

Isomerization and Dimerization Reactions of Methyloxirane over Various Types of Zeolite and Zeotype

András Fási,* Ágnes Gömöry,* István Pálinkó,†¹ and Imre Kiricsi‡

*Chemical Research Center, Hungarian Academy of Sciences, P.O. Box 17, Budapest, H-1525 Hungary; †Department of Organic Chemistry, University of Szeged, Dóm tér 8, Szeged, H-6720 Hungary; and ‡Department of Applied and Environmental Chemistry, University of Szeged, Rerrich B. tér 1, Szeged, H-6720 Hungary

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The ring-opening reactions of methyloxirane on various zeolites and zeotypes (HZSM-5, CuZSM-5, HY, AlMCM-41, SiMCM-41, and BMCM-41) were investigated at 363 K either in a pulse reactor or in a circulation system, in the presence of hydrogen or nitrogen. The acidic molecular sieves were found to be active in isomerization (the products are propionaldehyde and acetone) and dimerization (the products are dioxolane and dioxane derivatives) reactions. Deoxygenation was of minor importance in hydrogen or nitrogen atmosphere. The major product formation pathway was dimerization on every catalytically active material. This transformation route was favored by the confined environment. © 2001

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Key Words: HY; HZSM-5; CuZSM-5; AlMCM-41; SiMCM-41; BMCM-41; propylene oxide; ring-opening reactions; dimerization.

INTRODUCTION

It is widely known that epoxides are important building blocks in the syntheses of complex organic molecules, because their preparation is relatively easy and they offer a variety of ways to carry out further transformations during or following ring opening. The methods of their preparation are well explored both in industrial and laboratory scales (for a recent review, see (1)). The laws which govern acid-catalyzed ring-opening reaction under homogeneous conditions (conducted in solution) are also well known and are even taught in fundamental organic chemistry courses (2). Curiously, significantly less knowledge has been accumulated about the reaction promoted by heterogeneous acidic catalysts. Among the catalysts used there were mainly oxides (Al_2O_3 , $\text{Al}_2\text{O}_3\text{-SiO}_2$, ZnO, WO_3 , ZrO_2 , CaO, BeO, Nb_2O_5 , etc. (3, 4)) or Nafion-H (5). The number of publications in which zeolites were chosen to catalyze the ring-opening reaction is relatively small (6–13). In most cases the reaction was used for synthetic purposes (9–13). Mechanistic types of investigations are described in only

a few works (6, 7). Beside ring opening via the rupture of one C–O bond, rearrangement was also observed (12) but dimerization reactions were not reported until our recent studies concerning the transformations of methyloxirane and *cis*- and *trans*-2,3-dimethyloxiranes over HZSM-5 and CuZSM-5 zeolites (14, 15). We have found that the isomerization method of ring opening was always accompanied by dimerization, providing dioxane and dioxolane derivatives. Generally, this latter pathway proved to be more important than isomerization through a simple cleavage of one C–O bond. Since, to our knowledge, dimer formation was not reported earlier over “flat” acidic contacts, we assumed that a constrained environment was necessary for dimerization to occur. In order to place this assumption under scrutiny, the scope of acidic catalysts was widened in such a way that the pore size was altered significantly. The results of this investigation are summarized in this contribution.

EXPERIMENTAL

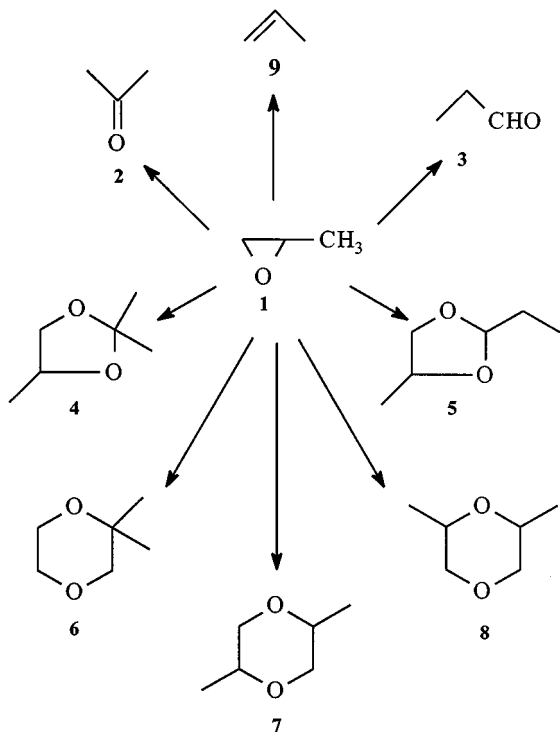
Materials

The catalysts used were HZSM-5 (Si/Al = 13.8), HY (Si/Al = 30), SiMCM-41, AlMCM-41, and BMCM-41 zeolites and zeotypes.

The H-zeolites were prepared by wet ion exchange starting from the Na forms. Four-fold ion exchange was performed in 1 mol/dm³ aqueous NH_4NO_3 solution. The duration of one exchange was 12 h and it was carried out at ambient temperature. The degree of ion exchange after the fourth repetition was nearly 100%. The resulting ammonium forms were then deammonized by calcination in a vacuum for 6 h at 873 K.

The MCM-41 derivatives were synthesized in our laboratory according to recipes published in the literature (16–19). Sodium silicate was always the silica source, aluminum isopropoxide was used for the preparation of AlMCM-41, boric acid was applied in the synthesis of BMCM-41, and hexadecyltrimethylammonium bromide was the surfactant for each material. NaOH and sulfuric acid solutions were

¹ To whom correspondence should be addressed. Fax: +36 62 544 619. E-mail: palinko@chem.u-szeged.hu.



SCHEME 1. Transformation pathways of methyloxirane on acidic zeolites/zeotypes.

used for adjusting the pH. The resulting gels were crystallized for 6 days under autogenous conditions at 373 K. They were then filtered and washed by distilled water, dried at 373 K, and, finally, calcined at 773 K for 10 h to burn the template off.

The CuZSM-5 catalyst was prepared by the solid-state ion-exchange method as described in the literature (20). A certain amount (5 mol%) of CuCl_2 was intimately mixed with well-powdered HZSM-5 in an agate mortar. The mechanical mixture was heat treated at 873 K for 8 h in air. The product was cooled to ambient temperature, washed free of chloride, and then dried at 373 K.

Methyloxirane (**1**; for the structure, please see Scheme 1) was a commercially (Fluka) available compound (racemic mixture was purchased) and was used as received. Hydrogen was produced in a Matheson generator. The high-purity nitrogen contained less than 0.0001% contamination.

Characterization

The samples were characterized by powder X-ray diffraction (DRON 3 diffractometer) and BET surface area measurements, and the metal content of CuZSM-5 was determined by X-ray fluorescence spectroscopy.

X-ray diffractograms were registered on well-powdered samples with a DRON 3 diffractometer in order to check crystallinity and to determine d_{100} distances for the MCM-41 samples.

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 a 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/cm^2 thickness) were pressed from the catalyst samples. They were pretreated in the optical cell at 573 K for 2 h in vacuum. Next, 1.33 kPa of pyridine was adsorbed on the activated samples at 363 K for 1 h followed by cooling to room temperature under continuous evacuation. Bands at 1540 cm^{-1} and 1450 cm^{-1} were used for calculating Brønsted and Lewis acidities, respectively.

Characteristic data of the zeolites and zeotypes collected by the different methods are displayed in Table 1.

Reactions and Analytical Method

The reactions of methyloxirane were studied in a pulse reactor system applying either hydrogen or nitrogen as carrier ($45 \text{ cm}^3/\text{min}$ gas flow). The reaction temperature was 363 K. The size of the pulse was $1 \mu\text{L}$ and 20 mg of catalyst was used. For comparison, the third and fourth pulses were used.

The ZSM-5 samples were also tested in a static closed recirculation reactor. A mixture of 1.33 kPa of methyloxirane and 20 kPa of H_2 was prepared and allowed to react on 20 mg of the dehydrated zeolite (1 h evacuation at 573 K). The reaction temperature was 363 K. Samples were withdrawn at 5 and 15 min and the mixture was analyzed.

Analysis of the product mixture of both reactors was done by using a GC-MS system (Hewlett Packard (HP) 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). Product identification

TABLE 1
Characterization Data for the Zeolites and Zeotypes

Zeolites	d_{001}^a (nm)	BET surface areas ($\text{m}^2 \text{ g}^{-1}$)	Brønsted/Lewis sites ^b
HZSM-5	—	336	0.88
CuZSM-5 ^c	—	318	0.09
HY	—	604	8.67
SiMCM-41	3.994	1169	0.03
BMCM-41	4.028	872	0.05
AlMCM-41	4.059	932	0.62

^a Calcined samples.

^b Calculated on the basis of IR spectra of adsorbed pyridine.

^c Prepared by solid-state ion exchange.

was based on the NBS/NIH/EPA/MSDC database, clean samples and chemical evidences detailed in Ref. (15), and molecular modeling (AM1 method included in the HyperChem 6.02 package (21)). The experimental, literature, and computational methods indicate that the most probable dimer products have *trans* configuration (*trans*-2-ethyl-4-methyl-1,3-dioxolane (5), *trans*-2,5-dimethyl-1,4-dioxane (7), and *trans*-2,6-dimethyl-1,4-dioxane (8)).

RESULTS

Transformation Pathways of Methyloxirane

The various acidic zeolite or zeotype catalysts used in this study behaved similarly as far as the main reaction channels are concerned. Cleavage of one C–O bond (single ring-opening pathway) provided acetone (2) and propionaldehyde (3). Rupture of both C–O bonds (double ring-opening pathway) gave propylene (9). Dimerization resulted in various 1,3-dioxolane (4, 5) and 1,4-dioxane (6, 7, 8) derivatives. The transformation pathways are depicted in Scheme 1.

When hydrogen was the carrier, the double ring-opening route was suppressed on every catalyst but HY. Applying hydrogen as carrier resulted in an induction period, and products were first observed after the third pulse.

Details are different, however, as far as specific products and product distribution are concerned. Before giving a more detailed overview, let us mention that the nonacidic SiMCM-41 was not active at all, and the weakly Lewis acidic BMCM-41 displayed only very little activity (conversion was less than 1%). Here, only dimerization occurred; however, even that reaction was very slow.

Reactions in the Pulse System

Product distributions in the pulse reactor on various zeolites and zeotypes are summarized in Table 2.

TABLE 2

Product Distribution in the Zeolite/Zeotype-Catalyzed Reactions of Methyloxirane (1) in the Pulse Reactor Using Hydrogen/Nitrogen as the Carrier—Data Correspond to the Third Pulse (20 mg of Catalyst, 45 cm³/min Gas Flow, 1 μL Pulse of Methyloxirane, 363 K)

	Composition/mol% ^a			
	HZSM-5	CuZSM-5 ^b	HY	AlMCM-41
2	4.5/4.9	3.8	21.0/18.2	10.0/10.5
3	7.1/9.8	3.6	41.9/47.8	65.5/62.4
4	0.9/1.5	2.7	0/0	0/0
5	51.9/47.3	35.1	17.6/12.4	15.1/15.9
6	8.6/8.3	5.8	6.9/8.0	0/0
7	14.7/14.4	20.1	5.6/2.6	9.4/10.7
8	12.3/12.9	28.9	0/0	0/0
9	0/0.9	0	7.0/11.0	0/0.5

^a Conversion of methyloxirane: HZSM-5, 67.8%/67.1%; CuZSM-5, 87.4%; HY, 90.4%/93.1%; AlMCM-41, 93.6%/98.7%.

^b Carrier: hydrogen.

It is to be seen that dimerization was predominant on the ZSM-5 zeolites, while HY and AlMCM-41 preferred single ring opening. Compared to dimerization the ZSM-5 catalysts performed poorly in single ring opening with some preference for the rupture of the sterically more hindered C–O bond on HZSM-5. Nearly equal isomerization activity was found in both directions on CuZSM-5. Deoxygenation was the most important pathway on HY in the first two pulses (100% and 80 % selectivities in the first and second pulses, respectively). From the third pulse isomerization and dimerization took over and deoxygenation became of minor importance. The formation of the single ring-opening products was overwhelming on HY and AlMCM-41 and, clearly, propionaldehyde (3) was always more significant than acetone (2). The proportion of dimerization decreases in the order CuZSM-5 ~ HZSM-5 > HY > AlMCM-41. Among the dimers 2-ethyl-4-methyl-1,3-dioxolane (5) is the predominant product. Dioxolane formation seems to be preferred on every zeolite except CuZSM-5 where the quantity of dioxanes surpasses that of dioxolanes. Interestingly, a significant dimerization product, 2,6-dimethyl-1,4-dioxane (8) that is, was not formed on HY and AlMCM-41 at all.

Finally, let us mention that changing the hydrogen carrier to nitrogen does not result in major alterations in product formation activities and selectivities.

Reactions in the Circulation Reactor on HZSM-5 and CuZSM-5 and Comparison of the Observed Characteristics to Those of the Pulse System

HZSM-5 and CuZSM-5 were picked for a more detailed investigation in a more sophisticated reactor system, since they provided the unexpected dimers in the highest proportion. In this reactor, similarly to the pulse system, methyloxirane was transformed through single C–O scission as well as dimerization (15). Product distribution data are displayed in Table 3.

First, let us describe features similar in both reactor types when hydrogen was added to methyloxirane. The products were essentially the same, except that 2,2,3-trimethyl-1,3-dioxolane (4) was not formed on HZSM-5 in the circulation reactor. However, one should note that the proportion of this compound was also very low in the pulse reactor. The CuZSM-5 zeolite was more active than the HZSM-5 zeolite. The dimerization pathway was more important than the single ring-opening route on both zeolites. 2-Ethyl-4-methyl-1,3-dioxolane (5) was the most important product, even taking into account the overall transformation. And, finally, deoxygenation (double C–O scission) did not occur.

Besides the above-listed similarities, considerable differences could be observed. They are as follows. Among the single C–O scission pathways the opening of the sterically more hindered C–O bond was clearly overwhelming in the circulation reactor. Although 2-ethyl-4-methyl-1,3-dioxolane (5) remained the most important product in the

TABLE 3

Product Distribution in the Zeolite-Catalyzed Reactions of Methyloxirane (1) under Reductive Atmosphere in the Circulation Reactor (20 mg of Catalyst, 1.33 kPa Methyloxirane, 20 kPa Hydrogen, 363 K)

	Product distribution/mol% ^a			
	5 min		15 min	
	HZSM-5	CuZSM-5	HZSM-5	CuZSM-5(s)
2	4.4	5.4	7.7	6.1
3	22.7	16.1	26.4	18.3
4	0	2.4	0	2.4
5	35.3	32.3	30.9	31.8
6	27.1	18.9	23.4	17.9
7	2.4	10.6	2.5	10.3
8	8.1	14.3	9.1	13.2

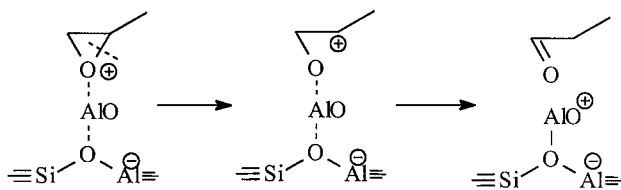
^a Conversion of methyloxirane. HZSM-5: 5 min, 29.5%; 15 min, 36.4%. CuZSM-5: 5 min, 76.4%; 15 min, 94.4%.

circulation system too, the sum of dioxane derivatives exceeded that of the dioxolanes.

DISCUSSION

The Reactions

Dimerization is a kind of ring opening; thus, ring opening may be considered to be the sole transformation pathway for methyloxirane under the conditions applied. Three types of this reaction may be distinguished on these substances: (i) single C–O bond cleavage leading to aldehyde and ketone; (ii) dimerization involving simultaneous bond making breaking; and (iii) olefin formation meaning double C–O bond scission. Single ring opening is a typical acid-catalyzed reaction proceeding on Brønsted as well as Lewis acid sites. It is known to proceed via carbenium ions. Since the secondary carbenium ion is more stable than the primary, the ring-opening route using the former cation (propionaldehyde is forming) is preferred (Scheme 2). However, steric factors favor the cleavage of the sterically less hindered C–O bond (acetone is forming). The two effects compete; nevertheless, electronic factors tend to overwhelm steric factors.



SCHEME 2. Schematic representation of the suggested mechanism for single ring opening of methyloxirane leading to aldehyde formation on a Lewis acid site.

As far as dimerization is concerned, it is clear that a more constrained environment (smaller pore size) is advantageous for dimerization to occur. The decreasing proportion of dimerization correlates with the increasing pore diameters (ZSM-5, 5.3 Å × 5.6 Å; Y, 7.4 Å; AlMCM-41, 40.6 Å). It is important to note, however, that dimerization remains an important reaction pathway even on AlMCM-41. In the following the suggested mechanism of one five-membered-ring product is detailed as an example, since the formation of five-membered-ring dimerization products is preferred on every zeolite/zeotype applied. Moreover, the 2-ethyl-4-methyl-1,3-dioxolane (**5**) is always the major product. The first step of its formation is proposed to be the formation of propanal precursors via the opening of the more hindered C–O bond of two methyloxirane molecules. These adsorbed species are then combined by establishing new C–O bonds. During ring formation a 1,2-hydride shift should also occur.

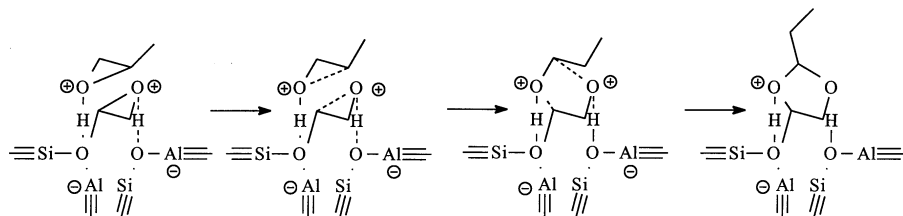
The above proposal is summarized in Scheme 3.

It is thought that C–O bond scission, C–O bond formation, and the hydride shift are probably sequential reactions. The first and second pulses, that are largely adsorbed in/on the materials, react with the following pulses and the combined products are observed as dimers. (In the static circulation reactor there is plenty of time for reactions like these to occur.) This suggestion is supported by the product distribution in the ring-opening reactions of methyloxirane performed in the liquid phase (but otherwise under similar conditions as described in this work) on HZSM-5 (22). Here, dimerization is suppressed relative to what was experienced in the gas phase. Solvation certainly hinders the interaction of the reactants; nonetheless, dimerization was not completely ceased. This observation indicates that a dimerization pathway with concomitant C–O scission and formation of new C–O bonds may also be operable.

The Molecular Sieves

The complete lack of reactivity on the all-Si zeotype strongly indicates the necessity of acid sites for the reaction to occur. Moreover, relatively strong acid sites are needed, since the activity of BMCM-41 possessing only weak acid sites is negligibly low. The transformations should proceed on Brønsted or Lewis centers—the activity of CuZSM-5 containing mostly Lewis sites was comparable to that of HZSM-5 containing mostly Brønsted sites—or their combination. Although the initial CuZSM-5 zeolite has predominantly Lewis sites, the working zeolite possibly contains a steady state composition of Cu(II), Cu(I), and Cu(0) clusters together with extra protonic sites, due to the interplay of autoreduction, the reducing environment (hydrogen or nitrogen as added gas), trace amounts of water, and the oxidizing effect of methyloxirane.

As has been mentioned already, the nature of added gas (hydrogen/nitrogen) does not influence product



SCHEME 3. Schematic representation of the suggested mechanism for the dimerization of methyloxirane leading to dioxolane formation on Brønsted acid sites.

distribution to a significant extent; however, added hydrogen suppresses or even stops deoxygenation.

CONCLUSIONS

Methyloxirane undergoes single (isomerization) and double (deoxygenation) ring-opening as well as dimerization reactions over various types of acidic zeolites and zeotypes. The transformations proceed on Brønsted or relatively strong Lewis acid sites or their combination. The major products are dimers: dioxolane and dioxane derivatives. It was found that a confined environment is advantageous for dimerization to occur; however, this reaction route also is viable when the pore size is large and possibly on nonporous but acidic substances as well.

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