Catalysis Letters Vol. 101, Nos. 1–2, May 2005 (© 2005)
DOI: 10.1007/s10562-005-3757-1

The ring transformations of 1,2,3,4-diepoxybutane (2,2′-bioxirane) catalysed by various aluminosilicates

András Fási[a], István Pálinkó[b,]*, and Imre Kiricsi[a]

[a]*Department of Applied and Environmental Chemistry, University of Szeged, Rerrich B. tér 1, Szeged, H-6720 Hungary*
[b]*Department of Organic Chemistry, University of Szeged, Dóm tér 8, Szeged, H-6720 Hungary*

Received 20 October 2004; accepted 10 January 2005

The transformations of a molecule containing two adjacent epoxide rings, 2,2′-bioxirane that is, were studied over various acidic aluminosilicates (HZSM-5, HY-FAU, AlMCM-41), for the first time, In the 373–473 K temperature range, in a pulse reactor, a ring-opening–ring-enlargment reaction producing furan only occured over the zeolites and it was the predominant reaction on AlMCM-41 as well. The driving force of this transformation route is water formation *via* elimination from 2,2′-bioxirane. Suprising is the lack of the mono- or dialdehyde, the would-be products of the cleavage of the sterically more hindered C–O bonds – an acid-catalysed reaction typical for alkyl-substituted oxiranes.

KEY WORDS: 1,2,3,4-diepoxybutane (2,2′-bioxirane); HZSM-5; HY; ALMCM-41; ring enlargement; pulse system.

Introduction

Over the last period of time much has been learnt about the ring transformations of simple alkyl-substituted oxiranes over acidic aluminosilicates [1–5] as well as other solid acids and bases [6]. It became clear that over moderately acidic molecular sieves the main reaction was dimerisation leading to five- or six-membered rings containing two non-adjacent oxygen atoms (dioxolanes and dioxanes) [5]. It has been established that moderately confined environment (medium pore size) is advantageous for this reaction to occur. Over highly acidic catalysts, however, dimerisation was overwhelmed by linear oligomerisation [6]. To further our understanding concerning the behaviour of this important class of molecules – their importance lies in the versatility of ring transformation easily exploited by synthetic organic chemists in building more complicated structures, for a variety of recent papers, see refs. [7–13] – it was decided to study the ring transformation reactions of 1,2,3,4-diepoxybutane (2,2′-bioxirane) – a molecule which has never seen molecular sieves of any kind – over the catalysts of our previous investigations. Result of this work is communicated in this contribution.

Experimental

The catalysts applied were HZSM-5 (Si/Al = 13.8), HY-FAU (Si/Al = 2.31) and AlMCM- 41 (Si/Al = 40.0). The H-zeolites were prepared by wet ion exchange starting from the Na-forms (NaY – Union Carbide, NaZSM-5 – home made following the description in ref. [14]).

Fourfold ion exchange was performed in 1 mol/dm^3 aqueous NH_4NO_3 solution. The duration of one exchange was 12 h and it was carried out at 353 K. The degree of ion exchange after the fourth repetition was nearly 100%. Then, the resulting ammonium forms were deammonised by calcination in vacuum for 6 h at 873 K. The AlMCM-41 derivative was synthesized in our laboratory following recipes published in the literature [15–18]. Sodium silicate and aluminium isopropoxide were the silica and the alumina sources, respectively. Hexadecyltrimethylammonium bromide was used as the surfactant. NaOH and sulfuric acid solutions were applied for adjusting the pH. The resulting gels were crystallised for 6 days under autogenous conditions at 373 K. Then, they were filtered and washed by distilled water, dried at 373 K and, finally, calcined at 773 K for 10 h to bum the template off.

The catalysts were characterized by powder X-ray diffractometry, BET surface area measurements, pyridine adsorption followed by FT-IR spectroscopy (Table 1).

X-ray diffractograms were registered on well-powdered samples with a DRON 3 diffractometer in order to check crystallinity and to determine the pore diameter for the AlMCM-41 sample. BET measurements were performed in a conventional volumetric adsorption apparatus cooled to the temperature of liquid nitrogen (77.4 K). Prior to measurements the samples were pretreated in vacuum at 573 K for 1 h.

The acid-base properties were studied by pyridine adsorption followed by IR spectroscopy (Mattson Gen-

---

* To whom correspondence should be addressed.

Table 1
Characterising data of the molecular sieves

Mol. sieves	Pore diameter^{a} (nm)	BET surface areas (m^{2} g^{-1})^{a}	Brønsted/Lewis sites^{b}
HZSM-5	0.53×0.56; 0.51×0.55^{c}	336	0.88
HY-FAU	0.74^{c}	604	8.67
A1MCM-41	4.059^{d}	932	0.62

[a] Calcined samples (for conditions, see text).
[b] calculated on the basis of IR spectra of adsorbed pyridine.
[c] from ref. [19].
[d] caculated from the position of the 001 reflection.

esis I FT-IR spectrometer, 128 scans for one spectrum, WIN-IR software package). Self-supported wafers (10 mg/cm^2 thickness) were pressed from the aluminosilicate samples. They were pretreated in the optical cell at 573 K for 1 h in vacuum. About 1.33 kPa of pyridine was introduced into the cell at ambient temperature, which was then heated to 473 K. After 1-h equilibration the cell was evacuated for 1 h at the same temperature. Then, the sample was cooled to ambient and the spectrum was recorded. Bands at 1540 cm^{-1} and 1450 cm^{-1} were used for calculating Brønsted and Lewis acidities, respectively.

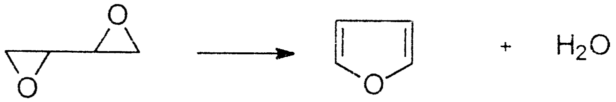
1,2,3,4-Diepoxybutane (2,2′-bioxirane **1**, for the structure, see Scheme 1) was commercially (Fluka) available and was used as received. Its reactions were studied in a pulse microreactor in the 373–473 K temperature range applying H_2 as carrier gas (45 cm^3/min gas flow) with the following pulse sequence (pulse size: 1 μl, amount of catalyst: 10 mg): three subsequent pulses at 393 K, followed by a pulse at 423 K, then a pulse at 473 K. Half an hour was allowed to elapse between the pulses. Blank experiments (experiments without catalysts) have been performed at the temperatures applied in catalytic experiments and no transformations of 2,2′-bioxirane have been found.

Analysis of the product mixture was done by a GC-MS system (Hewlett Packard 5890 gas chromatograph equipped with a HP 5970 quadrupole mass selective detector). Good separation was achieved on a 50-m long CPWAX 52CB coated CHROMPACK WCOT fused silica capillary column by applying a temperature program (303 K for 15 min, 323 K for 20 min and 473 K for 10 min). Now, the separation of the stereoisomer products were successful. Product identification was based on the NBS/NIH/EPA/MSDC database and clean samples.

Thermodynamic (standard) heats of formation for the reactant as well as the products were calculated after unrestricted geometry optimisation of the molecules to gradient 0.01 with the PM3 semiempirical code [20] included in the HyperChem package [21].

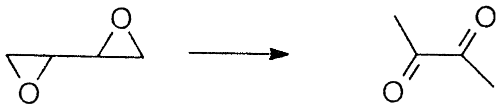
3. Results and discussion

The 2,2′-bioxirane molecule underwent ring enlargement resulting in furan (**2**) and water (**3**):



1 2 3

This was the only reaction over HZSM-5 and HY-FAU and the main transformation on AIMCM-41. Over AlMCM-41 the opening of both epoxide rings could also be observed as a minor transformation pathway. The resulting isomer was butane-2,4-dione (**4**). The reaction is as follows:



1 4

Table 2
Composition of the reaction mixture (mol%) after pulses at various temperatures (10 mg of catalyst, 40 cm^3/min H_2 flow rate, 1μl pulse size)

T/K	HZSM-5			HY-FAU			AIMCM-41			
	1	2	3	1	2	3	1	2	3	4
393	32.7	35.1	33.2	0	51.3	47.3	0	48.3	47.7	4.0
393	91.4	3.7	4.9	0	48.0	52.0	11.8	41.8	43.3	3.1
393	93.4	3.6	3.0	44.5	27.4	28.1	69.5	15.6	13.7	1.2
423	95.6	2.6	2.0	98.2	1.1	0.7	89.3	5.0	5.4	0.3
473	90.1	5.1	4.8	90.4	4.6	5.0	74.2	11.4	13.5	0.9

It is intriguing that there are no other transformation pathways under the conditions applied. Neither deoxygenation nor ring opening *via* the scission of the sterically more hindered C–O bond occurred. The latter means the lack of an ionic ring-opening mechanism. This is surprising, since these reactions readily take place with the alkyl-substituted monooxiranes over these acidic aluminosilicates [1,5].

The ring transformation proceeds with high conversion at temperature as low as 393 K over the freshly calcined catalyst. However, rapid deactivation takes place even on the subsequent pulse. Quite probably, the furan molecule undergoes polymerisation and the resulting polymer remains attached to the aluminosilicates rapidly covering the active sites. Even raising the reaction temperature to 423 K did not help – further deactivation could be observed. Only at 473 K there was some reactivation but merely relative to the conversion at 423 K. Data collected are displayed in Table 2.

Ring enlargement of 2,2′-bioxirane is complex involving the rupture of both C–O bonds followed by the elimination of a water molecule, then ring closure. All these steps are catalysed by either Brønsted or Lewis acid sites.

The first step is the attachment of one of the ring oxygens onto an acid site. Water elimination is not followed by desorption but an attack of the nucleophilic oxygen after the opening of the other epoxide ring onto the triple bond inducing a shift in one of the π electron pairs. The five-membered ring thus formed undergoes electron rearrangements, which is driven by the possibility of aromatic ring formation. Water elimination-formation is the most important step, it is the real driving force of the reaction according to calculated thermodynamic data ($\Delta H_{22'-\mathrm{bioxirane}} = -13.38$ kcal/mol, $\Delta H_{\mathrm{furan}} = -4.16$ kcal/mol, $\Delta H_{\mathrm{water}} = -53.46$ kcal/mol, $\Delta H_{\mathrm{reaction}} = -44.2$ kcal/mol).

Conclusions

2,2′-Bioxirane, a molecule new in catalytic investigations, underwent an unexpected ring opening-ring enlargement reaction over acidic molecular sieves. Surprisingly, the acid-catalysed ring opening *via* the rupture of the sterically more hindered C-O bond in one or both epoxide rings, typical for alkyl-substituted epoxides, did not occur.

Acknowledgments

This work was supported by the National Science Fund of Hungary through grant OTKA T034184. The financial help is highly appreciated.

References

[1] A. Fási, I. Pálinkó and I. Kiricsi, J. Catal. 188 (1999) 385.
[2] A. Fási, I. Pálinkó and I. Kiricsi, Stud. Surf. Sci. Catal. 130 (2000) 839.
[3] A. Fási, I. Pálinkó, Á. Gömöry and I. Kiricsi, Stud. Surf, Sci. Catal. 135 (2001) 233CD -ROM edition 23P15.
[4] A. Fási, I. Pálinkó and I. Kiricsi, React. Kinet. Catal. Lett. 74 (2001) 187.
[5] A. Fási, Á. Gömöry, I. Pálinkó and I. Kiricsi, J. Catal. 200 (2001) 340.
[6] A. Fási, I. Pálinkó, Á. Gömöry and I. Kiricsi, J. Mol. Catal., A 208 (2004) 307.
[7] M. Blagoev, A. Linden and H. Heimgartner, Helv. Chim. Acta 83 (2000) 3163.
[8] A.B. Smith III, S.M. Pitram, A.M. Boldi, M.J. Gaunt, C. Sfouggatakis and W.H. Moser, J. Am. Chem. Soc. 125 (2003) 14435.
[9] J.R. Vyvyan, J.A. Meyer and K.D. Meyer, J. Org. Chem. 68 (2003) 9144.
[10] K. Suda, T. Kikkawa, S. Nakajima and T. Takanami, J. Am Chem. Soc. 126 (2004) 9554.
[11] F. Badalassi, G. Klein, P. Crotti and J.-L. Reymond, Eur. J. Org. Chem. (2004) 2557.
[12] P. Naknayakkara and H. Alper, J. Org. Chem. 69 (2004) 4686.
[13] N. Kato, D. Tomita, K. Maki, M. Kanai and M. Shibasaki, J. Org. Chem. 69 (2004) 6128.
[14] Lechert H., Kleinwort R. in: *Verified Syntheses of Zeolitic Materials*, 2nd revised edition ed. H. Robson, (Elsevier, 2001) p.198..
[15] J.M. Kim, J.H. Kwak, S. Jun and R. Ryoo, J. Phys. Chem. 99 (1995) 16742.
[16] J.S. Beck, J.C. Vartuli, G.J. Kennedy, C.T. Kresge, W.J. Roth and S.E. Schramm, Chem. Mater. 6 (1994) 1816.
[17] R. Schmidt, D. Akporiaye, M. Stöcker, O.H. Ellestad, J. Chem. Soc., Chem. Commun. (1994) 1493.
[18] K.M. Reddy and C. Song, Catal. Lett. 36 (1995) 103.
[19] X. Zhao, G.Q. Lu and J. Millar, Ind. Eng. Chem. Res. 35 (1996) 2075.
[20] J.J.P. Stewart, J. Comput. Chem. 10 (1989) 209, 221.
[21] HyperChem 7.0, Hypercube, Inc., 2001, Gainesville, FL, USA.