Ring-opening of 1,2-epoxyalkane with alcohols over H-ZSM-5 in liquid phase

Haruo Ogawa [1], Yasuhiro Miyamoto, Tamiki Fujigaki and Teiji Chihara [a]

Department of Chemistry, Tokyo Gakugei University, Koganei, Tokyo 184, Japan
[a] *The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-01, Japan*

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H-ZSM-5 readily catalyzed the ring-opening of 1,2-epoxyalkane with alcohols to give alkoxy alcohols. The reaction proceeded accompanying the shape-selective properties of H-ZSM-5. The rate of the ring-opening was retarded by use of alcohols with larger numbers of carbon atoms such as hexanol. The selectivities for the substitution of nucleophile alcohols at the sterically more hindered position of the epoxide were improved to be almost higher than those under basic conditions.

Keywords: H-ZSM-5; ring-opening; epoxide; shape-selective property; regioselective reaction

1. Introduction

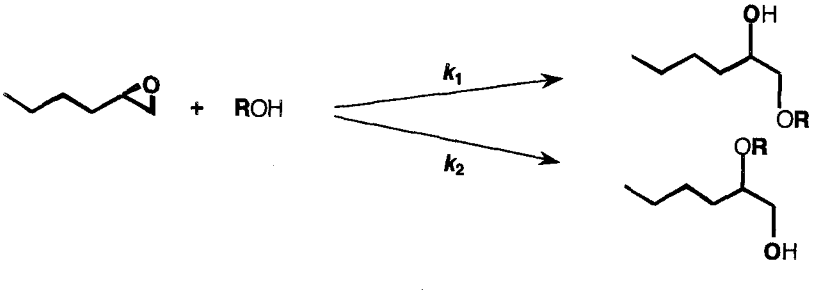
Highly selective reactions have been achieved by the use of inorganic porous solids in which the substrate molecules orientate in the cavity or channels with suppression of their translational movement [1]. Zeolites have been extensively studied as catalysts in gas-phase reactions. Recently, they are attracting much attention of organic chemists because they exhibit remarkable shape-selective properties besides the acid–base properties due to their homogeneous crystalline structures. Examples of recent reports using zeolites in organic syntheses are the photolysis of alkanophenones [2] and dibenzyl ketone [3], and ring-opening reactions of 2,3-epoxy alcohols [4].

We have been interested in the application of zeolites to organic reactions in the liquid phase and have reported that ZSM-5 performed the hydrolysis of esters [5] and the hydration of epoxides [6]. This paper reports the application of H-ZSM-5 to the ring-opening of 1,2-epoxyalkane, mainly 1,2-epoxyhexane as a model compound, with alcohols as nucleophiles (scheme 1). The application of H-ZSM-5 as a solid acid to the reaction improves the proportion of substitution of the nucleophile alcohol at the sterically more hindered position of the epoxide compared with that obtained under neutral or basic conditions, and, moreover, facilitates separation of the catalyst.

2. Experimental

H-ZSM-5-25 was prepared from ZSM-5-25Na ("standard" zeolite samples of Mobil Oil Co.) by a conventional cation exchange procedure using 1 mol ℓ^{-1} NH_4Cl aqueous solution followed by calcination in air at 500°C.

The ring-opening of 1,2-epoxyalkane with alcohol was investigated as follows. H-ZSM-5 (40 mg) and the epoxide (13.0 mmol) were added to a certain alcohol (10 ml), and the suspension was refluxed.



Scheme 1.

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[1] To whom correspondence should be addressed.

3. Results and discussion

3.1. Reaction rate and shape-selective property of H-ZSM-5

Ring-opening of 1,2-epoxyhexane with various alcohols was demonstrated over H-ZSM-5-25 catalyst. Alcohols play a dual role, both as nucleophilic reactant and as solvent in the reaction. Reaction rates over H-ZSM-5-25 were measured, and results are summarized in table 1 besides results observed with H_2SO_4 catalyst as a reference standard. Higher alcohols show higher values of the rate constant k. The value of k appears to be affected by the boiling point of the solvent alcohol under reflux conditions. Relative rate constants, k' and k'', based on the rate in methanol solvent indicate that both k' and k'' show larger values in higher alcohols.

The ratios of relative rate constants, k'/k'', denote the relative magnitude of each reaction rate using a certain organic solvent, where the influence of factors such as a boiling point and permittivity on the reaction rate could be counterbalanced taking account of the comparison based on the relative rate constants using H_2SO_4 catalyst. A smaller value of the ratio means a larger retardation of the rate by use of H-ZSM-5-25. The value would be ascribed primarily to the size of the solvent molecule. The larger retardation was observed in the reactions using hexanol and butanol. The retardation in the hydration of epoxide by bulky solvents such as *m*-xylene has been also reported [6a]. Larger tight fits of hexanol or butanol in the ZSM-5 pore might cause the larger retardation of the rate.

3.2. Selectivities for the substitution of nucleophile alcohols

The rate constants, k_1 and k_2, for the formation of 1-alkoxy-2-hexanol and 2-alkoxyhexanol, respectively, were measured and the k_2/k_1 ratios in various alcohols over H-ZSM-5-25 are listed in table 2 besides those obtained with NaOH and H_2SO_4 catalysts. Ratios were improved to be consequently almost higher than those using NaOH catalyst, while the values over H-ZSM-5-25 were lower than those using H_2SO_4. The higher value means higher selectivity for the substitution of the nucleophile alcohol at the sterically more hindered position of the epoxide. The highest value of 0.86 was observed in ethanol despite the lower value of 0.038 using NaOH and 1.00 using H_2SO_4. Na-ZSM-5-25 causes the ratio drastically to fall, and the ratio becomes lower than that under NaOH to give the value 0.015. This fact indicates that the ring-opening over H-ZSM-5-25 proceeds being influenced to a great extent by acid sites of the zeolite.

Table 1
Ring-opening of 1,2-epoxyhexane with various alcohols [a]

Alcohol	b.p. (°C)	H-ZSM-5-25		H_2SO_4	k'/k''
		k [b]	k' [c]	k'' [c]	
methanol	64.7	10.8	1.0	1.0	1.0
ethanol	78.5	11.7	1.08	1.15	0.94
1-propanol	97.2	18.0	1.67	1.80	0.93
1-butanol	118	25.0	2.31	8.27	0.28
1-hexanol	157	41.8	3.87	14.74	0.26

[a] A certain amount of catalyst and 1,2-epoxyhexane (13 mmol) was added in methanol (10 ml) and refluxed: zeolite (40 mg), H_2SO_4 (0.0216 mmol, 2.12 mg).
[b] First-order rate constant in the epoxide: k in 10^{-2} g^{-1} h^{-1}.
[c] Relative rate constant based on methanol.

Table 2
Selectivity for the substitution of the nucleophile alcohols [a]

Alcohol	H-ZSM-5-25 k_2/k_1 [c]	NaOH [b] k_2/k_1 [c]	H_2SO_4 k_2/k_1 [c]
methanol	0.347 (0.015) [d]	0.324 [e]	1.01
ethanol	0.860	0.038	1.00
1-propanol	0.385	0.151	0.614
1-butanol	0.028	0.000	0.436
1-hexanol	0.001	0.000	0.775

[a] Reaction conditions are the same as described in table 1.
[b] NaOH: 0.040 mmol, 1.6 mg.
[c] k_1 and k_2 are first-order rate constants in the epoxide for the formation of the representative 1-alkoxy-2-hexanol and 2-alkoxyhexanol, respectively: k_i in 10^{-2} g^{-1} h^{-1}.
[d] Na-ZSM-5-25, Na ion-exchanged ZSM-5, was used.
[e] The ratio of the yield of 2-methoxyhexanol to that of 1-methoxy-2-hexanol after 1 h reaction time.

3.3. Ring-openings of 1,2-epoxyalkanes

Results over H-ZSM-5-25 with methanol are summarized in table 3. Both the rate constant k and the ratio k_2/k_1 decreased with the number of carbon atoms of the epoxides. 1,2-epoxypropane shows the highest reactivity and selectivity for the substitution of methanol at the position of the hindered carbon. There is usually a greater tendency for a nucleophile to attack at the position of the more substituted carbon atom of the epoxide

Table 3
Ring-openings of epoxides with methanol [a]

Epoxide	H-ZSM-5-25	
	k [b]	k_2/k_1 [c]
1,2-epoxypropane	49.8	0.833
1,2-epoxybutane	22.4	0.383
1,2-epoxyhexane	10.8	0.347
1,2-epoxyoctane	10.9	0.151

[a] Reaction conditions are the same as described in table 1.
[b] First-order rate constant in the epoxide: k in 10^{-2} g^{-1} h^{-1}.
[c] k_1 and k_2 are rate constants for the formation of 1-methoxy-2-alkanol and 2-methoxyalkanol, respectively.

ring in an acidic solution, while under neutral or basic conditions a nucleophile attacks predominantly the sterically less hindered carbon atom [7,8]. In this reaction, it is considered that acid sites of the zeolite play the role of a catalyst and moderate linkage of the acid site to the less hindered carbon atom proceeds in comparison with the reaction performed by NaOH catalyst. Under acidic conditions, the first step is the preequilibrium addition of a proton to the epoxide, thereby producing an oxonium ion that can react further [7]. The oxonium ion with acid site might be formed in this work and successive ring-opening in the next step would proceed. Details of the mechanism for the selectivity could not be interpreted clearly at present. Further research on zeolite-catalyzed ring-opening of functionalized epoxides is under way.

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