with the addition of 18 mmol of carbon tetrachloride to the aqueous alkali containing 3.0 mmol of naphthalene, 3.0 mmol of β-CyD and 0.8 mmol of copper powder, and is continued for 10 h by adding 18 mmol of carbon tetrachloride and aqueous alkali containing 3.0 mmol of β-CyD and 0.8 mmol of copper powder to the reaction mixture every 2 h. The yield of 2,6-NDA increases with the number of addition, and reaches a maximum (65 mol% with 79% selectivity) at five additions, where the yields of 2,7-NDA and 2-NCA are 16 mol% and 1.4 mol%, respectively. The synthesis of 2,6-NDA from naphthalene was usually carried out by four main steps: alkylation of naphthalene, isomerization of dialkylnaphthalene, separation of 2,6-dialkylnaphthalene, and oxidation of 2,6-dialkylnaphthalene [4,5]. Another process also consisted of four

Table 2
Carboxylation of naphthalene by intermittent addition method[a]

Number of addition	Yield (mol%)		
	2,6-NDA[b]	2,7-NDA	2-NCA[c]
1	19	4.9	3.0
2	39	9.7	4.4
3	49	12	3.9
4	55	12	3.0
5	65	16	1.4

[a]Conditions: 3.0 mmol of naphthalene, 84°C, additional intervals of 2 h. Amount of one addition: 30 ml of 30 wt.% NaOHaq, 3.0 mmol of β-CyD, 18 mmol of carbon tetrachloride, 0.8 mmol of copper powder.
[b]NDA: naphthalenedicarboxylic acid.
[c]NCA: naphthalenecarboxylic acid.

main steps: separation of 2-methylnaphthalene from coal-tar, acylation of 2-methylnaphthalene, separation of 2-methyl-6-acylnaphthalene, and oxidation of 2-methyl-6-acylnaphthalene [6,7]. Therefore, the conventional process is comprised of more than four steps which are not easy to be carried out. We succeeded in the introduction of two carboxyl groups into 2- and 6-positions of naphthalene by the one-pot preparation of naphthalene at 84°C by the use of β-CyD as catalyst, producing 2,6-NDA in 65 mol% yield with 79% selectivity.

3.3. Conformation of cyclodextrin–2-NC inclusion complex in alkaline aqueous solution

The 400 MHz ^{1}H NMR spectrum of a solution containing β-CyD (0.1 mol l^{-1}) and 2-NC (0.1 mol l^{-1}) was compared with that of a solution of β-CyD (0.1 mol l^{-1}). The 2-NCA molecule was converted to 2-NC anion in aqueous alkaline solution. The C-1–C-6 protons on the glucose unit of β-CyD are defined as H-1–H-6, respectively, as shown in Fig. 1. The C-1–C-8 protons on naphthalene group of 2-NCA are defined as the H-1–H-8, respectively (see Scheme 1). In the presence of 2-NC anion, the chemical shifts of H-1, H-2, H-3, H-4, H-5 and H-6 of β-CyD shifted upfield by $\Delta \delta = 0.04$, 0.03, 0.09, 0.03, 0.27 and 0.15 ppm, respectively. According to the literature [19], H-3 and H-5 atoms are directed toward the interior of the cavity of β-CyD, whereas H-1, H-2, and H-4 atoms are located on the exterior. The larger changes in the chemical shifts of H-3 and H-5, compared with those of H-1, H-2 and H-4, indicate that the 2-NC anion is included in the cavity of the β-CyD molecule. The upfield shifts are dependent on the magnetic anisotropy effect of the naphthalene group of 2-NC.
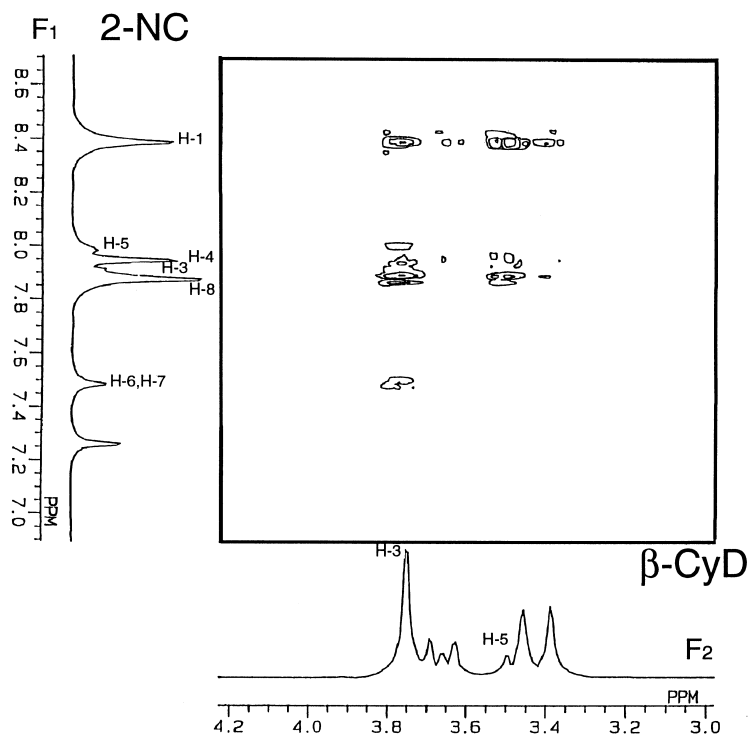

Fig. 3. 2D-ROESY spectrum of a solution containing β-CyD (0.1 mol l^{-1}) and 2-NC anion (0.1 mol l^{-1}) in 1 wt.% NaOD/D$_2$O at 27°C. Projection spectra on the F_1-axis and F_2-axis, respectively, were obtained from the *J*-resolved 2D spectrum.

Fig. 3 shows the ROESY spectrum of the solution containing β-CyD and 2-NC anion, where the *J*-resolved spectrum of 2-NC is shown on the F_1-axis and that of β-CyD on the F_2-axis. The intensity of the cross-peaks connecting the H-3 resonance of β-CyD to the H-1, H-3, H-4, and H-8 resonances of 2-NC are very strong, and those to the H-5, H-6, and H-7 resonances of 2-NC are strong. The cross-peaks connecting the H-5 resonance of β-CyD to the H-1 and H-3 resonances of 2-NC are appreciable. The cross-peaks connecting the H-5 resonance of β-CyD to the H-4 and H-8 resonances of 2-NC are observable. However, the cross-peaks between the H-5 resonance of β-CyD and the H-6 and H-7 resonances of 2-NC do not appear. The intensity of the cross-peak connecting the H-5 resonance of β-CyD to the H-1 resonance of 2-NC is stronger than that of the cross-peak connecting the H-3 resonance of β-CyD to the H-1 resonance of 2-NC. These facts indicate that the H-1 and H-3 atoms of 2-NC are situated near the H-5 atom of β-CyD and the H-4 and H-8 atoms of 2-NC are located near the H-3 atom of β-CyD. The H-6 and H-7 atoms of 2-NC are located far from the H-5 atom of β-CyD. On the basis of these results, the conformation of β-CyD–2-NC inclusion complex in aqueous alkali is proposed, as shown in Fig. 4. In this figure, β-CyD is illustrated simply; the

inner diameter of cavity 6.0 Å for the primary hydroxyl side, 6.4 Å for the secondary hydroxyl side, and the depth of the cavity is 7.9 Å, according to the literature [20]. The 2-NC molecule is axially included in the cavity of β-CyD with an orientation such that the carboxylate group is at the primary hydroxyl side of β-CyD and the 5-, 6-, and 7-positions of 2-NC, at the secondary hydroxyl side of β-CyD. The circular dichroism spectroscopy of β-CyD complexes with 2-NC anion and 2-naphthylacetate anion revealed that the structure of the 2-substituted naphthalene complex was an axial inclusion [16]. However, the orientation of the guest molecule was not determined in this literature [16]. The ROESY method is useful for NOE measurement of moderately large molecules (molecular weight of about 1000). This method is effective to measure the complex of β-CyD (molecular weight of 1135) with a compound. We determined the conformation of β-CyD–2-NC inclusion complex in aqueous alkali by the ROESY method.

3.4. Formation of the active species from carbon tetrachloride

The active species formed from carbon tetrachloride and copper powder in the reaction mixture was proposed to be trichloromethyl radical [10] on the basis of the following facts: (1) *p*-Benzoquinone, which strongly quenches the trichloromethyl radical, showed the remarkable suppression for the formation of terephthalic acid in the carboxylation of benzoic acid using β-CyD. (2) In the reaction under oxygen, oxygen exhibited significant retardation. (3) In the reaction even at reaction time 1 h, all of copper powder were consumed. (4) Copper(II) ion which formed between carbon tetrachloride and copper powder, was identified in the reaction mixture. As shown in Formula (1) and (2), carbon tetrachloride probably reacts with metallic copper powder, generating copper(I) chloride and the trichloromethyl radical. The copper(I) chloride possibly transfers an electron to carbon
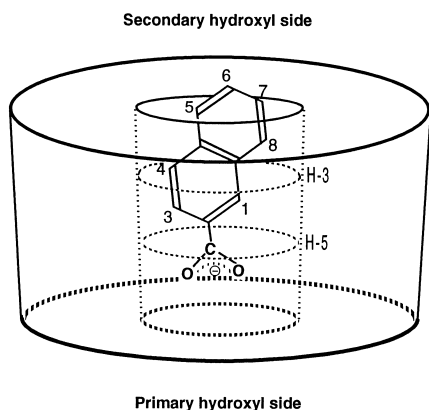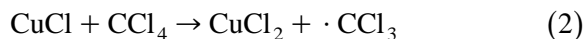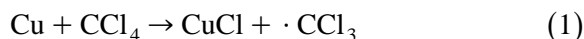

Fig. 4. Proposed conformation of the β-CyD–2-NC inclusion complex; ——-H-3 and ——-H-5 show planes comprised of the corresponding atoms of β-CyD.

tetrachloride leading to formation of the trichloromethyl radical and copper(II) chloride.

$$Cu + CCl_4 \rightarrow CuCl + \cdot CCl_3 \qquad (1)$$

$$CuCl + CCl_4 \rightarrow CuCl_2 + \cdot CCl_3 \qquad (2)$$

The solubility of carbon tetrachloride in water is poor (0.024 wt.% at 50°C) [21]. However, carbon tetrachloride can be soluble in aqueous alkali when it is included in the cavity of the β-CyD. The carbon tetrachloride was included in the cavity of β-CyD by measurement of the ^{1}H chemical shifts of β-CyD [10]. The carbon tetrachloride included in β-CyD is probably converted into the trichloromethyl radical by the reaction with the fine metallic copper powder dispersed in aqueous alkali, as shown in Formula (1). The β-CyD may protect the trichloromethyl radical from the deactivation by hydroxide ion and another molecule of trichloromethyl radical. When α-CyD was used instead of β-CyD, α-CyD formed a white precipitate with carbon tetrachloride in aqueous alkali. According to the literature [22], the formation constant $(42 \pm 17 \ M^{-1})$ of the α-CyD–carbon tetrachloride complex was much smaller than that $(150 \pm 35 \ M^{-1})$ of the β-CyD–carbon tetrachloride complex. The carbon tetrachloride molecule was partially included in α-CyD due to the size limitation of α-CyD. Precipitation seemed to occur through decrease in the solubility of α-CyD caused by including carbon tetrachloride partially. The association between γ-CyD and carbon tetrachloride was not perceived by our measurement of ^{1}H chemical shifts of γ-CyD. It was consistent with the results by Nishimura et al. [22], which the association between γ-CyD and carbon tetrachloride was not observed by the volatilization rate measurement of a guest molecule, carbon tetrachloride, from the aqueous phase into the gaseous phase. The cavity of γ-CyD is too large to be fitted with carbon tetrachloride molecule. Consequently, the inclusion complex formation of β-CyD with carbon tetrachloride is attributable to the fitness of cavity size with carbon tetrachloride molecule.

3.5. Mechanism of selective carboxylation

The proposed mechanism of the formation of 2,6-NDA from 2-NCA using β-CyD as catalyst is shown in Fig. 5. Carbon tetrachloride may be little concerned with the reaction in aqueous alkali owing to the poor solubility, as described above. When carbon tetrachloride is included in the cavity of the β-CyD, it can be soluble in aqueous alkali and concerned with the reaction. The carbon tetrachloride included in β-CyD is probably converted into the trichloro-methyl radical by the reaction with the fine metallic copper powder dispersed in aqueous alkali, as shown in Formula (1). The β-CyD may protect the trichloromethyl radical from the deactivation by hydroxide ion and another molecule of trichloromethyl radical. The solubility of 2-NCA in water is also poor (0.058 g l^{-1} at 25°C) [21]. Therefore, 2-NCA itself may take little part in the reaction in aqueous alkali. When 2-NCA is included in the cavity of the β-CyD, it can be soluble in aqueous alkali. The 2-NCA molecule was converted to 2-NC anion in aqueous alkaline solution. As shown in Fig. 4, the 2-NC anion is axially included in the cavity of β-CyD with an orientation such that the carboxylate group is at the primary hydroxyl side of β-CyD and the 5-, 6-, and 7-positions of 2-NC, at the secondary hydroxyl side of β-CyD. The 5-, 6-, and 7-positions of 2-NC are located outside the
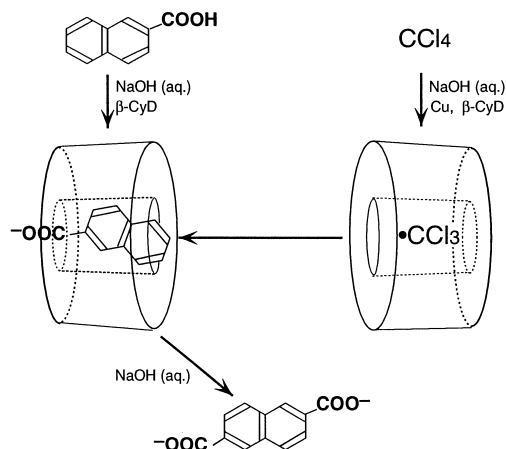

Fig. 5. Proposed mechanism of formation of 2,6-NDA from 2-NCA using β-CyD as catalyst.

β-CyD in the conformation of β-CyD–2-NC inclusion complex. The order of jutting-out is as follows: 6- > 7- > 5-position. The reaction of 2-NC anion included in β-CyD is attacked by trichloromethyl radical and forms a trichloromethyl adduct of 2-NC anion as an intermediate. The trichloromethyl adduct of 2-NC anion is rapidly hydrolyzed to give naphthalenedicarboxylate anion in aqueous alkali. When the 6-, 7-, and 5-positions of 2-NC are attacked by trichloromethyl radical, 2,6-naphthalenedicarboxylate, 2,7-naphthalenedicarboxylate, and 1,6-naphthalenedicarboxylate, respectively, are produced. The reaction of 2-NCA with carbon tetrachloride and copper powder in aqueous alkali using β-CyD as catalyst gave 2,6-NDA in 67 mol%, 2,7-NDA in 10 mol% and 1,6-NDA in 2.4 mol% yield, as described above. From the distribution of the reaction products in the carboxylation of 2-NCA, the proposed conformation is consistent with the positional selectivity of the reaction. The primary hydroxyl group of β-CyD has considerable freedom of movement about the C-5–C-6 bond [8]. The inner diameter of primary hydroxyl side of β-CyD (6.0 Å) [20] is smaller than that of the secondary side (6.4 Å) [20]. The trichloromethyl radical may not attack at the 2-NC anion included in β-CyD from primary hydroxyl side due to steric hindrance of the C-5–C-6 bond.

Fig. 6 illustrates the proposed mechanism of the synthesis of 2,6-NDA from naphthalene using β-CyD as catalyst. The solubility of naphthalene in water is small (0.030 g l^{-1} at 25°C) [21]. When naphthalene is included in the cavity of the β-CyD, it can be soluble in aqueous alkali and concerned with the reaction. We may propose that the naphthalene molecule is axially included in the cavity of β-CyD with an orientation such that the 2- and 3-positions of naphthalene are at the secondary hydroxyl side of β-CyD and the 6- and 7-positions of 2-NC, at the primary hydroxyl side of β-CyD. The proposed conformation is supported by the study of Fujiki et al. [23]. They reported that the naphthalene molecule was axially included in the cavity of
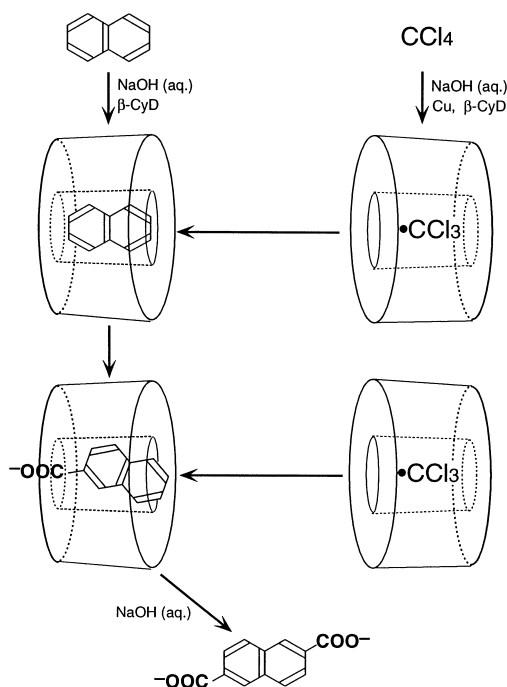

Fig. 6. Proposed mechanism of formation of 2,6-NDA from naphthalene using β-CyD as catalyst.

β-CyD by the volatilization rate of a guest molecule, naphthalene, from the aqueous phase into the gaseous phase. A naphthalene molecule included in β-CyD is predominantly attacked at the 2- or 3-position by trichloromethyl radical and forms 2-trichloromethylnaphthalene as an intermediate. The 2-trichloromethylnaphthalene dissociates from the cavity of β-CyD and is rapidly hydrolyzed to give 2-NC anion in aqueous alkali. The 2-NC anion associated with β-CyD forms a more stable conformation of β-CyD–2-NC inclusion complex, as shown in Fig. 4. In this conformation, the 2-NC anion included in β-CyD is preferentially attacked at the 6-position by trichloromethyl radical, producing 2,6-NDA in high yield with high selectivity, as described above.

4. Conclusions

The selective synthesis of 2,6-NDA from 2-NCA with carbon tetrachloride, copper powder,

and aqueous alkali was attained by using of β-CyD as catalyst at 60°C under nitrogen of atmospheric pressure, producing 2,6-NDA in 67 mol% yield with 84% selectivity. The introduction of two carboxyl groups into the 2- and 6-positions of naphthalene was achieved by the one-pot preparation of naphthalene, carbon tetrachloride, and copper powder in aqueous alkali at 84°C by the use of β-CyD as catalyst, producing 2,6-NDA in 65 mol% yield with 79% selectivity. The 2-NC anion is axially included in the cavity of β-CyD with an orientation such that the carboxylate group is at the primary hydroxyl side of β-CyD and the 5-, 6-, and 7-positions of 2-NC, at the secondary hydroxyl side of β-CyD. The 2-NC anion included in β-CyD is predominantly attacked at the 6- position by trichloromethyl radical and forms 2,6-NDA with very high selectivity. The conformation of β-CyD–2-NC inclusion complex is consistent with the positional selectivity of the reaction.

Acknowledgements

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