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Deuterium distribution in two major products obtained during the cyclic dimerisation of methyloxirane over acidic molecular sieves

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Abstract

The ring-transformation reactions of methyloxirane on DZSM-5 and DAIMCM-41 aluminosilicates were studied in a pulse microreactor at 363 K. Cyclic dimerisation was found to be the major reaction pathway. Deuterium distribution in two important products of this reaction route was monitored. The positions of the deuterium atoms were determined giving help in proposing a more accurate dimerisation mechanism.

1. Introduction

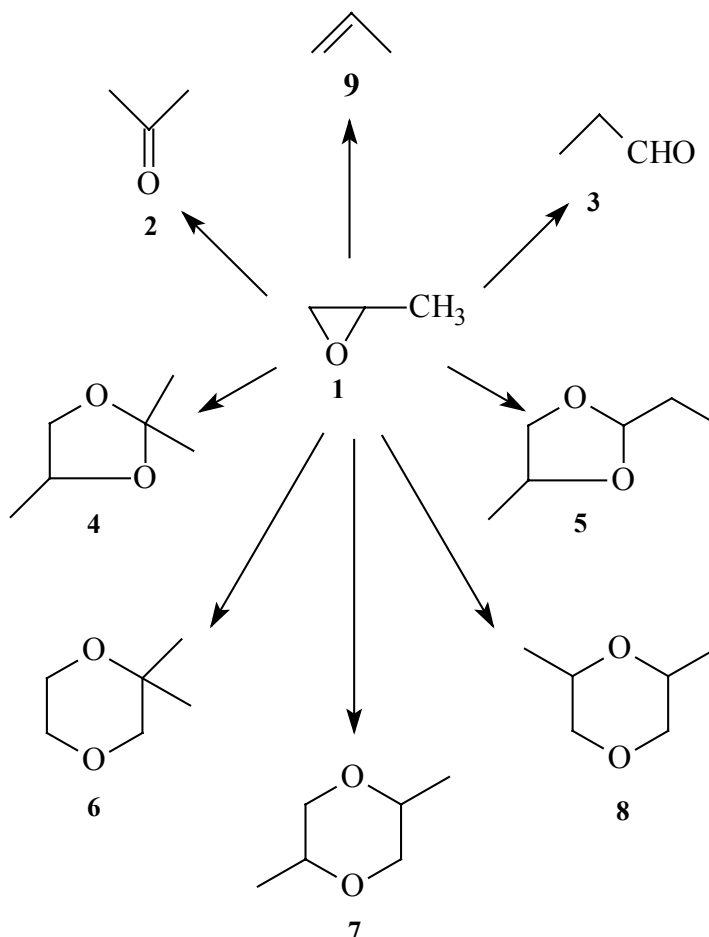
Epoxides are extremely useful building blocks in the synthesis of various complex organic molecules and macromolecules [1]. Their versatility lies in the fact that they can be easily prepared [2], under normal circumstances (room temperature, atmospheric pressure) they are stable yet the rings are reactive enough: they can be opened by acids [3] or bases [3] even in catalytic reactions as well as by electrophiles (very rare) [5] or nucleophiles (significantly more abundant) [6] in stoichiometric transformations. The epoxide ring can be opened on solids and for this purpose various oxides [7], molecular sieves [8], clays [9], acidic membranes [10] and even metals in the homogeneous [11] or the heterogeneous phase (supported transition metals) [12] may be used. Part of the versatility is the ability of these compounds to transform in various ways especially if the rings are substituted.

During our earlier investigations concerning the ring-opening reactions of methyloxirane over aluminosilicates of various types [13-16] it was found that single as well as double C-O scission occur producing oxo compounds and olefins. It also became clear that the major reaction pathway is a kind of ring opening too, cyclic dimerisation that is, producing various dioxolane and dioxane derivatives (Scheme 1).

Applying D₂O-treated molecular sieves (DZSM-5 and DAIMCM-41) it was observed that the ring transformations occurred through various channels [17]. The main reaction channel, where deuterium exchange did not occur, involved exclusively the Lewis sites at the potential exchange sites. For deuterium exchange to occur during ring opening at least one Brønsted site is necessary. For dimerisation when deuterium exchange took place many active site combinations may be envisaged, however, for the formation of the dioxolane derivatives two neighbouring Brønsted-Lewis site pairs, while for the formation of dioxane derivatives the interplay of one Brønsted-Lewis acid

pair and a Lewis-Lewis acid pair seem to be the most advantageous.

A more accurate picture about the main ring-transformation route might emerge if the positions of the exchanged deuteriums could be determined. In this contribution this is attempted for the major products of the cyclic dimerisation transformation pathway.



Scheme 1. Transformations of methyloxirane on acidic molecular sieves

2. Experimental

The catalysts applied were DZSM-5 (Si/Al = 13.8) and DAIMCM-41 (Si/Al = 40.0) molecular sieves. The HZSM-5 zeolite was prepared by wet ion exchange starting from the Na-form. Fourfold ion exchange was performed in 1 mol/dm³ aqueous NH₄NO₃ 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 demonised by calcination in vacuum for 6 h at 873 K. The AIMCM-41 molecular sieve was synthesized in our laboratory following recipes published in the literature [18-21]. Sodium silicate and aluminium isopropoxide were the silica and aluminium sources, respectively, and hexadecyltrimethylammonium bromide was the surfactant. NaOH and sulfuric acid solutions were used for adjusting the pH. The resulting gel was crystallized for 6 days

under autogeneous conditions at 373 K. Then, it was 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 ion-exchange procedure was the same as for the ZSM-5 zeolite. The H-form molecular sieves were transformed to D-forms right before the reaction by injecting pulses of D₂O (of 99.9+ purity) into a nitrogen stream passing through samples of the materials in the reactor at 523 K, while monitoring the deuterium content of water leaving the reactor by the GC-MS method. The size of the pulse was 5 µl and ten pulses always assured complete OH-OD exchange.

Characteristic data on the aluminosilicates collected by the different methods are to be seen in Table 1.

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 | 0.53x0.56; 0.51x0.55 ^c | 336 ± 10 | 0.88 |
| 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. [22]; d – calculated from the position of the 001 reflection corrected with the wall thickness (2.00 nm)

Methyloxirane (**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.

The reactions of methyloxirane were studied in a pulse reactor system applying nitrogen as carrier (45 cm³/min gas flow). The reaction temperature was 363 K. The size of a pulse was 1 µl. The quantity of the catalyst was 20 mg and it was activated before the reaction at 573 K for 1 h under nitrogen flow.

Analysis of the product mixture was performed by 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 was based on the NBS/NIH/EPA/MSDC database, clean samples and chemical evidences detailed in ref. [13].

The deuterium content was determined in the GC-MS system using the chemical ionisation technique (NH₃ was used as collision partner). This technique is mild enough to provide with easily observable molecular ions and only few fragments. The analysis of fragments, allowed to determine the position of the deuteriums in (**5**) and (**8**). The natural isotope abundance was taken into account in calculating deuterium content. Since the first pulse remained irreversibly adsorbed on the catalysts, the second pulse was used for determining deuterium content and distribution and the positions of exchanged deuterium atoms.

3. Results and Discussion

Product as well as deuterium distribution data over the two molecular sieves are summarised in Tables 2 and 3.

Table 2
Deuterium distribution in the products of methyloxirane ring transformations catalysed by DZSM-5

| Products (mol%) | Deuterium distribution/% | | | | | |
|-----------------------|--------------------------|-------|-------|-------|-------|-------|
| | d_0 | D_1 | d_2 | d_3 | d_4 | d_5 |
| 2 (4.9) | 45.9 | 24.2 | 18.5 | 8.9 | 2.2 | 0.3 |
| 3 (9.8) | 68.7 | 27.5 | 3.8 | – | – | – |
| 4 (1.5) | 44.1 | 25.6 | 23.2 | 6.9 | 0.2 | – |
| 5 (47.3) | 53.7 | 29.1 | 16.7 | 0.5 | – | – |
| 6 (8.3) | 67.9 | 29.7 | 2.4 | – | – | – |
| 7 (14.4) | 69.3 | 27.6 | 3.1 | – | – | – |
| 8 (12.9) ^a | 68.0 | 29.3 | 2.7 | – | – | – |

a – plus 0.9 mol% propene (no H–D exchange)

Table 3
Deuterium distribution in the products of methyloxirane ring transformations catalysed by DAIMCM-41

| Products (mol%) | Deuterium distribution/% | | | | | |
|-----------------------|--------------------------|-------|-------|-------|-------|-------|
| | d_0 | D_1 | d_2 | d_3 | d_4 | d_5 |
| 2 (10.5) | 60.8 | 19.0 | 11.1 | 5.9 | 2.6 | 0.6 |
| 3 (62.4) | 48.5 | 36.8 | 14.7 | – | – | – |
| 5 (15.9) | 56.6 | 31.1 | 12.3 | – | – | – |
| 7 (10.7) ^a | 72.1 | 26.7 | 1.2 | – | – | – |

a – plus 0.5 mol% propene (no H–D exchange)

It is to be seen that cyclic dimerisation is the major transformation pathway over DZSM-5 and very significant over DAIMCM-41. There are two types of cyclic dimerisation: the C5-route gives 1,3-dioxolane and the C6-route provides with 1,4-

dioxane derivatives. Cyclic products appearing over both aluminosilicates are 2-ethyl-4-methyl-1,3-dioxolane (**5**) and 2,5-dimethyl-1,4-dioxane (**7**), thus, positions of the deuterium atoms are attempted in these molecules. It is to be noted that they are representatives of the C5- and C6-routes, respectively.

Relevant data in Tables 2 and 3 reveal that there is no significant difference in the deuterium distribution over the two catalysts for these molecules. More than half the quantity formed does not contain deuterium at all. Those molecules which do, are mainly single- and a smaller proportion is double-exchanged. Some and insignificant triple exchange only occurred with the dioxolane derivative over DZSM-5.

Studying the fragmentation pattern of the dioxolane derivative and the fragments themselves revealed that deuterium enters into the ring at the tertiary carbon of the methyloxirane over both catalysts indicating that this is the adsorption site beside the ring oxygen. The predominance of the single-exchanged product indicates that among the pathways leading to H–D exchange that one is the most important, which proceeds on a combination of Brønsted and Lewis sites. The other, less important pathway involves two Brønsted sites. The H-D exchange sites even in this case remain the tertiary carbon atoms of the two methyloxirane molecules over both molecular sieves.

The fragmentation pattern and the fragments showed that the deuterium in the dioxane-*d*₁ derivative changes positions. It sweeps through each ring carbon atom between the oxygen atoms of the dioxane ring indicating π -allyl adsorbed species in the pathway proceeding over a combination of Brønsted acid – Lewis acid site pairs over both aluminosilicates. Two π -allyl adsorbed species make up the dioxane derivative when the active site is a combination of Brønsted acid – Brønsted acid pairs: the two deuterium atoms sweep through each ring carbon over both catalysts.

4. Conclusions

The positions of the deuterium atom(s) were determined in the cyclic dimerisation reaction of methyloxirane over DZSM-5 and DA1MCM-41 molecular sieves. In the C5 dimerisation pathway the tertiary carbon atom of the methyloxirane molecule is involved: in one of the two molecules upon single exchange or in both molecules upon double exchange. The dioxane derivative (C6 dimerisation pathway) was formed *via* π -allyl adsorbed species.

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