ISSN 0965-5441, Petroleum Chemistry, 2007, Vol. 47, No. 6, pp. 402–408. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © E.A. Karakhanov, Yu.S. Kardahseva, A.L. Maksimov, S.V. Egazar'yants, L.M. Karapetyan, O.A. Zatolochnaya, 2007, published in Neftekhimiya, 2007, Vol. 47, No. 6, pp. 435–441.

Oxidation of 2-Naphthol in the Presence of Catalysts Based on Modified β-Cyclodextrins

E. A. Karakhanov, Yu. S. Kardahseva, A. L. Maksimov, S. V. Egazar'yants, L. M. Karapetyan, and O. A. Zatolochnaya

Faculty of Chemistry, Moscow State University, Leninskie gory, Moscow, 119992 Russia
e-mail: kar@petrol.chem.msu.ru

Received April 15, 2007

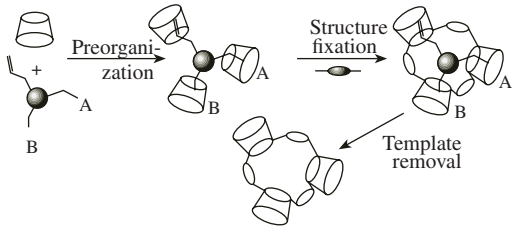
Abstract—The oxidation of 2-naphthol to 1,1'-bi-2-naphthol in a biphasic system in the presence of β-cyclodextrins was studied. It was found that the use of macrocyclic receptors leads to substantial enhancement of the activity of catalytic systems. It was shown that the product yield and the reaction rate substantially increase when ligands obtained via molecular imprinting in the presence of 1,1'-bi-2-naphthol as a template are added.

DOI: 10.1134/S0965544107060047

The use of molecular receptors (cyclodextrins, calixarenes, urea-based macrocycles) opens up a wide range of opportunities for designing new high-performance metal complex catalysts. Owing to the ability in molecular recognition, their use as components of catalyst systems makes it possible to substantially enhance the substrate-binding selectivity and to attain a uniquely high selectivity of processes [1, 2].

The activity and selectivity of such catalysts can be controlled in two ways. The first is targeted selective modification of the macromolecular receptor itself with complexing groups, whose arrangement predetermines the coordination of a substrate to the metal atom in the macromolecular catalyst formed. In this manner, a number of effective oxidation, hydrogenation, hydroformylation, etc. catalysts were synthesized [1].

The second way (molecular imprinting) is based on the targeted design of macroreceptors by means of template synthesis [3]. As a template, various organic molecules that determine the structure of the material to be synthesized are used. The macroligands prepared in this manner turn out to be able to selectively bind molecules similar to those used as templates. The imprinting process involving cyclodextrin molecules occurs as shown in Scheme 1 [4, 5].



Scheme 1. Imprinting process involving host (cyclodextrin) and guest (template) molecules.

At the first step, the preorganization of cyclodextrin and the template molecule takes place; as result, a host–guest inclusion complex is formed. The structure formed can be fixed with the use of agents containing two or more functional groups capable of reacting with the cyclodextrin hydroxyl groups.

The molecular imprinting technique has found application in catalysis as well; e.g., in the oxidation of ethylbenzene, cobalt complexes anchored to polymers in the presence of the substrate showed two to three times higher activity than the macrocomplexes prepared in the absence of the substrate [6]. We have found that the use of unsaturated macroligand compounds produced via the reaction of cyclodextrins with toluene-2,4-diisocyanate or *N,N'*-methylenebisacrylamide in the presence of some templates (dodecene-1, hexadecene-1, and *p-tert*-butylstyrene) as components of catalyst systems in Wacker oxidation substantially alters the substrate selectivity of the process. The activity of catalytic systems that contain β-cyclodextrins modified in the presence of templates turned out to be substantially higher than that of the same systems containing a macroligand produced without a template [7].

In this work, we studied the efficiency of cyclodextrin-containing catalysts in the reaction of 2-naphthol oxidation into 1,1'-bi-2-naphthol in a two-phase system. Note that 1,1'-bi-2-naphthol (BINOL) and its derivatives are optically active ligands used in various organic reactions catalyzed by transition metal (Cu(I), VO(2+), etc.) complexes, e.g., in the synthesis of optically active crown ethers [5, 6].

Some BINOLs form structural units in many alkaloids and natural biologically active compounds. As components of catalyst systems, we used both conventional modified cyclodextrins (Scheme 1) and cyclodextrin-based materials prepared by means of molecular imprinting with the use of 1,1'-binaphthol as a tem-

Table 1. Macroligands synthesized by means of molecular imprinting

Template	Cyclodextrin/template ratio	Binding agent	Ligand
Bi-2-naphthol	2 : 1	Epichlorohydrin	β-CD1
Bi-2-naphthol	1 : 5	Epichlorohydrin	β-CD2
Bi-2-naphthol	2 : 1	Diepoxybutane	β-CD3
Bi-2-naphthol	1 : 5	Diepoxybutane	β-CD4
Bi-2-naphthol	2 : 1	Diglycidyl ether of glycerol	β-CD5
Without template		Epichlorohydrin	β-CD6
Without template		Diepoxybutane	β-CD 7
Without template		Diglycidyl ether of glycerol	β-CD 8

plate. In the latter case, as a linker for fixing the structure of the supramolecular ligand, we chose a number of bifunctional compounds capable of reacting with β-cyclodextrin hydroxyl groups: epichlorohydrin, diepoxybutane, diepoxyoctane, and diglycidyl ether of glycerol.

EXPERIMENTAL

β-Cyclodextrin from SigmaAldrich, 1,1'-bi-2-naphthol (BINOL), epichlorohydrin (Epy), diepoxybutane (DEB), diepoxyoctane, and glycerol diglycidyl ether (GDG) (SigmaAlrdich) were used without additional purification. As a reaction medium, distilled water was used.

Nuclear magnetic resonance measurements were carried out on an Avance Bruker instrument with an operating frequency of 400 MHz. To determine the fractional composition of the cyclodextrins obtained, we used matrix-activated laser desorption/ionization mass spectrometry with a time-of-flight analyzer (MALDI-TOF) and liquid chromatography–mass spectrometry with electrospray ionization (LC–MS–ESI). The analysis by the former method was carried out on a MALDI-TOF-MS Bruker (Germany) instrument operating in the reflecto-mol mode. Ionization was produced with a UV laser at an incident wavelength of 336 nm. The substrate was a nickel plate, and 2,5-dihydroxybenzoic and sinapic (4-hydroxy-3,5-dimethoxycinnamic) acids were used as references.

The analysis of oligomers by means of electrospray-ionization mass spectrometry in conjunction with liquid chromatography was carried out on a Agilent 1100 LC–MSD Trap SL instrument in the negative ion mode. Samples were prepared in DMSO (HPLC grade, Aldrich) at a concentration of ~ 1mg/ml. A 1 : 9 (by volume) methanol–water blend was used as an eluent.

A series of macroligands was synthesized by means of molecular imprinting in the presence and absence of the template via modification with epichlorohydrin, diepoxybutane, and diglycidyl ether (Table 1).

The procedure for the modification of β-cyclodextrin with epichlorohydrin in the presence of the template was as follows. To a β-cyclodextrin (0.44 mmol, 500 mg) solution in H_2O (5 ml) and NaOH (2.2 mmol, 88 mg), 0.5-,1-, 2-, 5-, and 10-fold excess of template was added and the mixture was stirred for 10 min. Then, 2.2 mmol of epichlorohydrin (176 μl) was introduced and stirring continued for 6 h at room temperature. The reaction was stopped by the addition of HCl (2.3 mmol). The product was precipitated with acetone and washed with the same solvent to remove template molecules. The precipitate was decanted and the product was dried in vacuum. Obtained in this manner were samples $\bar{\beta}$CD1-β-CD5.

In the synthesis of the macroligand in the absence of the template ($\bar{\beta}$CD6-β-CD8), 2.2 mmol of epichlorohydrin (176 μl) added to a solution of β-cyclodextrin (0.44 mmol, 500 mg) and NaOH (2.2 mmol, 88 mg) in H_2O (5 ml). The other operations were the same as for the template synthesis.

The samples were characterized by means of NMR spectroscopy and MALDI–TOF and ESI mass spectrometry.

To modify β-cyclodextrin with the binding agents diepoxybutane and glycerol diglycidyl ether, we followed that same procedure with reference to the absence or presence of the template. The amounts of the linking agents and the template were 2.2 and 0.22 mmol, respectively.

β-CD-1, β-CD-2 (template). ^{1}H NMR (DMSO-d_6, ppm) 5.75 (O**H**-2), 5.65 (O**H**-3), 4.9 (C^1**H**); 3.6–3.64 (C^3**H**, C^5**H**, C^6**H**^{a,b}, -O-CH$_2$-C**H**OH-C**H**$_2$OH);, 3.4 (C^4**H**), 3.39 (-O-C**H**$_2$-CHOH-CH$_2$OH), 3.2 (C^2**H**); ^{13}C NMR (DMSO-d_6, ppm): 101.76 (**C**^{1}). 81.5 (**C**^{4}), 74.5 (-O-**C**H$_2$-CHOH-CH$_2$OH), 72.9 (**C**^{3}), 72.3 (**C**^{2}), 72.1 (-O-CH$_2$-**C**HOH-CH$_2$OH), 71.9 (**C**^{5}), 66.7 (-O-CH$_2$-CHOH-**C**H$_2$OH), 59.86 (**C**^{6}). MALDI–TOF (*m/z*): 1157, 1231, 1305, 1379, 1453, 1527, 2347, 2421, 2495, 2569, 2643, 2717; LC–MS–ESI (target mass at *m/z* 1500): 1157, 1253, 1327, 1401, 1475, 1549, 2369, 2443, 2517, 2592, 2739.

β-CD-6. ^{1}H NMR (DMSO-d_6, ppm) 5.75 (O**H**-2), 5.65 (O**H**-3), 4.9 (C^1**H**), 3.6–3.64 (C^3**H**, C^5**H**, C^6**H**^{a,b}, -O-CH$_2$-C**H**OH-C**H**$_2$OH), 3.4 (C^4**H**), 3.39 (-O-**C**H$_2$-CHOH-CH$_2$OH), 3.2 (C^2**H**); ^{13}C NMR (DMSO-d_6, ppm): 101.76 (**C**^{1}). 81.5 (**C**^{4}), 74.5 (-O-**C**H$_2$-CHOH-CH$_2$OH), 72.9 (**C**^{3}), 72.3 (**C**^{2}), 72.1 (-O-CH$_2$-**C**HOH-CH$_2$OH), 71.9 (**C**^{5}), 66.7 (-O-CH$_2$-CHOH-**C**H$_2$OH), 59.86 (**C**^{6}). MALDI–TOF (*m/z*): 1157, 1231, 1305, 1379, 1453, 1527, 2347, 2421; LC–MS–ESI (target mass at *m/z* 1500): 1157, 1253, 1327, 1401, 1475, 1549, 2369, 2443.

β-CD-3, β-CD-4 (template). ^{1}H NMR (DMSO-d_6, ppm) 5.75 (O**H**-2), 5.65 (O**H**-3), 4.9 (C^1**H**), 3.6–3.64 (C^3**H**, C^5**H**, C^6**H**^{a,b}, -O-C**H**$_2$-C**H**OH-CHOH-C**H**$_2$OH), 3.4 (C^4**H**), 3.38 (-O-CH$_2$-CHOH-C**H**OH-C**H**$_2$OH), 3.2 (C^2**H**); ^{13}C NMR (DMSO-d_6, ppm): 101.76 (**C**^{1}), 81.5 (**C**^{4}), 75.0 (-O-CH$_2$-CHOH-**C**HOH-CH$_2$OH), 72.9 (**C**^{3}), 72.5 (-O-**C**H$_2$-**C**HOH-CHOH-CH$_2$OH), 72.3 (**C**^{2}), 71.9 (**C**^{5}), 64.2 (-O-CH$_2$-CHOH-CHOH-**C**H$_2$OH), 59.86 (**C**^{6}). MALDI–TOF (*m/z*): 1157, 1261, 1365, 1469, 1573, 2377, 2481, 2585, 2689; LC–MS–ESI (target mass at *m/z* 1500): 1157, 1283, 1387, 1595, 2399, 2503, 2607, 2711.

β-CD-7. ^{1}H NMR (DMSO-d_6, ppm) 5.75 (O**H**-2), 5.65 (O**H**-3), 4.9 (C^1**H**), 3.6–3.64 (C^3**H**, C^5**H**, C^6**H**^{a,b}, -O-C**H**$_2$-C**H**OH-CHOH-C**H**$_2$-OH), 3.4 (C^4**H**), 3.38 -O-CH$_2$-CHOH-C**H**OH-C**H**$_2$-OH); 3.2 (C^2**H**); ^{13}C NMR (DMSO-d_6, ppm): 101.76 (**C**^{1}), 81.5 (**C**^{4}), 75.0 (-O-CH$_2$-CHOH-**C**HOH-CH$_2$-OH); 72.9 (**C**^{3}); 72.5 (-O-**C**H$_2$-**C**HOH-CHOH-CH$_2$-OH); 72.3 (**C**^{2}); 71.9 (**C**^{5}); 64.2 (-O-CH$_2$-CHOH-CHOH-**C**H$_2$-OH); 59.86 (**C**^{6}). MALDI–TOF (*m/z*): 1157, 1261, 1365, 1469, 1573, 2377, 2481; LC–MS–ESI (target mass at *m/z* 1500): 1157, 1283, 1387, 1595, 2399, 2503.

β-CD-5 (template). ^{1}H NMR (DMSO-d_6, ppm) 5.75 (O**H**-2), 5.65 (O**H**-3), 4.9 (C^1**H**), 3.87 (-C^{DGD}**H**OH-), 3.6–3.64 (C^3**H**, C^5**H**, C^6**H**^{a,b}, -C^{DGD}**H**$_2$-), 3.4 (C^4**H**), 3.2 (C^2**H**); ^{13}C NMR (DMSO-d_6, ppm): 101.76 (**C**^{1}), 81.5 (**C**^{4}), 74.8 (-C^{DGD}H$_2$-), 72.9 (**C**^{3}), 72.3 (**C**^{2}), 71.9 (**C**^{5}), 69.9 (-**C**^{DGD}HOH-), 59.86 (**C**^{6}). MALDI–TOF (*m/z*): 1157, 1379, 1469, 1601, 1823; LC–MS–ESI (target mass at *m/z* 1500): 1157, 1401, 1623.

β-CD-8. ^{1}H NMR (DMSO-d_6, ppm) 5.75 (O**H**-2), 5.65 (O**H**-3), 4.9 (C^1**H**), 3.87 (-C^{DGD}**H**OH-), 3.6–3.64 (C^3**H**, C^5**H**, C^6**H**^{a,b}, -C^{DGD}**H**$_2$-), 3.4 (C^4**H**), 3.2 (C^2**H**); ^{13}C NMR (DMSO-d_6, ppm): 101.76 (**C**^{1}), 81.5 (**C**^{4}), 74.8 (-C^{DGD}H$_2$-), 72.9 (**C**^{3}), 72.3 (**C**^{2}), 71.9 (**C**^{5}), 69.9 (-**C**^{DGD}HOH-), 59.86 (**C**^{6}). MALDI–TOF (*m/z*): 1157, 1379, 1469, 1601, 1823; LC–MS–ESI (target mass at *m/z* 1500): 1157, 1401, 1623.

2,6-Perallyl-β-cyclodextrin was prepared as follows. β-Cyclodextrin (2g, 1.76 mmol) and dry DMF (100 ml) were placed in a three-necked flask (250 ml) equipped with a reflux condenser, a dropping funnel, and an argon supply system. Sodium hydride (0.963 g in oil mull) was added. To the mixture stirred with a magnetic stirrer, allyl bromide (2.6 ml, 30 mmol) was added and the reaction continued for 24 h at room temperature. The solvent was distilled off to dryness on a rotary evaporator, and the resulting viscous white material was dissolved in acetone and precipitated with water. The product was filtered off.

From the ^{1}H NMR spectrum, it follows that the degree of substitution of hydroxyl groups is close to 50%. The yield was 91.5%. ^{1}H NMR (DMSO-d_6, ppm) 6.06, 5.6, 5.3 (-C**H**=C**H**$_2$); 5.76 (O**H**-2); 5.61 (O**H**-3); 4.92 (C^1**H**); 4.12 (-C**H**$_2$-CH=CH$_2$) 3.7–3.6 (C^3**H**, C^5**H**, C^6**H**^{a,б}); 3.4–3.2 (C^4**H**, C^2**H**). MALDI–TOF (*m/z*): 1375.5, 1415.5, 1455.5, 1495.5. 11535.5, 1575.5, 116115.5, 1655.5.

Per(bromopropyl)-β-cyclodextrin was prepared as follows. Gaseous HBr was passed through a solution of perallyl-β-cyclodextrin persulfonic acid in CH_2Cl_2 at room temperature for 1.5 h. The solvent was distilled off and the products was purified by reprecipitation from acetone. The yield was 90%. According to ^{1}H NMR data, the addition involved a half of allyl groups. The relative amount of the bromide produced via the addition to the terminal allyl atom was 80%. ^{1}H NMR (DMSO-d_6, ppm) 6.06, 5.6, 5.3 (-C**H**=C**H**$_2$); 5.76 (O**H**-2); 5.61 (O**H**-3); 4.92 (C^1**H**); 4.12 (-C**H**$_2$-CH=CH$_2$) 3.9–3.5 (-C**H**$_2$-C**H**Br-CH$_3$, C^3**H**, C^5**H**, C^6**H**^{a,б}); 3.5–3.2 (C^4**H**, -C**H**$_2$-CH$_2$-C**H**$_2$Br); 1.85 (CH$_2$-C**H**$_2$-CH$_2$Br), 1.72 (-CH$_2$-CHBr-C**H**$_3$). MALDI–TOF (*m/z*): 1657.5, 1739.4, 1819.3, 1901.2, 1981.2.

Compound βCD-9 was prepared according to the following procedure. A 9% Na_2SO_3 aqueous solution (10 ml) was slowly added with vigorous stirring to a solution of per(bromopropyl)-β-cyclodextrin (0.80 g) in ethanol (10 ml). The resulting mixture was refluxed for 3 days. After the reaction, the solvent was distilled off to dryness. The product was dissolved in 10 ml of water, and inorganic salts were precipitated with 50 ml of acetone. The filtrate solvent was distilled off on a rotary evaporator. The precipitate was washed with ethanol and purified by means of dialysis. Yield 0.4 g. ^{1}H NMR (DMSO-d_6, ppm) 6.06, 5.6, 5.3 (-C**H**=C**H**$_2$); 5.76 (O**H**-2); 5.61 (O**H**–3); 4.92 (C^1**H**); 4.12 (-C**H**$_2$-CH=CH$_2$) 3.9–3.5 (-C**H**$_2$-C**H**SO$_3$Na-CH$_3$, C^3**H**, C^5**H**, C^6**H**^{a,б}); 3.5–3.2 (C^4**H**, -C**H**$_2$-CH$_2$-C**H**$_2$SO$_3$Na); 2.18 (CH$_2$-C**H**$_2$-CH$_2$SO$_3$Na), 1.79 (-CH$_2$-CHSO$_3$Na-C**H**$_3$)1. MALDI–TOF (*m/z*): 1870.4, 1766.5, 1661.5.

In catalytic experiments, iron(III) chloride and vanadyl sulfate were used as components.

The coupling reaction of 2-naphthol was carried out in the 1 : 1 (vol.) water–dichloroethane biphasic system with intense stirring at atmospheric pressure, a temperature of 60°C, and ratios between the catalyst components of 2-naphthol : $FeCl_3$: β-CD = 20 : 40 : 1 and of 2-naphthol : $VOSO_4$: β-CD = 5 : 1 : 1.

The catalyst system was prepared according to the following general procedure. A 10-ml flat-bottomed glass flask was charged with the components of the catalytic system in calculated amounts: 50 mg of 2-naphthol and distilled water and dichloroethane, 1 ml each; the reaction mixture was stirred upon heating. At cer-

Table 2. Characterization of materials based on epichlorohydrin-modified cyclodextrins

Sample	Linking agent	Ratio of peak areas on mass chromatogram $\frac{S_{2000-3500}}{S_{1000-1700}}$	Average number of glycerol units per cyclodextrin unit	
			for compounds containing 2 CD molecules	for compounds containing a CD molecule
β-CD-7	Diepoxybutane	0.11	3	4
β-CD-6	Epichlorohydrin	0.17	3–4	4
β-CD-3	Diepoxybutane	0.25	3–4	5–6
β-CD-1	Epichlorohydrin	0.32	3–4	5–6
β-CD-4	Diepoxybutane	0.51	5–6	6–7
β-CD-2	Epichlorohydrin	0.81	5–6	7–8

tain intervals, the organic layer was sampled and the small samples were dissolved in 1 ml of acetonitrile. The products of oxidative coupling of 2-naphthol with air as an oxidizing agent was studied by means of HPLC on an Agilent SL 1100 chromatograph using a Zorbax Eclipse XDB-C18 column of 2.1 × 150 mm size, 5 μl (the column was thermostated at 40°C). The mobile-phase flow rate was 0.5 ml/min, the mobile phase was a methanol/water blend with a gradient of 80% water at the beginning to 100% methanol by the 10th min. The detection was performed at a wavelength of 290 nm with a diode array detector.

RESULTS AND DISCUSSION

In the syntheses of 2,6-dimethyl-β-cyclodextrin, ethoxylated β-cyclodextrin, 6-deoxy(ethylenediamine)-β-cyclodextrin, and 2,6-persulfopropyl-β-cyclodextrin, we employed procedures reported in the literature [8, 9]. 2,6-Perallyl-β-cyclodextrinsulfonic acid was synthesized via successive allylation, hydrogen bromide addition, and $–SO_3$ group substitution for bromide. The modification of cyclodextrins with epichlorohydrin and diepoxybutane was carried out in an aqueous alkali solution for 6 h. The products was isolated by reprecipitation from the aqueous solution with acetone or methanol. The general scheme of imprinting is described by Schemes 2 and 3.

The cyclodextrin molecule contains 21 hydroxyl groups, whose reactions can lead to various mono-, di-, and trisubstituted compounds. Reacting in the presence of a template are its inclusion complexes with β-cyclodextrin, in which some hydroxyl groups of the host molecule are inaccessible to the reagents. As a result, isomers that form the most stable inclusion complexes with the template prevail in the mixture. As has been shown earlier, owing to the formation of guest–host complexes composed of two cyclodextrin molecules per template molecule, the proportion of the dimers can increase as well [4, 5, 7].

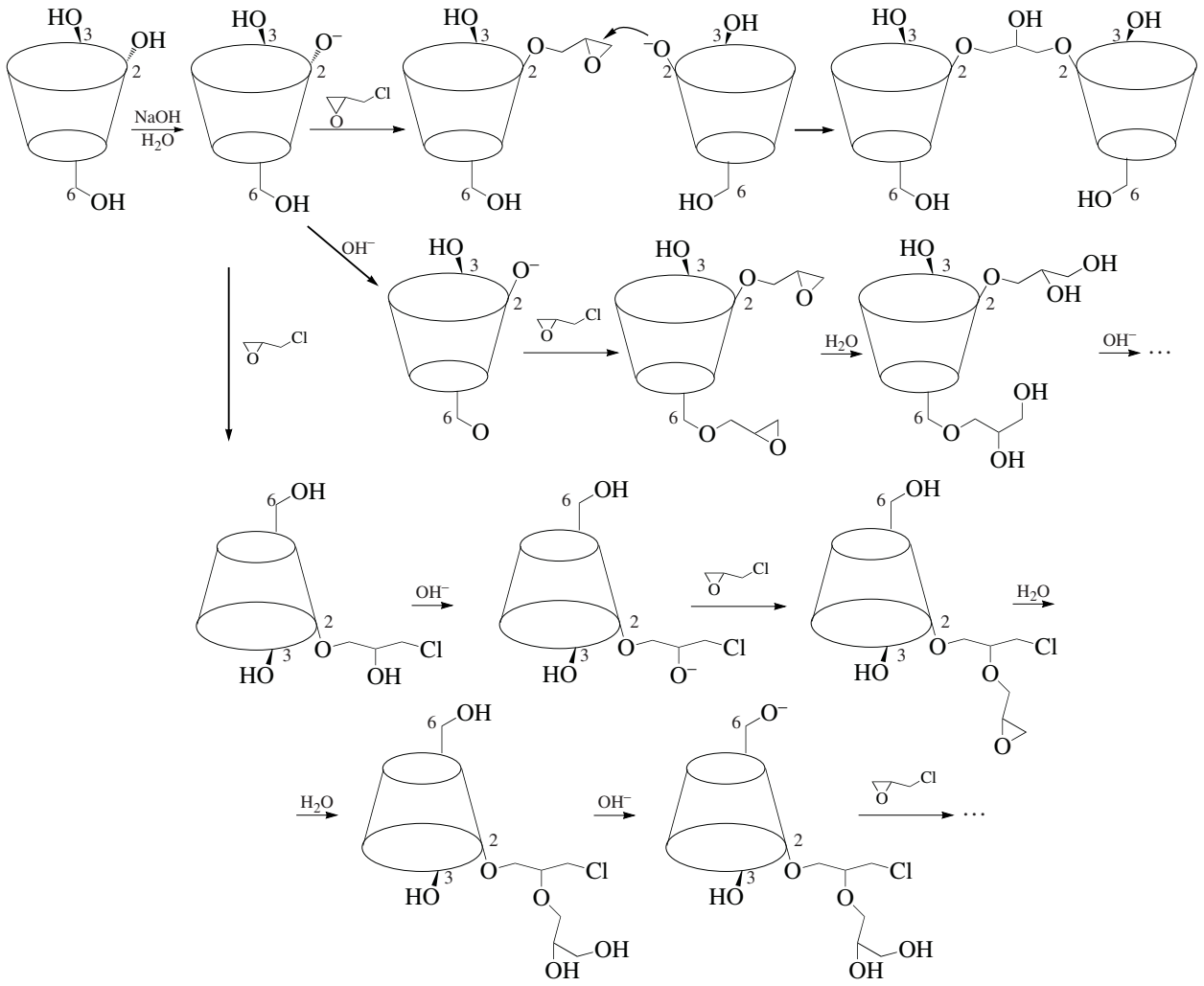
The macroligands obtained in the presence and absence of templates were studied by the NMR and mass spectrometry (MALDI–TOF and LC–MS) techniques. The mass spectra of modified cyclodextrins turned out to display peaks of molecular ions corresponding to compounds containing one and two cyclodextrin units. The number of added oligoglycidol units varied from 2 to 8 in these compounds.

The ratio between various isomers of modified cyclodextrins was determined by means of the LC–MS technique in the electrospray ionization mode. The ratio of peak areas in the molecular mass ranges 2000–3600 and 1000–17000 characterizes the proportion of dimers in the product.

It was shown that the average degree of polymerization of epichlorohydrin and the number of compounds that include two chemically linked cyclodextrin molecules strongly depends on the presence of the template and its concentration in the reaction mixture. The growth in the chain length of the linker on passing from epichlorohydrin to diepoxybutane leads to a decrease in the proportion of dimers and the degree of oligomerization. Moreover, the dimers were not found at all when the bulkier reagent diglycidyl ether of glycerol was used. The characteristics of the materials based on epichlorohydrin-modified cyclodextrins are given in Table 2.

The materials obtained via modification with epichlorohydrin and diepoxybutane were also characterized by means of ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectra of the samples showed a substantially lower intensity of signals due to hydroxyl groups and the appearance of signals at 3.8–4.9 ppm attributed to C1–H and C6–H protons of cyclodextrin, the chemical shifts of these protons being changed by modification, and to free hydroxyls of the oligoglycidyl segments. The most substantial changes were observed in the region of cyclodextrin OH protons.

It should be noted that hydroxyl groups at the third carbon atom (O**H**-3) remained practically intact in the case of β-cyclodextrins prepared with the use of templates. This conclusion follows from the intensity ratio of signals at 5.65 (O**H**-3) and 4.85 ppm (C^1**H**) in the proton NMR spectrum. This ratio was 0.7–0.8 for the



Scheme 2. Cyclodextrin-mediated oligomerization of epichlorohydrin.

samples prepared in the absence of templates and close to unity for the samples prepared in their presence. In addition, the ^{13}C NMR spectra of the latter samples did not display a signal at 73 ppm that would correspond to the modified carbon atoms C_3 of β-cyclodextrin. It is likely that the hydroxyl groups at C_2 and C_6 carbon atoms (OH-2 and OH-6) predominantly enter the reaction.

When aromatic compounds were oxidized in the water/dichloroethane biphasic medium with different

Table 3. Oxidation of 2-naphthol

Ligand	Metal salt	Metal/2-naphthol ratio	Time, h	1,1'-Bi-2-naphthol yield, %
Methylated β-CD	$FeCl_3$	2	2	39
Oxyethylated β-CD	$FeCl_3$	2	2	38
Perallyl β-CD sulfonic acid	$FeCl_3$	2	2	16
Sulfopropyl β-CD	$FeCl_3$	2	2	32
6-Ethylenediamino-β-CD	$FeCl_3$	2	2	39
Methylated β-CD	$VOSO_4$	0.2	240	81
6-Ethylenediamino-β-CD	Cu^{2+}	0.05	5	24
Methylated β-CD	Cu^{2+}	0.05	10	2

systems (iron(III) chloride [10, 11], oxygen/vanadyl ion [12, 13], oxygen in the presence of copper complexes as catalysts [14, 15]), the main product was 1,1'-bi-2-naphthol with the selectivity for this product exceeding 95%. In the absence of cyclodextrin, the reaction proceeds at an extremely slow rate and the product yield does not exceed 20% for 10 h (in the case of the iron salt) or 10% for 7 days (in the case of the vanadium salt). In the presence of copper salts, no formation of binaphthol was observed.

The use of modified cyclodextrins made it possible to substantially increase the rate of the process. It is likely that the rise in the reaction rate is primarily due to an increase in the concentration of the substrate 2-naphthol in the aqueous phase as a result of the formation of guest–host complexes with cyclodextrin. The yield of the corresponding dimeric products reaches 80% for 8 h of the reaction (with the use of $FeCl_3$) or for 10 days in the presence of vanadyl sulfate. It is essential that the double excess of the metal salt was used in the former case and a 10 mol % excess in the latter case, that is, the reaction proceeds in the catalytic mode involving air oxygen (Table 3). It should specially be noted that the copper complex of ethylenediamine-modified cyclodextrin exhibits a relatively high activity. The use of other cyclodextrins in combination with copper salts did not lead to the dimerization of the substrate.

Note that a nearly quantitative yield of the product was obtained when the reaction was run for a very long time.

We compared the activity of catalyst systems containing the macroligands synthesized via the same procedure in the presence and absence of template molecules. For this purpose, we calculated the reaction-rate enhancement factor $\frac{TON_1}{TON_2}$, where TON_1 is the number of moles of the product per mole of catalyst per hour in the case when the macroligands was synthesized in the presence of the template and TON_2 is the number of moles of the product per mole of catalyst per hour in the case when the same macroligand was synthesized in the absence of the template.

The use as catalyst components of cyclodextrins synthesized in the presence of 1,1'-bi-2-naphthol made it possible to substantially increase the rate of the reaction as compared with the catalyst system containing cyclodextrin obtained in the absence of the template, as well as methylated cyclodextrin. The yield of the dimer over the reaction time of 5 h was 65% (Fig. 1). It is important that the reaction rate and the product yield increase when the macroligand prepared in the presence of a large excess of the template is used. The reaction-rate enhancement factor was greater than two in this case.

The activity of the catalysts prepared via modification with diepoxybutane turned out to be somewhat lower; nonetheless, a similar trend was observed: the use of binaphthol as a template leads to a dramatic increase in the product yield relative to the catalyst prepared either in the absence of the template or in the

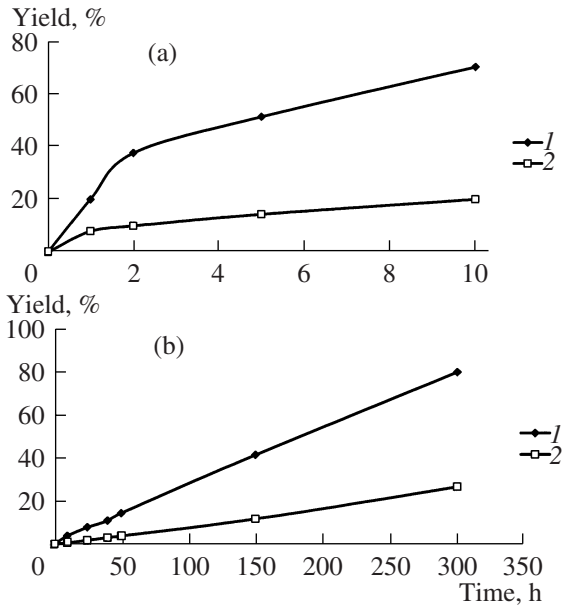


Fig. 1. Oxidative coupling of 2-naphthol into 1,1'-bi-2-naphthol catalyzed by (a) $FeCl_3$ and (b) $VOSO_4$ in the biphasic system (*1*) in the presence of 2,6-Me-CD and (*2*) in the absence of the macroligand.

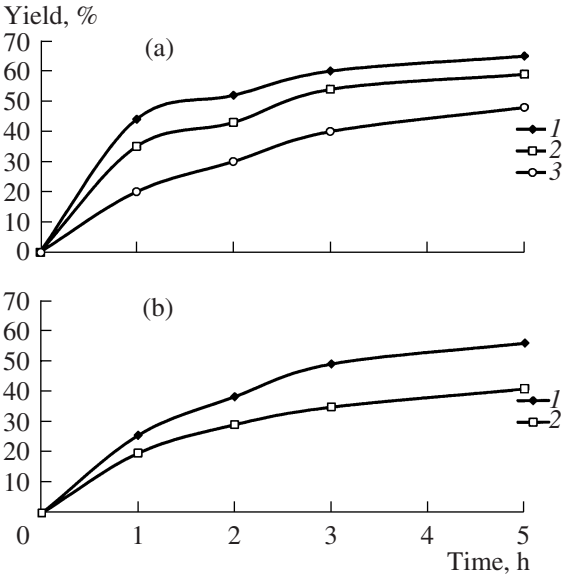


Fig. 2. (a) Catalytic activity of the system using the ligand prepared via modification with epichlorohydrin in the presence of (*1*) excess of epichlorohydrin template or (*2*) bi-2-naphthol and (*3*) in the absence of the template; (b) catalytic activity of the system using the ligand prepared via modification with diepoxybutane (*1*) in the presence of bi-2-naphthol and (*2*) in the absence of the template.

presence of 2-naphthol as a template. It should also be noted that the ligand that had been prepared via modification with epichlorohydrin in the presence of the linear substrate dodecanal and had contained a considerable amount of dimers exhibited a considerably lower activity than the ligand obtained with the use of bi-2-naphthol as a template. This difference indicates that a kind of preorientation of cyclodextrin molecules takes place to fit to the conformation of the product. In this case, the use of corresponding aromatic compounds as the bi-2-naphthol template must lead to a growth in the reaction rate owing to a kind of simulation of the transition state of the reaction with the use of the template.

Indeed, a mechanism that suggests the interaction of the naphthyl radical with naphthol has been proposed for oxidative coupling in the literature [10, 11].

The rate of this process depends on the distance between interacting molecules; the closer this distance to the distance in 1,1'-binaphthol itself, the higher the reaction rate. It is likely that the structure of the dimers in the case of catalysts obtained in the presence of 1,1'-binaphthol best satisfies this condition and the reaction rate turns out to be high.

In summary, studying the coupling of 2-naphthol, we have shown that the use, as catalyst components, of cyclodextrins modified under the molecular imprinting conditions leads to an increase in the reaction rate when an analog of the reaction transition state is taken as a template.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 04-03-32166a.

REFERENCES

1. E. A. Karakhanov, A. L. Maksimov, and E. A. Runova, Usp. Khim. **74**, 104 (2005).
2. R. Breslow, in *Artificial Enzymes*, Ed by R. Breslow (Wiley-VCH, Weinheim, 2005), p. 1.
3. M. Komiyama, T. Takeuchi, T. Mukawa, and H. Asanuma, *Molecular Imprinting: From Fundamentals to Applications* (Wiley, New York, 2003).
4. T. Hishiya, M. Shibata, M. Kakazu, et al., Macromolecules **32**, 2265 (1999).
5. E. A. Karakhanov, L. M. Karapetyan, Yu. S. Kardasheva, et al., Macromol. Symp. **235**, 39 (2006).
6. A. A. Efendiev and V. A. Kabanov, Pure Appl. Chem. **11**, 2077 (1982).
7. E. A. Karakhanov, A. L. Maksimov, A. Ya. Zhuchkova, et al., Neftekhimiya **45**, 97 (2005) [Pet. Chem. **45**, 79 (2005)].
8. US Patent No. 5,008,386 (1991).
9. L. Bruce, A. May, D. Suzanna, et al., J. Chem. Soc., Perkin Trans. 1, 3157 (1997).
10. K. Ding, Y. Wanf, L. Zhang, and Y. Wu, Tetrahedron **52**, 1005 (1995).
11. K. Ding, Q. Xu, Y. Wanf, et al., Chem. Commun., 693 (1997).
12. D. R. Hwang, Ch. P. Chen, and B. J. Uang, Chem. Commun., 1207 (1999).
13. Ch. Y. Chu, D. R. Hwang, Sh. K. Wang, and B. J. Uang, Chem. Commun., 980 (2001).
14. J. Brusse, J. L. G. Groenendidijk, J. M. Koppele, and A. C. Jansen, Tetrahedron **41**, 3313 (1985).
15. M. Hovorka, J. Gunterova, and J. Zavada, Tetrahedron Lett. **31**, 413 (1990).