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Immobilization of β-cyclodextrin onto Dowex resin as a stationary microvessel and phase transfer catalyst

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ABSTRACT

In this study, immobilization of β-cyclodextrin onto commercial Dowex resin by covalent bond was reported. The efficiency of this biocatalyst system as a stationary microvessel and new solid–liquid phase transfer catalyst in reduction of epoxides by $NaBH_4$ was studied.

1. Introduction

The use of cyclodextrins (CDs) as microvessels to perform chemical reaction has attracted the interest of chemist since the 1960s [1]. Cyclodextrins have hydrophobic cavities into which organic molecules of appropriate size and shape can be incorporated mainly through hydrophobic interactions in aqueous solutions [2–5]. Although water has many unique properties, it has not traditionally been the solvent of choice in which to perform organic reactions. One reason has been that the nonpolar nature of organic molecules results in low or no solubility in water [6].

As is well known, the solubility of apolar guest compounds in water is (in general) increased when they form inclusion complexes with CDs [7–11]. Thus, cyclodextrins are potent phase transfer catalysts (PTC) [12,13].

On the other hand, the practical utility of CDs could be extended further if they can be rendered water insoluble. Different strategies have been explored in the literature including polymerization procedures and immobilization onto solid particles such as silica, PEGylated Merrifield resins, and inside nanoporous oxides [14–16].

Immobilization of the phase transfer catalyst on an insoluble polymeric matrix has considerable advantages. Not only would the catalyst recovery and product isolation be greatly simplified but also, owing to the three-phase nature of the system, continuous flow methods could be employed, making the technique particularly attractive for industrial applications [17].

Recently, as part of our efforts to introduce novel PTC systems for the synthesis of organic compounds [18,19]; we have reported grafting of the poly(ethylene glycol) onto Dowex resins [20], as an efficient and reusable catalyst in the regioselective azidolysis of epoxides in water. Taking into account all this; we decided to immobilize β-CD as a stationary microvessel and new phase transfer system for organic transformation.

2. Experimental

2.1. General remarks

Epoxides and other chemical materials were purchased from Fluka and merck and used without further purification. Dowex H^+ resin (mesh 30–40) was washed with cold methanol, dried under vacuum at 50 °C and stored in airtight container. β-cyclodextrin was heated at 80 °C under vacuum for 30 min before use to remove traces of moisture. Products were characterized by comparison of their physical data, IR and ^1H NMR spectra with known samples. NMR spectra were recorded in $CDCl_3$ on a Bruker Advance DPX 400 MHz instrument spectrometer using TMS as internal standard. IR spectra were recorded on a BOMEM MB-Series 1998 FT-IR spectrometer. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates. GLC analyses were performed on a Shimadzu GC-12 A chromatograph equipped with a 3-m Thermon-1000 column.

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2.2. Typical procedure for immobilizing of β-cyclodextrin to Dowex Maraton C

An oven dried 50 mL flask equipped with a magnetic stirrer is charged with dried Dowex H^+ resin (2 g) under nitrogen atmosphere. Then freshly distilled $SOCl_2$ (5.0 mL, 67 mmol) was added slowly to the flask through an addition funnel and the reaction mixture was stirred under reflux conditions. After stirring for 6 h, the excess unreacted thionyl chloride was distilled out. Under nitrogen atmosphere, a solution of freshly dried β-cyclodextrin (3.4 g, 3 mmol) in dried pyridine (10 mL) was added dropwise to the resulting polymer. The solution was mixed at room temperature until no HCl was produced. The solid was filtered off and washed thoroughly with acetone and water. Then, the Dowex-β-CD was collected and dried in vacuum.

2.3. Typical procedure for the ring opening of epoxides

$NaBH_4$ (4.0 mmol) was added gradually to a mixture of epoxide (1.0 mmol) and Dowex-β-CD (0.1 g) in water (5.0 mL). The suspension was magnetically stirred at room temperature for the time shown in Table 2. After complete consumption of epoxide as judged by TLC (using *n*-hexane/ethylacetate (5:1) as eluent), the insoluble PTC was filtered off and the filtrate was extracted with ether (3 × 5). The extract was dried over Na_2SO_4, and evaporated in vacuo to give the alcohols. The crude products were purified by silica gel column chromatography.

3. Results and discussion

β-CD, a cyclic oligosaccharide composed of seven α-(1–4) linked D-glucopyranose units [21,22], can be easily immobilized to Dowex Maraton C resin in the reaction depicted in Scheme 1. In the first step, sulfonic acid functional groups of resin were converted to sulfonyl chloride. Cyclodextrine can be efficiently immobilized on the resin by reaction of sulfonyl chloride functional groups with β-CD. The reaction is very clean and does not require any work-up procedure because the evolved HCl gas can be removed from the reaction vessel immediately.

To determine the amount of β-CD supported on the resin, 0.5 g of the each resins, Dowex-SO_3H and Dowex-β-CD, were washed with methanol, dried and mixed with 20 mL of 0.5 M NaOH for 1 h. Then, the solutions were titrated with 0.5 M HCl. The degree of immobilization of β-CD units on the main backbone of the resin was 0.9 mmol/g resin.

It has been reported that CDs affected the reduction of epoxide with sodium borohydride [23]. But, to our knowledge, there is no example about application of supported cyclodextrin in the ring-opening reaction of epoxide with sodium borohydride in aqueous media. In order to investigate the efficiency of the immobilized β-Cyclodextrine onto polymer as a solid–liquid phase transfer catalyst, 2, 3-epoxypropyl phenyl ether was chosen as a model compound and reacted with Dowex-β-CD and $NaBH_4$ in water. TLC analysis of the mixture showed completion of the reaction in 8 h. The products, 1-phenoxypropan-2-ol (1a) and 3-phenoxypropan-1-ol (1b) were achieved after extraction and no evidence for the formation of diol as byproduct of the reaction was observed. This reaction was also tested, using Dowex and $NaBH_4$; the reaction was not completed and required much longer reaction time for the complete conversion. Also, the product, 3-phenoxypropan-1-ol was contaminated by diol. The promoting effect of supported catalyst was definitely confirmed by reaction of 2, 3-epoxypropyl phenyl ether under similar reaction condition, without adding catalyst, the substrate did not react with $NaBH_4$, even after two days and more than 90% of the substrate was recovered.

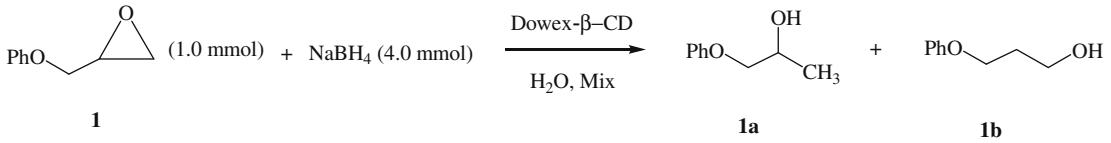
To confirm the effect of acidic sites on Dowex-β-CD in the rate and regioselectivity of the reduction reaction, the resin was first treated with 0.1 M NaOH solution and the reduction of 2, 3-epoxypropyl phenyl ether by $NaBH_4$ was investigated with the inactivated acidic sites resin. GLC analysis of the reaction mixture was clearly shown that the reaction completed in 12 h associated with remarkable decreasing in 1b, whereas the main product of the reaction was 1a (Table 1).

This method has been found to be applicable to a series of epoxides, under similarly mild experimental reaction conditions, and the results are illustrated in Table 2.

The catalytic property of the polymeric matrix, Dowex-β-CD, is due to the inclusion complex formation of epoxides via hydrogen bonding of the epoxide oxygen to the outer OH of the β-CD which then reacts with BH_4^- anion to form alcohol. Likewise, acidic media promote activation of the epoxide and increase the rate of the reduction by sodium borohydride (Scheme 2).

However, when an immobilized biocatalyst is prepared, it should be considered that the main goal of enzyme immobilization should be the reuse of the biocatalyst [24]. It is worthy to note that Dowex-β-CD does not suffer from extensive mechanical degradation after operating and could be quantitatively recovered by simple filtration and washing with water and methanol. The recovered resin has been reused three times for the reduction of cyclohexene oxide. The results were clearly shown that the catalyst does not show any loss in its activity and produced corresponding alcohol in 85%, 82% and 80% yield, respectively.

Table 1
Effect of Dowex- β-CD on the ring-opening reaction of 2, 3-epoxypropyl phenyl ether.

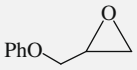
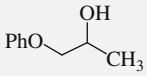
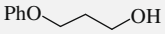
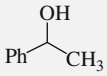
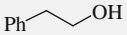
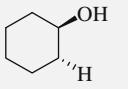
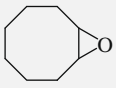
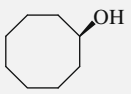
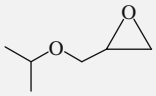
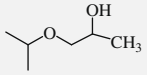


1 **1a** **1b**

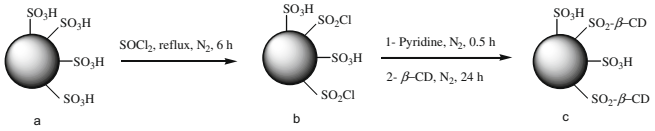
Entry	Catalyst	Time (h)	Conversion (%)	Isolated yields (%)
1	Dowex-β-CD	8	100	40 (1a), 55 (1b)
2	Dowex	8	40	12 (1b and some diol was isolated)
3	–	48	10	5 (1b)
4	Dowex-β-CD*	12	100	70 (1a), 15 (1b)

* Inactivated sites resins.

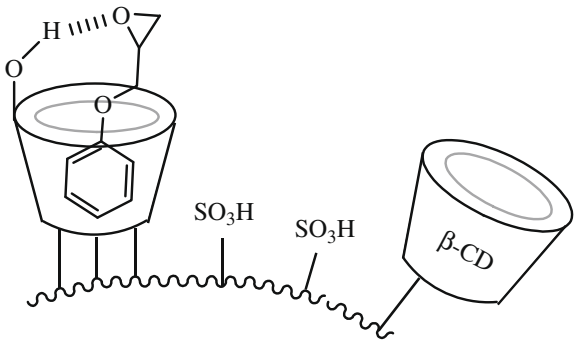
Table 2
Results of the treatment of epoxides with $NaBH_4$ catalyzed by Dowex-β-CD.

Entry	Epoxide	Product(s)[a]		Time (h)	Yield (%)[b]
1				8	40(55)[c]
2				6	40(50)[c]
3				8	85
4				12	75
5				24	10

[a] Products were identified by comparison of their physical and spectral data with those of authentic samples.
[b] Isolated yields.
[c] According to GLC analysis.



Scheme 1. Preparation of Dowex-β-CD.



Scheme 2. Dowex-β-CD mediated ring opening of epoxide.

4. Conclusion

In conclusion, we have described an efficient method for the immobilization of β-cyclodextrin onto a polymer matrix. Dowex-β-CD was objectified and evaluated as a heterogeneous catalyst by the reduction of epoxides to the corresponding alcohols with sodium borohydride, and was found to exhibit good activity. Extensive research to use this solid–liquid phase transfer catalyst system in organic transformation is currently underway in our group and will be reported in due course.

Acknowledgement

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References

[1] K. Takahashi, Chem. Rev. 98 (1998) 2013.
[2] L.X. Song, L. Bai, X.M. Xu, J. He, S.Z. Pan, Coord. Chem. Rev. 253 (2009) 1276.
[3] A. Kikuzawa, T. Kida, M. Akashi, Org. Lett. 9 (2007) 3909.
[4] M.S. Reddy, M. Narender, Y.V.D. Nageswar, K.R. Rao, Tetrahedron Lett. 46 (2005) 6437.
[5] S. Hamai, T. Ikeda, A. Nakamura, H. Ikeda, A. Ueno, F. Toda, J. Am. Chem. Soc. 114 (1992) 6012.
[6] H.C. Hailes, Org. Process Res. Dev. 11 (2007) 114.
[7] J. Szejtli, Chem. Rev. 88 (1998) 1743.
[8] B. Kaboudin, M. Sorbiun, Tetrahedron Lett. 48 (2007) 9015.
[9] Z. X Yang, Y. Chen, Y. Liu, Carbohydr. Res. 343 (2008) 2439.
[10] Z. Lu, B. Cheng, Y. Hu, Y. Zhang, G. Zou, Food Chem. 113 (2009) 17.
[11] S.N. Murthy, B. Madhav, A.V. Kumar, K.R. Rao, Y.V.D. Nageswar, Tetrahedron 65 (2009) 5251.
[12] H. Dodziuk, Cyclodextrins and Their Complexes, Wiley-Vch Verlag GmbH & Co, KGaA, Weinheim, 2006.
[13] J.T. Lee, H. Alper, J. Org. Chem. 55 (1990) 1854.
[14] M. Siu, V.A. Yaylayan, J.M.R. Belanger, J.R.J. Pare, Tetrahedron Lett. 46 (2005) 3737.
[15] Y. Wang, Y. Xiao, T.T.Y. Tan, S.-C. Ng, Tetrahedron Lett. 49 (2008) 5190.
[16] C. Lagrost, G. Alcaraz, J.-F. Bergamini, B. Fabre, I. Serbanescu, Chem. Commun. (2007) 1050.
[17] J. Chen, G. Yang, H. Zhang, Z. Chen, React. Funct. Polym. 66 (2006) 1434.
[18] A.R. Kiasat, M. Zayadi, Catal. Commun. 9 (2008) 2063.
[19] A.R. Kiasat, M. Fallah Mehrjardi, Catal. Commun. 9 (2008) 1497.
[20] A.R. Kiasat, R. Badri, B. Zargar, S. Sayyahi, J. Org. Chem. 73 (2008) 8382.
[21] S.V. Bhosale, S.V. Bhosale, Mini-Rev. Org. Chem. 4 (2007) 231.
[22] J.M. Casas-Solvas, M.C. Martos-Maldonado, A. Vargas-Berenguel, Tetrahedron 64 (2008) 10919.
[23] Y. Hu, M. Uno, A. Harada, S. Takahashi, Chem. Lett. (1990) 797.
[24] S.A. Ferrarotti, J.M. Bolivar, C. Mateo, L. Wilson, J.M. Guisan, R.F. Lafuente, Biotechnol. Prog. 22 (2006) 1140.