

The ring opening and oligomerisation reactions of an epoxide and an episulfide on aluminosilicates in the liquid phase

András Fási¹, István Pálinkó^{2*}, Ágnes Gömöry³, Imre Kiricsi¹

¹ *Department of Applied and Environmental Chemistry,
University of Szeged,
Rerrich B. tér 1, Szeged, H-6720 Hungary*

² *Department of Organic Chemistry,
University of Szeged,
Dóm tér 8, Szeged, H-6720 Hungary*

³ *Chemical Research Center,
Hungarian Academy of Sciences,
POBox 19, Budapest, H-1525 Hungary*

Received 4 November 2004; accepted 11 January 2005

Abstract: The ring opening reactions of propylene oxide (methyloxirane) or ethylene sulfide (thiirane) were studied in the liquid phase over HZSM-5, HY-FAU or AlMCM-41 at 363 K or 423 K and under 1 or 20 bar pressure in a batch reactor. The proportion of these routes were identified: (i) single C-O scission providing non-cyclic products, (ii) double C-O cleavage leading to the loss of the heteroatom, (iii) oligomerisation resulting in cyclic dimers and the trimer of thiirane and a non-cyclic dimer of methyloxirane. The reaction pathway depended on the conditions and the solid acids used. Findings are compared to those in the gas phase over the same solid acids. Transformation mechanisms are also suggested.

© Central European Science Journals. All rights reserved.

Keywords: Propylene oxide (methyloxirane), ethylene sulfide (thiirane), HZSM-5, HY-FAU, AlMCM-41, liquid phase, transformation channels, comparison to the gas-phase reactions

1 Introduction

Epoxides and episulfides are extremely useful building blocks in the synthesis of various complex organic molecules and macromolecules [1, 2]. Their versatility lies in the fact

* E-mail: palinko@chem.u-szeged.hu

that they can be easily prepared [3, 4], they are stable under normal circumstances (room temperature, atmospheric pressure) yet the rings are reactive enough: they can be opened by acids [5] or bases [6] in catalytic reactions and by electrophiles (very rare) [7] or nucleophiles (significantly more abundant) [8] in stoichiometric transformations. The epoxide ring can be opened in the solid state and for this purpose various oxides [9], molecular sieves [10], clays [11], acidic membranes [11, 12] and even metals in the homogeneous [13] or the heterogeneous phase (supported transition metals) [14] may be used. Although the ring transformation reactions of episulfides has been less studied, examples exist of electrophilic [15], nucleophilic [16] as well as molecular sieves catalysed [17] ring opening. However, this reaction does not take place in presence of transition metals due to the strong poisoning effect of sulfur. Part of the versatility is attributed to the ability of these compounds to transform in various ways especially if the rings are substituted. Of course, it is advantageous only if the reactions can be driven onto the required pathways but to achieve this, gathering information about the possible transformation routes under various conditions is of utmost importance. We have learnt much about the gas-phase reactions of these molecules over aluminosilicates of various types [17-19]. To be able to at least partially replace stoichiometric reactions by environmentally more benign heterogeneous catalytic processes in epoxide or episulfide related syntheses, we decided to extend our knowledge of the ring opening reactions of methyloxirane and thiirane over acidic aluminosilicates to the liquid phase at atmospheric pressure or above. These conditions are now close to those applied by synthetic organic chemists.

Results of this work, together with mechanistic considerations and a comparison with those obtained in gas-phase reactions are communicated here.

2 Experimental

2.1 Materials

The catalysts applied were HZSM-5 (Si/Al = 13.8), HY-FAU (Si/Al = 2.31) and AIMCM-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. [20]). Fourfold ion exchange was performed in 1 mol/dm³ aqueous NH₄NO₃ solution. The duration of one exchange was 12 hours 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 AIMCM-41 derivative was synthesized in our laboratory following recipes published in the literature [21-24]. 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 used for adjusting the pH. The resulting gels were crystallised for 6 days under autogenous conditions at 373 K, filtered and washed with distilled water, dried at 373 K and, finally, calcined at 773 K for 10 h

to burn the template off.

Propylene oxide [methyloxirane – racemate was purchased], **1**, (for the structure, see Scheme 1) and ethylene episulfide, **10**, (for the structure, see Scheme 2) are commercially (Fluka) available compounds and were used as received. Hydrogen (with purity of 99.99+ %) was used for pressurising the reactor.

2.2 Characterization

The catalysts were characterised by powder X-ray diffractometry, BET surface area measurements and pyridine adsorption followed by FT-IR spectroscopy

Mol. sieves	pore diameter ^a (nm)	BET surface areas (m ² g ⁻¹) ^a	Brønsted/Lewis sites ^b
HZSM-5	0.53x0.56; 0.51x0.55 ^c	336 ± 10	0.88
HY-FAU	0.74 ^c	604 ± 15	8.67
AIMCM-41	3.08 ^d	932 ± 21	0.62

^a - calcined samples (for conditions, see text);

^b - calculated on the basis of IR spectra of adsorbed pyridine;

^c - from ref. [25];

^d - calculated from the position of the 001 reflection corrected with the wall thickness (2.00 nm).

Table 1 Characterizing data of the molecular sieves.

X-ray diffractograms were acquired on well-powdered samples with a DRON 3 diffractometer to check for crystallinity and to determine the pore diameter of the AIMCM-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 Genesis I FT-IR spectrometer, 128 scans for one spectrum, WIN-IR software package). Self-supported wafers (10 mg/cm² thickness) were pressed from the aluminosilicate samples. They were pretreated in the optical cell at 573 K for 1 h in vacuum. 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. The sample was then cooled to ambient temperature and the spectrum recorded. Bands at 1540 cm⁻¹ and 1450 cm⁻¹ were used for calculating Brønsted and Lewis acidities, respectively.

2.3 The reaction and the analytical method

The reactions of methyloxirane (**1**) and thiirane (**10**) were studied in a magnetically stirred autoclave (with volume of 30 cm³) under 1 bar or 20 bar pressure over HZSM-5 and 1 bar over the other molecular sieves. The reaction temperature was 363 K or 423 K for compound **1** and 423 K for compound **2**. The reacting mixture contained 100 mg of the catalyst, 2 cm³ of the cyclic compound, 2 cm³ of CH₂Cl₂ and was pressurised to 1

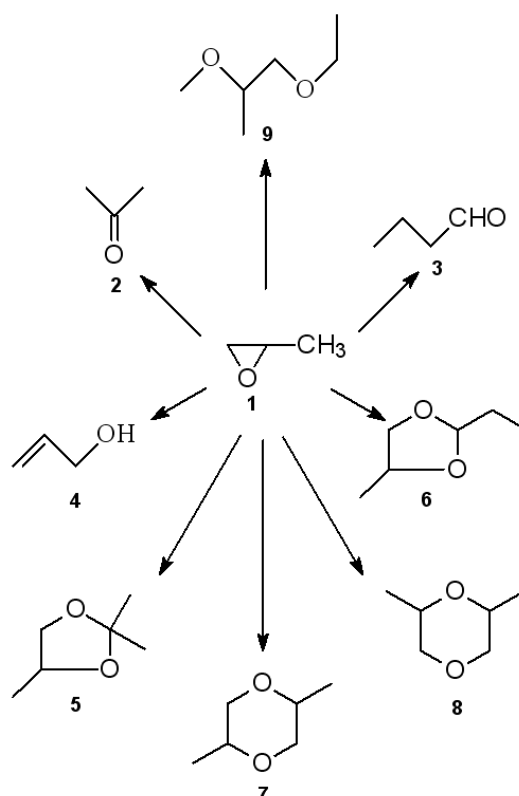
bar or 20 bar with hydrogen. After 3 or 9 hours the reactor was cooled in liquid nitrogen, depressurised and was allowed to warm up gradually to facilitate the analysis of ethylene, the other low- and higher-boiling products and, the reactants. Prior to characterisation and catalytic use the molecular sieves were calcined at 573 K for 2 hours under vacuum and hydrogen, respectively.

A GC-MS system of Hewlett Packard 5890 gas chromatograph equipped with a HP 5970 quadrupole mass selective detector was used for analysis of the product mixture. A good separation of stereoisomeric products was achieved on a 50-m long CPWAX 52CB coated CHROMPACK WCOT fused silica capillary column. The temperature program used was 303 K for 15 min, 323 K for 20 min and 473 K for 10 min. Product identification was based on the NBS/NIH/EPA/MSDC database and standard compounds.

3 Results and discussion

3.1 The reactions of propylene oxide

Propylene oxide (methyloxirane) underwent various reactions on the molecular sieves (Scheme 1).



Scheme 1 Transformation routes of methyloxirane (propylene oxide) (1) over various aluminosilicates in the liquid phase.

Product distributions at the two temperatures and pressures are summarised in Table 2.

		Composition of the reacting mixture/mol%											
	time/h	1	2	3	4	5	6 <i>cis</i>	6 <i>trans</i>	7 <i>cis</i>	7 <i>trans</i>	8 <i>cis</i>	8 <i>trans</i>	9
		HZSM-5											
1 bar, 363 K	3	98.0	0.1	0.3	0	0	0.3	0.4	0.2	0.3	0.1	0.3	0
	9	97.1	0.2	0.3	0.1	0	0.3	0.4	0.3	0.6	0.2	0.5	0
1 bar, 423 K	3	93.4	0.1	1.1	0.1	0.1	1.0	1.1	0.5	1.1	0.5	0.9	0.1
	9	89.9	0.3	3.8	0.2	0.1	1.0	1.2	0.6	1.1	0.5	1.1	0.2
20 bar, 363 K	3	95.4	0.1	2.3	0	0	0.4	0.8	0.2	0.4	0.1	0.2	0
	9	93.3	0.2	3.2	0	0	0.5	1.1	0.3	0.7	0.2	0.5	0
20 bar, 423 K	3	75.6	0.7	9.1	0.2	0.1	3.0	5.6	0.9	2.2	0.7	1.8	0.1
	9	71.3	1.0	12.6	0.3	0.2	3.2	5.7	1.0	2.2	0.7	1.8	0.2
		HY-FAU											
1 bar, 363 K	3	89.8	0.4	4.9	0.1	0.1	0.6	1.5	0.5	1.1	0.3	0.5	0.2
	9	77.8	1.7	11.1	0.3	0.2	1.0	2.0	1.1	2.1	0.9	1.1	0.7
1 bar, 423 K	3	71.1	2.2	8.4	0.8	0.4	2.2	3.5	2.1	4.3	1.7	2.2	1.1
	9	49.9	3.0	18.5	0.9	0.5	3.2	5.3	4.0	7.2	2.5	3.4	1.6
		AIMCM-41											
1 bar, 363 K	3	66.6	1.4	9.3	0.1	0.7	2.6	6.5	2.9	4.1	2.5	2.9	0.4
	9	28.6	2.8	20.9	0.2	2.3	8.5	17.4	3.7	6.6	4.0	4.4	0.6
1 bar, 423 K	3	8.9	6.0	45.9	0.4	1.2	6.9	13.8	2.4	4.6	2.8	3.9	3.2

Table 2 Composition of the reacting mixture in an autoclave (30 cm³) in the transformations of methyloxirane (**1**) at 363 K (first entry at each pressure) or 423 K (second entry at each pressure) over various molecular sieves (catalyst 100 mg, starting mixture: 2 cm³ of **1** and 2 cm³ of CH₂Cl₂).

Single C-O scission gave acetone (**2**), propionaldehyde (**3**) and allylic alcohol (**4**). Products **3** and **4** from the cleavage of the sterically more hindered C-O bond were always predominant over acetone, which was produced *via* the scission of the less hindered C-O bond. Dimerisation leading to the production of dioxolane (**5**, **6**) and dioxane (**7**, **8**) derivatives also occurred. The proportion of this transformation channel was always comparable to that of single C-O cleavage and occasionally even exceeded it. Another type of dimerisation providing acyclic diether **9** was also observed. This reaction did not take place in the gas phase [18, 19]. However, deoxygenation found in the gas phase did not occur in the liquid phase under the reaction conditions applied. It is worth mentioning that in accordance with their higher thermodynamic stabilities, among the geometric isomers, the *trans* compounds were always formed in higher quantities than the corresponding *cis* isomers. It is also to be noted that increasing the pressure accelerated the overall transformation of methyloxirane, probably by increasing the availability of methyloxirane molecules for transformations.

To summarise, there were three transformation routes: single C-O cleavage, cyclic dimerisation (with two subclasses, C₅ and C₆ routes) and acyclic dimerisation. Their proportions, listed in Table 3, varied with varying catalysts and experimental conditions.

	Selectivity of the transformation pathways/%				
	time/h	single C-O scission	C ₅ route	C ₆ route	acyclic dimer.
HZSM-5					
1 bar, 363 K	3	20	35	45	0
	9	21	24	55	0
1 bar, 423 K	3	20	33	45	2
	9	43	22	33	2
20 bar, 363 K	3	52	26	22	0
	9	51	24	25	0
20 bar, 423 K	3	41	35.5	23	0.5
	9	48	31	20	1
HY-FAU					
1 bar, 363 K	3	53	21	24	2
	9	59	15	23	3
1 bar, 423 K	3	39	21	36	4
	9	45	18	34	3
AIMCM-41					
1 bar, 363 K	3	32	30	37	1
	9	33	40	26	1
1 bar, 423 K	3	57	24	15	4

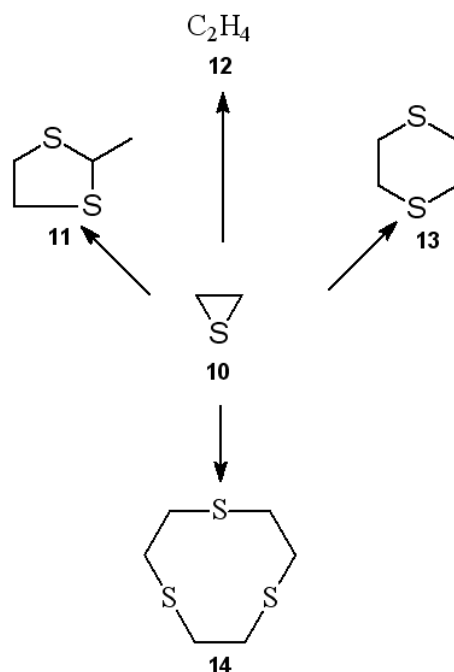
Table 3 Proportions of the reaction channels in the transformations of methyloxirane (**1**) over various molecular sieves (catalyst 100 mg, starting mixture: 2 cm³ of **1** and 2 cm³ of CH₂Cl₂).

As was indicated above single C-O cleavage and cyclic dimerisation are the main

transformation routes. Acyclic dimerisation if it occurred, remained a minor reaction pathway. The two main reaction channels are comparable in most cases. However, over HZSM-5 at lower temperature or at smaller contact time at higher temperature, cyclic dimerisation was favoured. Between the two cyclic dimerisation reaction pathways, in the majority of cases the C₆ route was found to be more significant. The C₅ route seems to be more important on HZSM-5 at the higher temperature and pressure and also over AlMCM-41 at the higher temperature.

3.2 The reactions of ethylene sulfide

Ethylene oxide (thiirane) underwent desulfurisation, cyclic dimerisation and cyclic trimerisation reactions (Scheme 2).



Scheme 2 Transformation routes of thiirane (ethylene sulfide) (**10**) over various aluminosilicates in the liquid phase.

The product distribution is displayed in Table 4.

Though dimerisation forming 1,4-dithiane, **13** was always the main transformation route, desulfurisation, giving ethylene **12** with the sulfur retained by the molecular sieves occurred on every catalyst. A dimer, 2-methyl-1,3-dithiolane, **11**, and a cyclic trimer **14** were also formed. However, on the HZSM-5 catalyst, the former could not be detected while the latter was always found at the higher pressure (except after 3 hours contact time). In contrast to the oxygen-containing ring, isomerisation products from single C-S cleavage were not observed here. The proportions of the main transformation channels double C-S scission leading to desulfurisation and cyclic dimerisation via C₅ and C₆ routes are listed in Table 5.

The predominance of the C₆ dimerisation route is emphasised by the data obtained

	Composition of the reacting mixture/mol%					
	time/h	10	11	12	13	14
	HZSM-5					
1 bar, 423 K	3	5.4	0	3.7	74.1	16.8
20 bar, 423 K	3	99.3	0	0.1	0.6	0
	9	81.0	0	0.3	17.4	1.3
	HY-FAU					
1 bar, 423 K	3	4.6	1.3	3.3	86.8	4.0
	AlMCM-41					
1 bar, 423 K	3	2.5	2.3	3.6	89.8	1.8

Table 4 Composition of the reacting mixture in an autoclave (30 cm³) in the transformations of thiirane (**10**) at 423 K over various molecular sieves (catalyst 100 mg, starting mixture: 2 cm³ of **10** and 2 cm³ of CH₂Cl₂).

	Selectivity of the transformation pathways/%				
	time/h	desulfuri- sation	C ₅ route	C ₆ route	cyclic trimerisation
	HZSM-5				
1 bar, 423 K	3	4	0	78	18
20 bar, 423 K	3	14	0	86	0
	9	2	0	91	7
	HY-FAU				
1 bar, 423 K	3	3	1	82	4
	AlMCM-41				
1 bar, 423 K	3	4	2	82	2

Table 5 Proportions of the reaction channels in the transformations of thiirane (**10**) at 423 K over various molecular sieves (catalyst 100 mg, starting mixture: 2 cm³ of **10** and 2 cm³ of CH₂Cl₂).

and are detailed below. 1,4-dithiane was always the overwhelming product and reaction products from other pathways seem to be insignificant in nearly all cases. The exception is HZSM-5. The formation of the cyclic trimer (either at the first sampling in the 1-bar reaction or the second in the pressurised one) is significant on this zeolite, just as desulfurisation in the pressurised reaction at the first sampling. It is to be noted here that, unexpectedly, thiirane reacted slower at the pressure of 20 bar than at 1 bar. This behaviour was different from the one experienced with the oxygen-containing analogue. Perhaps for thiirane oligomerisation occurs over the catalytic surface more extensively than for methyloxirane, and due to the relatively high pressure these oligomers do not desorb and thus block a large part of the potentially active surface.

3.3 Comparing the characteristics of liquid-phase reaction to those of the gas-phase

First, let us take a look at the available reaction channels. As has already been mentioned for methyloxirane, double C-O scission (deoxygenation) did not occur in the liquid phase over any of the catalysts, while this was an important pathway for HY-FAU in the gas phase [19]. Acyclic dimerisation was observed in the liquid phase, while only cyclic dimerisation took place in the gas phase. Single C-O scission did occur in both the liquid and the gas phase, but allylic alcohol was only formed in the liquid phase. Among the cyclic dimers 2,2-dimethyl-1,4-dioxane was an important product over HZSM-5 and HY-FAU in the gas phase [19] although it was not found over AlMCM-41 and it was not formed at all in the liquid phase over any of the catalysts. For thiirane the same reaction channels were detected in both the gas phase and the liquid phase, except for the fact that sulfur which was fully retained by the catalysts in the liquid phase was partially released in the gas-phase reaction in the form of H₂S [17].

As far as selectivity was concerned the major reaction pathway was dimerisation *via* the C₅ route on any of the catalysts in the gas phase with exceptionally high selectivity over the HZSM-5 zeolite. In the liquid phase single C-O ring opening was of comparable or, occasionally, even of higher importance than the cyclic dimerisation pathway. Moreover, among the cyclic dimers, the C₆ products predominated most often. For thiirane the C₆ dimerisation route predominated in both the gas phase and the liquid phase, i.e. thiirane transformed to 1,4-dithiane very selectively. Selectivity was exceptionally high over HY-FAU in the gas phase and equally high over each catalyst in the liquid phase. Since from dithianes advanced fragments for complex molecule synthesis may be prepared through Linchpin coupling [26] this reaction may prove to be very useful. The selectivity was meaningfully decreased by cyclic trimerisation over AlMCM-41 in the gas phase and over HZSM-5 in the liquid phase.

Generally speaking, reactions in the gas phase were always faster than those in the liquid phase. However, since the gas-phase reactions were run in a pulse microreactor [19] or a closed circulation system [18], a scale-up to obtain synthetically useful amounts of products could be problematic which is not the case for the liquid-phase transformations. In addition, these types of reactions will be more convenient for a synthetic organic chemist to handle. Considering the two factors mentioned above, the reactions in the liquid phase may be of more value for practical purposes.

Hydrogen gas was used in the case of both compounds in the gas-phase and the liquid-phase reactions. Its intended role in the gas-phase reactions was to slow down deactivation. However, it was found to be inert like nitrogen [19] and did not take part in the reaction either as a reactant (since no hydrogenation occurred) or as an agent decelerating deactivation. In the liquid-phase with hydrogen as the gas, hydrogenated products were not found, thus hydrogen was not a reactant here either implying that its ionic dissociation did not take place.

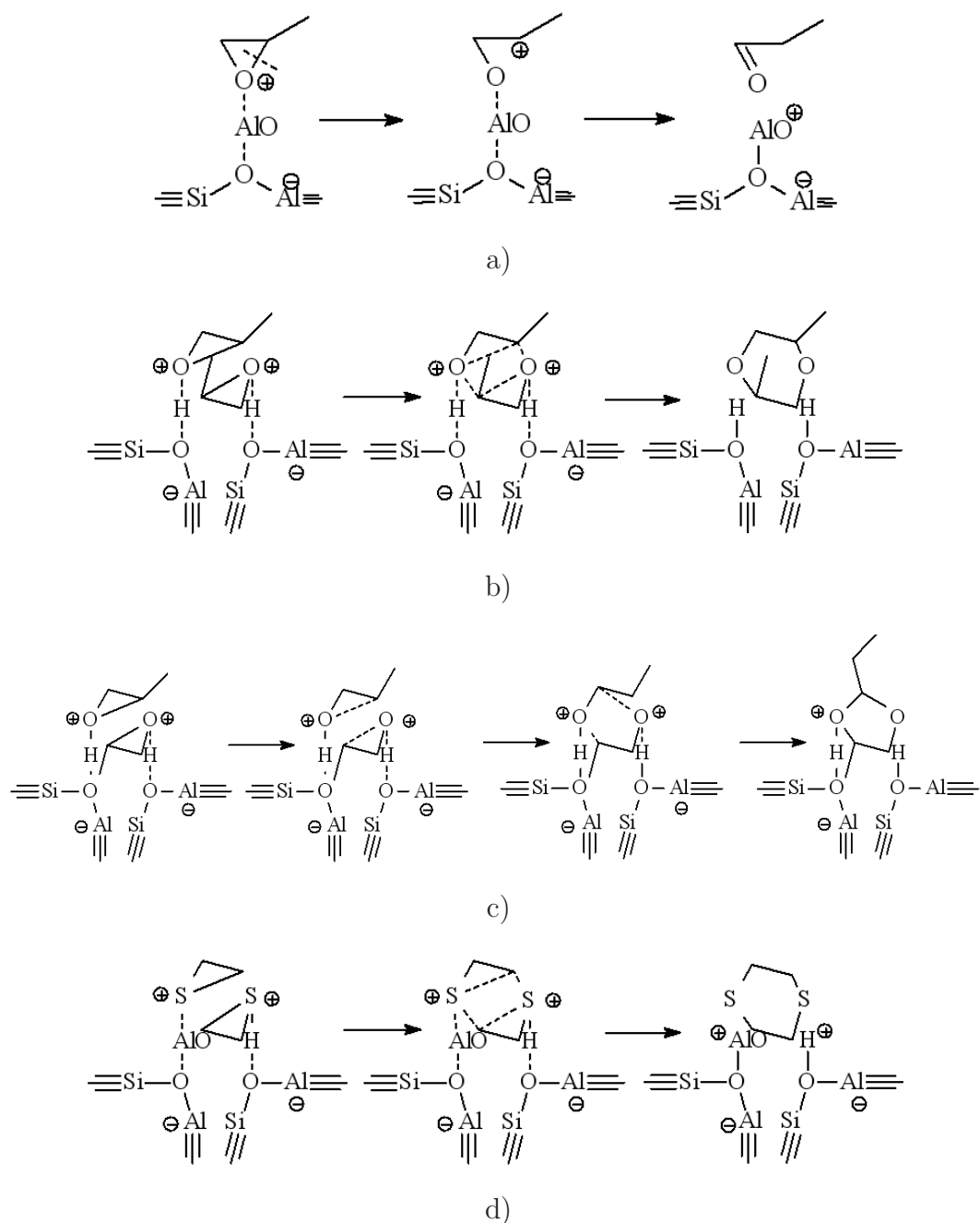
3.4 Possible transformation mechanisms

It is known from any fundamental organic chemistry course that in general, the reactions of substituted epoxide in the homogeneous phase gives a mixture of products even on simple ring opening (i.e. a single C-O scission and no further reaction of the ring-opened products) when the reaction is initiated by an acid and a single product when the attacking agent is a base [27]. The former is a mixture of S_N1 and S_N2 reactions, while the latter is a typical S_N2 transformation. The S_N1 reaction proceeds *via* a "free" carbenium ion, while the S_N2 does not have "free" carbenium ion intermediate but a pentacovalent transition state although being ionic in character. In the presence of solid acid or base ring opening analogous to the S_N1 reaction gives an aldehyde and that analogous to S_N2 results in a ketone. It is also well known that epoxide easily undergoes polymerisation providing polyethers of various lengths. It is a recent discovery that when propylene oxide is the reactant, dimerisation occurs on acidic zeolites/zeotypes producing dioxane and dioxolane derivatives [18, 19]. It has been established for this molecule as well as for thiirane (where cyclic oligomerisation was always predominant over the molecular sieves [17]) that for cyclic dimerisation or trimerisation reaction to occur a constrained environment is advantageous.

The molecular sieves used in this study are acidic with the ratio of Brønsted to Lewis acid sites close to one for HZSM-5, a higher proportion of Lewis sites for the AIMCM-41 and overwhelmingly Brønsted acid sites for the HY-FAU zeolite. The Lewis sites are most probably extra framework alumina, their presence was qualitatively indicated by ^{27}Al MAS NMR results obtained for the HY-FAU zeolite earlier [28]. Of course, basic sites are also available, the skeletal oxygens, due to their lone electron pairs, are basic. Since all the important transformation pathways were present on all the catalysts of this study, it is clear that the observed reactions are catalysed either by the Brønsted or the Lewis sites or their combinations. Examples representing the major reaction routes are shown in Schemes 3 (a)-(d).

The schemes do contain speculative elements, since the actual structures of the surface intermediates could not be determined under reaction conditions. However, some key elements are supported by experimental observations and common knowledge. It is widely accepted that over acidic materials the adsorption starts with the ring oxygen (or sulfur). It was found experimentally [29] that in the gas phase d_2 -dimerised products were found to be abundant over DZSM-5 and DAIMCM-41. It is also to be mentioned that deuterium-free dimers were formed as well indicating that Lewis site pairs can also be reaction centres.

One may argue for an Eley-Rideal-like mechanism for the dimerisation reactions where the second epoxide or thiirane reacts upon the arrival from the gas phase with the already adsorbed and somewhat transformed epoxide molecule. In our view this mechanism should not be predominant since we see no driving force for the ring distortion of the second incoming molecule that is necessary for the reaction to occur in the dimerisation of methyloxirane. In the liquid phase, especially under pressure when the number of molecules



Scheme 3 The suggested mechanisms for the typical transformation pathways: (a) single C-O scission of methyloxirane over Lewis acid sites; (b) the C₆ route of dimerisation for methyloxirane over Brønsted acid sites; (c) the C₅ route of dimerisation for methyloxirane over Brønsted acid sites; (d) the C₆ route of dimerisation for thiiirane over the combination of Lewis and Brønsted acid sites.

in the close proximity of the catalysts is increased relative to the gas-phase reaction, there is even less chance for the dimerisation proceeding through an Eley-Rideal mechanism. Therefore, dimerisation is thought to take place *via* a Langmuir-Hinshelwood-like mechanism mainly over Brønsted-Brønsted and Lewis-Lewis acid site pairs or their combinations over the HY-FAU and the other aluminosilicates.

4 Conclusions

In the liquid phase the transformation pathways of methyloxirane over various acidic aluminosilicates differed from those in the gas phase by the appearance of acyclic dimerisation and the disappearance of double C-O scission. Single C-O cleavage and cyclic dimerisation remained the two most important pathways, but the relative importance of the C₆ route of cyclisation increased, with no exceptional selectivity with respect to pore size. Thiirane transformed almost exclusively *via* the C₆ route providing a synthetically promising way for the preparation of dithiane.

The reactions proceed on either Brønsted and Lewis acid sites or in their combinations.

Acknowledgment

The financial support from the National Science Fund of Hungary (Grant OTKA T034184) is highly appreciated.

References

- [1] Some of the very recent references: J.-A. Ma and D. Cahard: "Towards perfect catalytic asymmetric synthesis: Dual activation of the electrophile and the nucleophile", *Angew. Chem. Int. Ed.*, Vol. 43, (2004), pp. 4566–4583;
N. Kato, D. Tomita, K. Maki, M. Kanai and M. Shibasaki: "Practical synthesis of chiral ligands for catalytic enantioselective cyanosylation of ketones and ketoimines", *J. Org. Chem.*, Vol. 69, (2004), pp. 6128–6130.
- [2] M.G. Silvestri and C.-H. Wong: "Opening of thiiranes: Preparation of orthogonal protected 2-thioglyceraldehyde", *J. Org. Chem.*, Vol. 66, (2001), pp. 910–914;
R.D. Adams, K.M. Brosius and O. Sung-Kwon: "The catalytic synthesis of thiacrowns from thiiranes by Group VI and VII transition metal carbonyl complexes", *J. Organomet. Chem.*, Vol. 652, (2002), pp. 51–59.
- [3] J.C. Zomerdijk and M.W. Hall: "Technology for the manufacture of ethylene oxide", *Catal. Rev. Sci. Eng.*, Vol. 23, (1981), pp. 163–185;
R.A. van Santen and H.P.C.E. Kuipers: "The mechanism of ethylene epoxidation", *Adv. Catal.*, Vol. 35, (1987), pp. 265–321.
- [4] B. Tamami and K.P. Borujeny: "Synthesis of thiiranes from oxiranes using cross-linked polystyrene supported aluminium chloride as a catalyst", *Synth. Commun.*, Vol. 34, (2004), pp. 65–70.
- [5] Some very recent exemplary references: S. Gil, M. Torres, N. Ortúzar, R. Wincewicz and M. Parra: "Efficient addition of acid enediolates to epoxides", *Eur. J. Org. Chem.*, (2004), pp. 2160–2165;
K. Suda, T. Kikkawa, S. Nakajima and T. Takanami: "Highly regio- and stereoselective rearrangement of epoxides to aldehydes catalyzed by high-valent metalloporphyrin complex, Cr(TPP)OTf", *J. Am. Chem. Soc.*, Vol. 126, (2004), pp. 9554–9555;
A.K., Chakraborti, S. Rudrawar and A. Kondaskar: "Lithium bromide, an inexpensive and efficient catalyst for opening of epoxide rings by amines at room

- temperature under solvent-free conditions”, *Eur. J. Org. Chem.*, (2004), pp. 3597–3600;
- P.-Q. Zhao, L.-W. Xu and C.-G. Xia: ”Transition metal-based Lewis acid catalyzed ring opening of epoxides using amines under solvent-free conditions”, *Synlett*, (2004), pp. 846–850.
- [6] R.-H. Fan and X.-L. Hou: ”Efficient ring-opening reaction of epoxides and aziridines promoted by tributylphosphine in water”, *J. Org. Chem.*, Vol. 68, (2003), pp. 726–730;
- V. Polshettiwar and M.P. Kaushik: ”CsF–Celite catalyzed regio- and chemoselective S_N2 type ring opening of epoxides with thiol”, *Catal. Commun.*, Vol. 5, (2004), pp. 515–518;
- H. Shargi, M.M. Eskandari and R. Ghavami: ”A facile conversion of epoxides to halohydrins with elemental halogen using isonicotinic hydrazide (isoniazide) as a new catalyst”, *J. Mol. Catal. A*, Vol. 215, (2004), pp. 55–62.
- [7] G. Islas-Gonzales, C. Puigjaner, A. Vidal-Ferran, A. Moyano, A. Riera and M.A. Pericas: ”Boron trifluoride-induced reactions of phenylglycidyl ethers: a convenient synthesis of enantiopure, stereodefined fluorohydrins”, *Tetrahedron Lett.*, Vol. 45, (2004), pp. 6337–6341.
- [8] F. Badalassi, G. Klein, P. Crotti and J.-L. Reymond: ”Fluorescence assay and screening of epoxide opening by nucleophiles”, *Eur. J. Org. Chem.*, (2004), pp. 2557–2566;
- O. Equey, E. Vrancken and A. Alexakis: ”Regioselective S_N2 opening of vinylic epoxides with trialkylzincates and trialkylaluminates”, *Eur. J. Org. Chem.*, (2004), pp. 2151–2159;
- D.M. Hodgson, C.D. Bray and N.D. Kindon: ”Enamines from terminal epoxides and hindered lithium amides”, *J. Am. Chem. Soc.*, Vol. 126, (2004), pp. 6870–6871.
- [9] Á. Molnár, I. Bucsi and M. Bartók: ”Selective ring-opening of isomeric 2-methyl-3-phenyloxiranes on oxide catalysts”, *Stud. Surf. Sci. Catal.*, Vol. 59, (1991), pp. 549–556;
- Á. Molnár, I. Bucsi, M. Bartók, G. Resofszki and G. Gáti: ”Characterization of acid-base properties of oxides via the selective ring-opening of 2-methyloxirane”, *J. Catal.*, Vol. 129, (1991), pp. 303–306.
- [10] T. Imanaka, Y. Okamoto and S. Teranishi: ”Isomerization of propylene oxide on zeolite catalysts”, *Bull. Chem. Soc., Jpn.*, Vol. 45, (1972), pp. 3251–3254;
- S. Matsumoto, M. Nitta and K. Amoura: ”Catalytic properties of synthetic A-type zeolite. III. Effect of ion exchange on the 1,2-epoxybutane-isomerization activity”, *Bull. Chem. Soc., Jpn.*, Vol. 47, (1974), pp. 1537–1538;
- H. Takeuchi, K. Kitajima, Y. Yamamoto and K. Mizuno: ”The use of proton-exchanged X-type zeolite in catalyzing ring-opening reactions of 2-substituted epoxides with nucleophiles and its effect on regioselectivity”, *J. Chem. Soc., Perkin Trans.*, Vol. 2, (1993), pp. 199–2023;
- M. Onaka, K. Sugita, H. Takeuchi and Y. Izumi: ”Regioselective ring openings of 2,3-epoxy alcohols with ammonium halides and sodium benzenethiolate supported on zeolite CaY”, *J. Chem. Soc., Chem. Commun.*, (1988), pp. 1173–1174;
- W. Hölderich and H. van Bekkum: ”Zeolites in organic synthesis”, *Stud. Surf. Sci. Catal.*, Vol. 58, (1991), pp. 631–727;
- A. Liebens, C. Mahaim and W.F. Hölderich: ”Selective isomerization of α -pinene oxide with heterogeneous catalysts”, *Stud. Surf. Sci. Catal.*, Vol. 108, (1997), pp. 587–594;

- R. Dimitrova, V. Minkov and N. Mincheva: "Zeolite catalyzed ring opening of styrene oxide", *Appl. Catal. A*, Vol. 145, (1996), pp. 49–55;
- H. Ogawa, Y. Miyamoto, T. Fujigaki and T. Chihara: "Ring-opening of 1,2-epoxyalkane with alcohols over H-ZSM-5 in liquid phase", *Catal. Lett.*, Vol. 40, (1996), pp. 253–255;
- M.V.R. Reddy, S.V. Pitre, I. Bhattacharya and Y.D. Vankar: "General synthetic methods. 5. Zeolite (H-ZSM5) catalyzed regioselective isomerization of glycidic esters to α -hydroxy- β,γ -unsaturated esters", *Synlett*, (1996), pp. 241–242;
- R.A. Sheldon, J.A. Elings, S.K. Lee, H.E.B. Lempers and R.S. Downing: "Zeolite-catalyzed rearrangements in organic synthesis", *J. Mol. Catal. A*, Vol. 134, (1998), pp. 129–135;
- C. Meyer, W. Laufer and W.F. Hölderich: "Selective isomerization of isophorone epoxide over zeolites", *Catal. Lett.*, Vol. 53, (1998), pp. 131–134;
- A. Liebens, W. Laufer and W.F. Hölderich: "Ring opening reaction of 4,4,5,8-tetramethyl-1-oxaspiro-[2,5] octane to 2,2,3,6-tetramethyl-cyclohexane-carbaldehyde with heterogeneous catalysts", *Catal. Lett.*, Vol. 60, (1999), pp. 71–75.
- [11] A. Fási, I. Pálincó and I. Kiricsi: "Ring-opening, dimerization and oligomerization reactions of methyloxirane on solid acid and base catalysts", *J. Mol. Catal. A*, Vol. 208, (2004), pp. 307–311.
- [12] G.K.S. Prakash, T. Matthew, S. Krishnaraj, E. Marinez and G.A. Olah: "Nafion-H catalysed isomerization of epoxides to aldehydes and ketones", *Appl. Catal. A*, Vol. 181, (1999), pp. 283–288.
- [13] P. Nanayakkara and H. Alper: "Palladium-catalyzed alkylation of vinyl oxirane with substituted allenes. Direct access to bifunctionalized allylic alcohols", *J. Org. Chem.*, Vol. 69, (2004), pp. 4686–4691;
- K. Nakano, M. Katayama, S. Ishihara, T. Hiyama and K. Nozaki: "An alternative route to protected alcohols: Cobalt-catalyzed hydroformylation of epoxides and in situ protection of β -hydroxyaldehydes by $\text{HC}(\text{OMe})_3$ ", *Synlett*, (2004), pp. 1367–1370.
- [14] I. Pálincó and J. Ocskó: "Hydrogen pressure dependence in the ring opening of methyloxirane over silica-supported Pd and Rh catalysts; Effect of high temperature on ring-opening routes", *J. Mol. Catal. A*, Vol. 104, (1996), pp. 261–265;
- I. Pálincó: "Activity and regioselectivity in the ring-opening reaction of methyloxirane at metal-metal oxide interfaces", *J. Mol. Catal. A*, Vol. 140, (1999), pp. 195–198.
- [15] A. Sadorge, P. Sauvageot, O. Blacque, M.M. Kubicki, C. Moise and J-C. Leblanc: "Desulfurization and ring opening of thiirane induced by tantalocene trihydride complexes: synthesis, reactivity and X-ray structure of $\text{Cp}'_2\text{Ta}(\text{:S})(\text{S-iPr})$ with $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{tBu}$ ", *J. Organomet. Chem.*, Vol. 575, (1999), pp. 278–285.
- [16] A. Kameyama, M. Kiyota and T. Nishikubo: "New ring-opening reaction of thiiranes with carboxylic acid derivatives catalyzed by quaternary onium salts", *Tetrahedron Lett.*, Vol. 35, (1994), pp. 4571–4574.
- [17] A. Fási, Á. Gömöry, I. Pálincó and I. Kiricsi: "Cyclodimerisation and cyclotrimerisation during the ring-opening reactions of ethylene sulfide (thiirane) over acidic molecular sieves and alumina", *Catal. Lett.*, Vol. 76, (2001), pp. 95–98.
- [18] A. Fási, I. Pálincó and I. Kiricsi: "Ring-opening and dimerization reactions of methyl- and dimethyloxiranes on HZSM-5 and CuZSM-5 zeolites", *J. Catal.*, Vol. 188, (1999), pp. 385–392.

- [19] A. Fási, Á. Gömöry, I. Pálinkó and I. Kiricsi: "Isomerization and dimerization reactions of methyloxirane over various types of zeolite", *J. Catal.*, Vol. 200, (2001), pp. 340–344.
- [20] H. Lechert and R. Kleinwort: "High-alumina ZSM-5", In: H. Robson (Ed.): *Verified Syntheses of Zeolitic Materials*, 2nd revised Ed., Elsevier, 2001, p. 198.
- [21] J.M. Kim, J.H. Kwak, S. Jun and R. Ryoo: "Ion exchange and thermal stability of MCM-41", *J. Phys. Chem.*, Vol. 99, (1995), pp. 16742–16747.
- [22] J.S. Beck, J.C. Vartuli, G.J. Kennedy, C.T. Kresge, W.J. Roth and S.E. Schramm: "Molecular or supramolecular templating: defining the role of surfactant chemistry in the formation of microporous and mesoporous molecular sieves", *Chem. Mater.*, Vol. 6, (1994), pp. 1816–1821.
- [23] R. Schmidt, D. Akporiaye, M. Stöcker and O.H. Ellestad: "Synthesis of a mesoporous MCM-41 material with high levels of tetrahedral aluminum", *J. Chem. Soc., Chem. Commun.*, (1994), pp. 1493–1494.
- [24] K.M. Reddy and C. Song: "Synthesis of mesoporous molecular sieves: influence of aluminum source on Al incorporation in MCM-41", *Catal. Lett.*, Vol. 36, (1995), pp. 103–109.
- [25] X. Zhao, G.Q. Lu and J. Millar: "Advances in mesoporous molecular sieve MCM-41", *Ind. Eng. Chem. Res.*, Vol. 35, (1996), pp. 2075–2090.
- [26] A.B. Smith III, S.M. Pitram, A.M. Boldi, M.J. Gaunt, C. Sfougataki and W.H. Moser: "Multicomponent Linchpin couplings. Reaction of dithiane anions with terminal epoxides, epichlorohydrin, and vinyl epoxides: Efficient, rapid, and stereocontrolled assembly of advanced fragments for complex molecule synthesis", *J. Am. Chem. Soc.*, Vol. 125, (2003), pp. 14435–14445.
- [27] J.M. McMurry: *Organic Chemistry*, 5th Ed., Brooks/Cole, 2000, p. 720.
- [28] I. Hannus, Z. Kónya, P. Lentz, J.B. Nagy and I. Kiricsi: "Multinuclear MAS NMR investigation of zeolites reacted with chlorofluorocarbons", *J. Mol. Struct.*, Vol. 482–483, (1999), pp. 359–364.
- [29] A. Fási, I. Pálinkó, Á. Gömöry and I. Kiricsi: "Ring opening reactions of methyloxirane over DZSM-5 and DAlMCM-41 zeolites - A mechanistic study", *Stud. Surf. Sci. Catal.*, Vol. 135, (2001), p. 233; CD-ROM edition 23P15.