Diastereoselective epoxidation of allylic alcohols with hydrogen peroxide catalyzed by titanium-containing zeolites or methyltrioxorhenium versus stoichiometric oxidation with dimethyldioxirane: Clues on the active species in the zeolite lattice

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Abstract

Chiral, acyclic allylic alcohols **1** are epoxidized chemoselectively to the epoxy alcohols **2** by hydrogen peroxide, catalyzed by titanium-containing zeolites (TS-1, Ti-beta). For substrates with 1,3-allylic ($A^{1,3}$) strain, a high diastereoselectivity is observed with preference for the *threo* isomer, while derivatives with 1,2-allylic ($A^{1,2}$) strain or no allylic strain give a low *threo* diastereomeric excess. Comparison of the diastereomeric ratios of the titanium-containing zeolites with those for *meta*-chloroperbenzoic acid shows a good correspondence which suggests that the active species for the oxygen transfer in the epoxidations for zeolites is peracid- rather than peroxo-type. Comparison of the diastereomeric ratios achieved with the three-membered ring peroxide oxidants dimethyldioxirane and MTO/UHP (metal peroxo complex) disfavor the peroxo species since significantly lower *threo* diastereoselectivities for substrates with 1,3-allylic strain were obtained. Direct coordination of the allylic alcohol through a metal alcoholate bond is unlikely because of the different diastereomeric ratios obtained for the heterogeneous and homogeneous titanium species with allylic alcohols that possess 1,2-allylic strain. Moreover, the number of coordination sites at the titanium atom in the zeolite framework is limited for steric reasons and the constrained space around the active center in the zeolite lattice presents severe geometrical problems for the stereoelectronically controlled linear S_N2-type alignment of the oxygen donor (metal-activated peroxide bond) and the acceptor (metal–alcoholate-bonded substrate) during the epoxidation process.

Keywords: Catalysis; Hydrogen peroxide; Dimethyldioxirane; Zeolites; Titanium; Diastereoselectivity; Epoxidation; Allylic alcohols; Mechanism

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1. Introduction

The last decades of the twentieth century will be historically declared as the age of 'environmental consciousness', with a great demand for cleaner and environmentally acceptable products, e.g. the need for 'green gasoline'. The imposition has been placed on the chemical industry to develop more effective, more targeted, and environmentally friendly processes [1]. Since oxidations are important industrial reactions as a source of oxyfunctionalized molecules from a wide variety of cheap hydrocarbons, new oxidation catalysts play an increasingly important role in chemical manufacture. New selective processes have been designed to avoid undesired chemoisomers, regioisomers or diastereomers, and enantiomers. In this context, the highlight in recent years is the reagent of the year 1994, namely Jacobsen's chiral Mn(salen) oxidation catalyst, which shows high enantioselectivities in the epoxidation of many olefins.

Improvements in the production of bulk chemicals are more pressing than in fine chemical synthesis, because in the former even small amounts of side products may generate tons of waste which then incur high disposal costs. Many worldwide, well-established processes still involve the use of dangerous or toxic oxidants [1]. A critical example is the industrial vitamin K_3 synthesis, which is carried out with $K_2Cr_2O_7$ as oxidant in stoichiometric amounts [2]. In the last few years it was demonstrated that this hazardous process may be replaced by catalytic methods. These include the Pd/CH_3CO_3H oxidant [3] and a procedure in which methyltrioxorhenium (MTO) serves as catalyst and hydrogen peroxide as oxygen source, with water as the only by-product [4]. Besides the catalytic nature and higher yields, an additional advantage is the excellent regioselectivity [Eq. (1)].
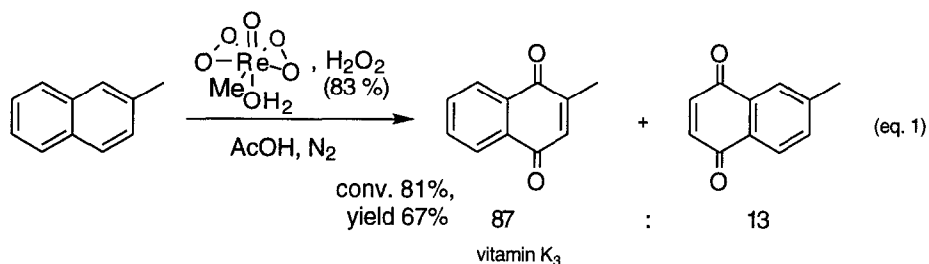

A completely different approach for a new class of catalysts is to incorporate metals by isomorphous substitution into the framework of zeolites, the so-called 'redox molecular sieves'. These heterogeneous materials use hydrogen peroxide or even molecular oxygen as oxygen source and can easily be removed by filtration. Although such oxidation catalysts have become only recently available, their definite advantages have stimulated much interest in catalytic oxidations as documented for titanium silicate 1 (TS-1) [1], the best-known zeolite with a ZSM-5 structure (Scheme 1).

Another mild and clean reagent of the last decade is dimethyldioxirane (DMD), which is easily available from caroate in isolated form as acetone solution (Scheme 2) [11] [2]. Most of the reactions can be carried out at room temperature (ca. 20°C) or for sensitive substrates under subambient conditions. The most important advantage of DMD is that the oxidant is reduced to acetone, which is

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[1] For CH insertions, see Ref. [5], for epoxidations [6], for arene oxidations [7], for amine oxidation [8], for sulfide oxidation [9], for a recent review see [10].

[2] For preparation of DMD see Ref. [12] for the in-situ method see Ref. [13].
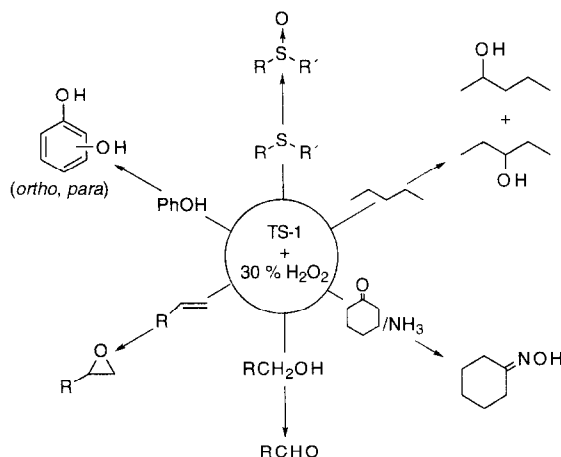
Scheme 1. Catalytic oxidations with titanium silicate 1 (TS-1) and aqueous hydrogen peroxide.

also the solvent, so that the work-up only requires evaporation of the acetone and usually the product is obtained pure enough for direct further use.

In the present article we compare the new heterogeneous, catalytic oxidants TS-1/H_2O_2 and Ti-beta/H_2O_2 (the titanium analog of H-beta) with the homogeneous, catalytic one MTO/H_2O_2 and the stoichiometric DMD as peroxo species in the diastereoselective epoxidation of chiral allylic alcohols **1**. As a homogeneous titanium catalyst, Ti($OiPr)_4$/tBuOOH(TBHP) was chosen and contrasted with the literature-known stoichiometric oxidation by m-chloroperbenzoic acid (m-CPBA) and catalytic oxygen transfer by VO(acac)$_2$/TBHP [Eq. (2)]. The chiral allylic alcohols **1**, particularly derivative **1e**, in which the methyl group geminal to the stereogenic center provides 1,2-allylic ($A^{1,2}$) strain and the *cis* methyl group for 1,3-allylic ($A^{1,3}$) strain, should be helpful as a stereochemical probe to identify the active species in the catalytic epoxidations with titanium-containing zeolites. For the latter, the peracid type **A** and the titanium peroxo **B** structures have been proposed as the active oxygen transfer species (see Scheme 4). In addition to these mechanistic features, also the preparative
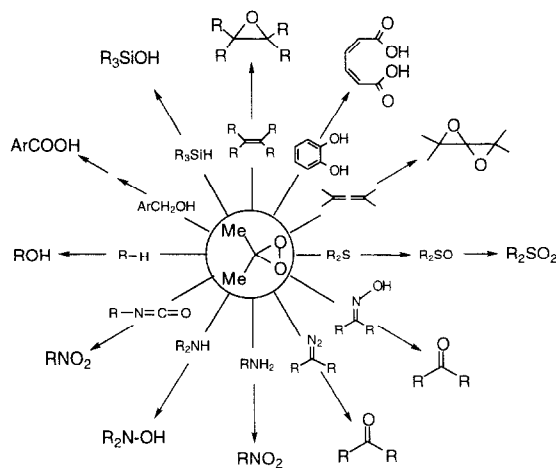
Scheme 2. Selected DMD oxidations of common substrates.

incentives should be stressed since epoxy alcohols with defined stereochemistry are valuable building blocks in natural product synthesis [14].
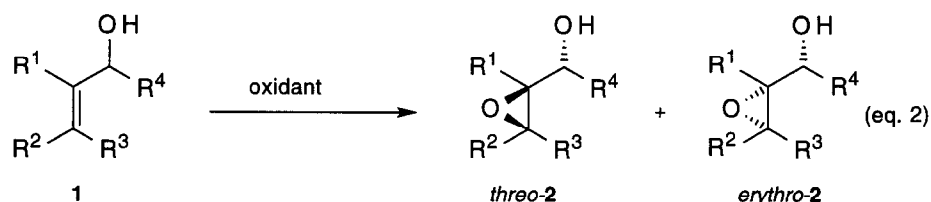
2. Results and discussion

For epoxidations catalyzed by the Ti-containing zeolites, the epoxy alcohols were obtained in high chemoselectivity without rearrangement when 30% aqueous hydrogen peroxide is replaced by its concentrated 85% form in the presence of $MgSO_4$ or by the waterfree crystalline urea adduct of hydrogen peroxide (UHP) [15]. For the latter oxygen source, the hydrophobic TS-1 catalyst is not poisoned as it is the case for the hydrophilic Ti-beta catalyst. The epoxy alcohols are obtained highly *threo*-selectively when $A^{1,3}$ strain is present in the allylic alcohol, i.e. substrates **1d–g** (Table 1, entries 4–7). For the zeolite with a larger pore size, namely Ti-beta, the *threo* preference is a little higher for the alcohols **1d** and **1e** (Table 1, entries 4 and 5). Allylic alcohols without strain, i.e. **1a** and **1c** (Table 1, entries 1 and 3), or with $A^{1,2}$ strain such as substrate **1b** (Table 1, entry 2), give only a low diastereomeric excess, but here also the *threo* product is favored.

The homogeneous $Ti(OiPr)_4$/TBHP catalytic oxidation system distinguishes more effectively between the three substrates **1a–c** than the heterogeneous ones. Allylic alcohols without allylic strain, i.e. **1a** and **1c** (entries 1 and 3), also react in a low *threo*-selective fashion, but for substrate **1b** (entry 2) a significant *erythro* selectivity is obtained. The other substrates are epoxidized in high *threo* selectivities, e.g. the derivatives **1f** and **1g** (entry 6 and 7) give essentially exclusively the *threo* epoxy alcohol.

The $VO(acac)_2$/TBHP oxidant is more *erythro*-selective. The allylic alcohol **1b** (entry 2) is converted to the corresponding *erythro* alcohol, for the substrates **1a, c** and **e** (entries 1, 3 and 5) the *erythro* product is also preferred. Only the epoxy alcohols **2d** and **2f** (entries 4 and 6) are obtained *threo*-selectively.

For the MTO/UHP oxidant, analogous to the TS-1 catalyst, the use of the urea adduct of hydrogen peroxide improves the chemoselectivity in favor of the epoxides [19]. No diastereoselectivity is displayed for substrate **1b** (entry 2), which signifies that $A^{1,2}$ strain is not important. The allylic alcohols **1a** and **1c** (entries 1 and 3) without any strain are modestly *threo*-selective, the substrates **1d** and **1f** (entries 4 and 6) with $A^{1,3}$ strain exhibit appreciable *threo* selectivity, while the highest *threo* selectivities are displayed by the derivatives **1e** and **1g**.

For the stoichiometric oxidant *m*-CPBA, $A^{1,3}$ strain is decisive, as evidenced by the fact that the alcohols **1d–g** (entries 4–7) afford the *threo* epoxy alcohol essentially exclusively. The allylic alcohols **1a–c** without $A^{1,3}$ strain exhibit expectedly low diastereoselectivity.

In contrast, for dimethyldioxirane the *threo–erythro* ratio varies greatly and shows a small but significant solvent dependence for substrates with allylic strain. Thus, the moderate *threo* selectivity

Table 1

Diastereomeric ratios (d.r.) for the epoxidation of the allylic alcohols 1 with TS-1/UHP, Ti-beta/H_2O_2, Ti(OiPr)$_4$/TBHP, MTO/UHP, m-chloroperbenzoic acid (m-CPBA) and dimethyldioxirane

		catalyst:	TS-1[a]	Ti-beta[a]	Ti(OiPr)$_4$[b]	VO(acac)$_2$[c]	MTO[d]	m-CPBA[e]	DMD	
		donor:	UHP	H_2O_2(85%)	TBHP	TBHP	UHP			
		solvent:	CH$_3$COCH$_3$	CH$_3$CN	CH$_2$Cl$_2$	C$_6$H$_6$	CDCl$_3$	CH$_2$Cl$_2$	CH$_3$COCH$_3$	CCl$_4$
entry	substrate					diastereoselectivities[f]				
1	OH (1a)		60 : 40	62 : 38	71 : 29	20 : 80	60 : 40	60 : 40	50 : 50	---
2	OH (1b)		55 : 45	56 : 44	22 : 78	05 : 95	50 : 50	45 : 55	60 : 40	70 : 30
3	OH (1c)		65 : 35	62 : 38	66 : 34	29 : 71	67 : 33	64 : 36	53 : 47	56 : 44
4	OH (1d)		87 : 13	91 : 09	91 : 09	71 : 29	82 : 18	95 : 05	67 : 33	85 : 15
5	OH (1e)		81 : 19	89 : 11	83 : 17	33 : 67	91 : 09	90 : 10	87 : 13	91 : 09
6	OH (1f)		95 : 05	95 : 05	95 : 05	86 : 14	83 : 17	95 : 05	76 : 24	82 : 18
7	OH (1g)		90 : 10		95 : 05		95 : 05	90 : 10[g]	95 : 05	---

[a] 2.5 mol% Ti based on the allylic alcohol, all reactions were monitored by TLC until > 95% conversion, after 12–24 h the epoxy alcohols were isolated in 72–95% yields.

[b] Carried out by a modified literature procedure [16], Ti(OiPr)$_4$ was used in stoichiometric amounts.

[c] 0.5 mol% VO(acac)$_2$.

[d] 1 mol% MTO.

[e] For substrates 1a–d, f see Ref. [17], for substrate 1e see Ref. [18].

[f] Diastereomeric ratios (d.r.) of threo:erythro products, determined by ^{1}H NMR analysis of the characteristic signals in the crude reaction mixture, error ±5% of the stated values.

[g] In CDCl$_3$ as solvent.

in polar solvents (acetone) is increased in unpolar ones (CCl$_4$), e.g. for substrate 1b (entry 2) with A^{1,2} strain and 1d (entry 4) with A^{1,3} strain. Except for the alcohols 1e and 1g (entries 5 and 7), the diastereomeric excess is always lower for DMD than for m-CPBA.

A comparison of the stereochemical data (Table 1) for the epoxidation of the chiral allylic alcohols 1 with the various oxidants provides valuable information on the transition state geometry of the oxygen transfer process. Thus, the chiral allylic alcohol 1b serves as test of A^{1,2} strain and derivatives 1d or 1f of A^{1,3} strain, while substrate 1e constitutes a differentiating stereochemical probe because it possesses both A^{1,2} and A^{1,3} strain in competition. The derivatives 1a, 1c and 1g are not useful as mechanistic probes because the first two are both equally unselective for all oxidants except for Ti(OiPr)$_4$/TBHP, whilst the alcohol 1g is converted essentially exclusively to its threo diastereomer for all cases.
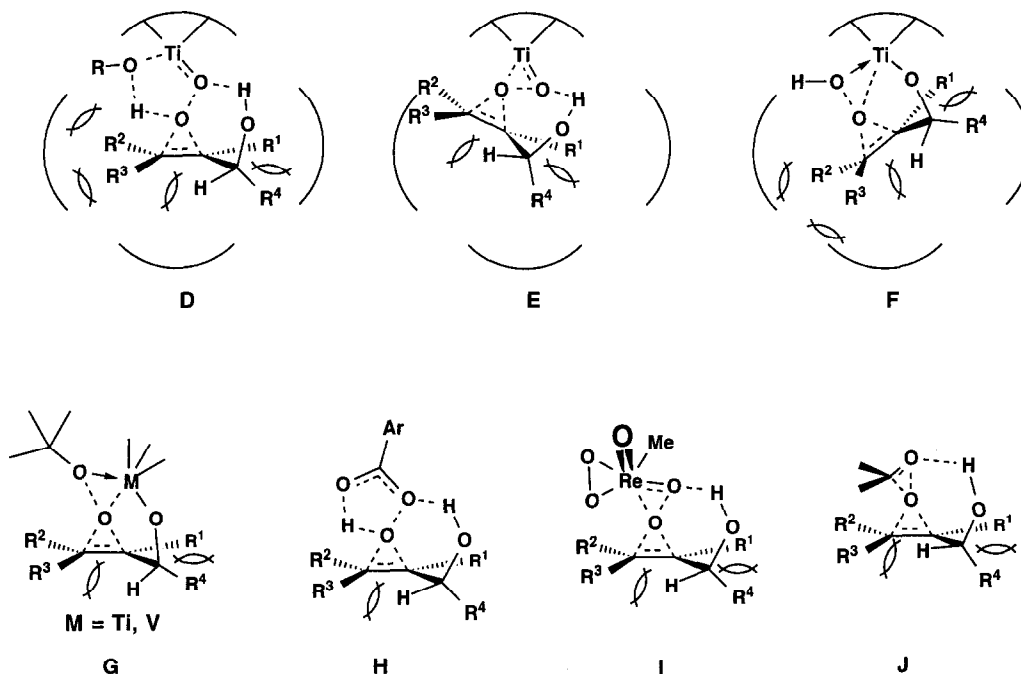
Fig. 1. Proposed transition states for the epoxidations catalyzed by the heterogeneous titanium-containing zeolites for a peracid-type species (D) and a titanium-peroxo-type one (E), or for direct coordination of the allylic alcohol through a metal–alcoholate bond (F), for the homogeneous metal-catalyzed oxidants $Ti(OiPr)_4$/TBHP, $VO(acac)_2$/TBHP (G), and MTO/UHP (I), and the stoichiometric, nonmetal-activated oxygen transfer agents m-CPBA (H) and DMD (J).

The diastereomeric ratios of the epoxidation of the four stereochemically informative allylic alcohols 1b, 1d, 1e and 1f (Table 1) show that the transition state geometry for oxygen transfer by the titanium zeolites (D, Fig. 1) is similar to that of m-CPBA (H, Fig. 1). The latter associates with the substrate by hydrogen bonding for which a dihedral angle of 120° in the allylic alcohol (O–C–C=C) is optimal. As a consequence, $A^{1,3}$ strain has a strong influence on the transition state geometry, whereas the effect of $A^{1,2}$ strain is essentially negligible; consequently, the threo epoxy alcohols are obtained preferentially (Scheme 3). This is in good harmony with the peracid-type structure C for the active species (Scheme 4). The latter is very similar to the structure A (Scheme 4), which has been proposed for these epoxidations on the basis of solvent, acid and base effects on the reaction kinetics [20]. The only change is the metal–alcoholate bond of a water or a protic solvent molecule to the active center (structure C) instead of the weak coordination without deprotonation (structure A). In the case that the Ti atom possesses a higher coordination number, additional ligation is possible (R'OH in C, Scheme 4). In addition to hydrogen bonding of the substrate to the active species, the transition state for the epoxidation in the resulting complex D' (Scheme 4) is similar to that of peracids (K, Scheme 3) in which multiple H-bonding assists the electronic reorganization in the oxygen transfer. Thus, like for the m-CPBA, also for the titanium zeolite $A^{1,3}$ dominates $A^{1,2}$ strain in the transition state of the oxygen transfer to optimize hydrogen bonding between the allylic alcohol and the active catalytic species. The consequences of the latter are documented in the high threo diastereoselectivities for the alcohols 1d and 1f and most definitively for the stereochemical probe 1e. In view of these identical (within the error limits) stereochemical data for m-CPBA and Ti-beta, we conclude that, analogous to the peracid epoxidation, also for the Ti-beta/H_2O_2 oxidant the substrate
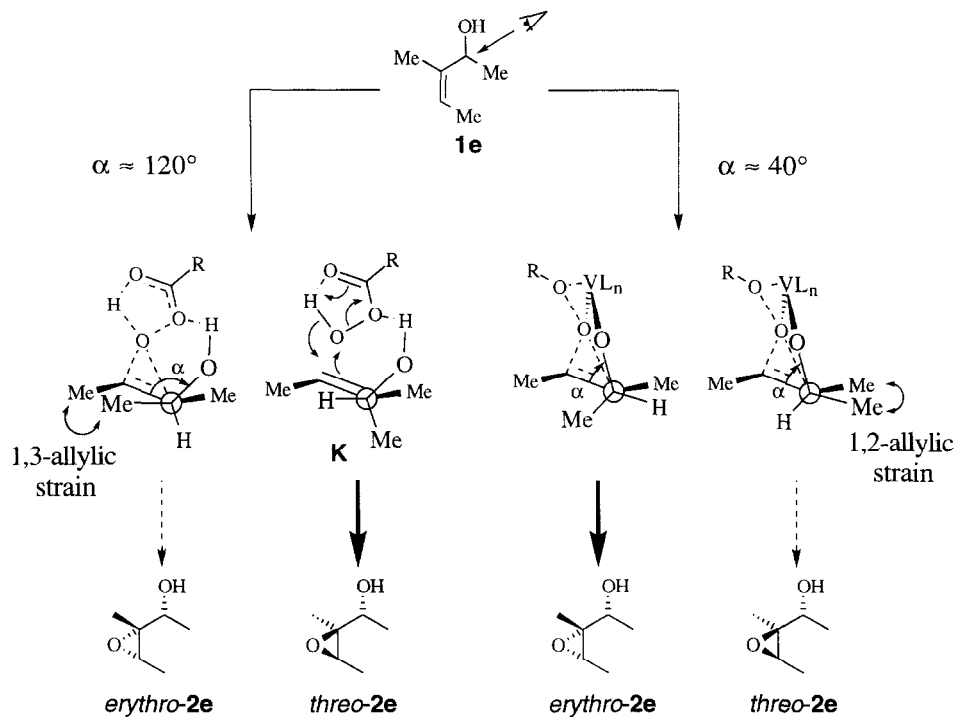
Scheme 3. Preferred dihedral angles α (C=C–C–O) in the allylic alcohol controlled by 1,2- or 1,3-allylic strain.
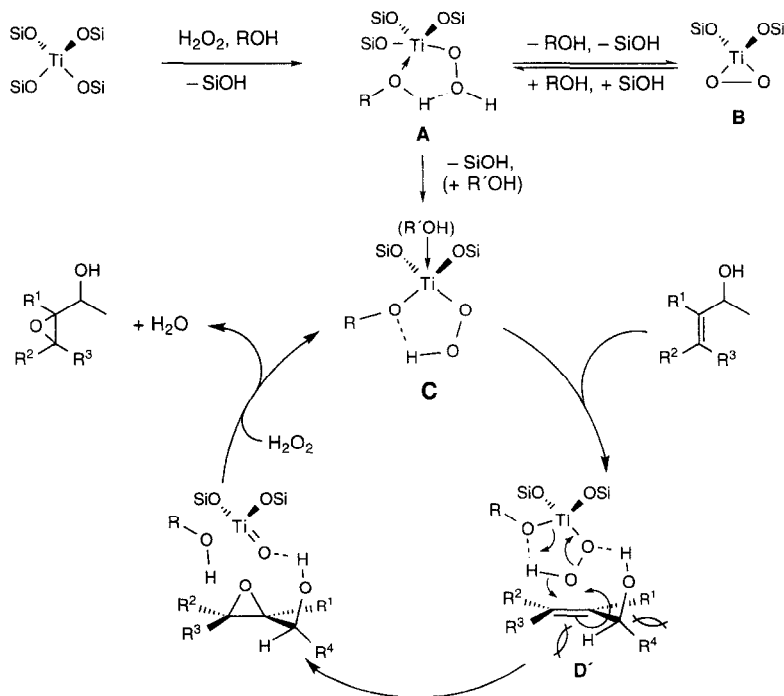
Scheme 4. Catalytic cycle and proposed structures of the active species **A**, **B** and **C** for the oxygen transfer of the titanium-containing zeolites.

molecule is coordinated by hydrogen bonding of the allylic hydroxy group with the oxidant at an optimal dihedral angle (O–C–C=C) of 120° in the allylic alcohol. The slightly different diastereoselectivities for the TS-1 catalyst compared to Ti-beta surely are influences of the different zeolite framework on the transition state geometry.

The comparison of the diastereoselectivities (Table 1) of the peroxo-type oxidants, i.e. dimethyldioxirane (**J**, Fig. 1) and the diperoxo–rhenium complex (**I**, Fig. 1), permits to exclude unequivocally the participation of the peroxo species **B** (Scheme 4) in the epoxidation by the titanium-containing zeolites. For example, for DMD it has been established with conformationally fixed cyclic substrates that the optimal angle in the allylic alcohol for oxygen transfer is greater than 130° [21]. Since the hydroxy group is further away from the oxidant, hydrogen bonding is expectedly weaker and the diastereoselectivity drops for the $A^{1,3}$-strained substrates **1d** and **1f** to 67:33 and to 76:24 in the polar solvent acetone compared to > 90:10 for Ti-beta (Table 1, entries 4 and 6). In the less polar solvent CCl_4, the diastereoselectivity is enhanced to > 80:20 because the polarized transition state is less effectively stabilized by the medium and the allylic hydroxy functionality must compensate this deficiency through intramolecular hydrogen bonding and thereby promote better stereocontrol. Also for the structurally similar metal peroxo complex derived from MTO/H_2O_2, the same diastereoselectivities (within the error limit) as for the dioxirane DMD are observed (Table 1). If the corresponding titanium peroxo complex **B** (Scheme 4) were involved in the Ti-containing zeolite epoxidations, analogous to the DMD and MTO/H_2O_2 oxidants, a significantly lower diastereoselectivity should have been observed. Since this is not the case (Table 1), the titanium peroxo transition state **E** (Fig. 1) is not likely as the active species and we favor the peracid-type structure **C** with the transition state **D** in this oxygen transfer.

The question whether the allylic alcohol is bound to the metal site through a metal–alcoholate bond (transition state **F**, Fig. 1) remains to be addressed. If the homogeneous $Ti(OiPr)_4/TBHP$ oxidant, as one would expect, were to display similar diastereoselectivities as the $VO(acac)_2/TBHP$ system, it would be straightforward to decide whether such direct bonding applies. For $VO(acac)_2/TBHP$ the allylic alcohol is bound by a metal–alcoholate bond and to minimize $A^{1,2}$ strain, the optimal dihedral angle of 40–50° applies in the oxygen transfer. In terms of diastereoselectivity this is expressed in a high yield of the *erythro* isomer (Scheme 3). In contrast, the $Ti(OiPr)_4/TBHP$ system gives in many cases very high *threo* selectivities. For example, the diastereomeric ratio for substrate **1b** drops from 5:95 for the vanadium catalyst to 22:78 for the homogeneous titanium catalyst (Table 1), i.e. although still mainly *erythro*-selective, a significantly higher *threo* yield is observed for the latter. Indeed, for the stereochemical probe **1e**, the diastereoselectivity is even reversed from 33:67 ($A^{1,2}$ strain) to 83:17 ($A^{1,3}$ strain) for vanadium versus titanium, and now for the former *erythro* and for the latter *threo* selectivity applies. Thus, although for both metals the chiral allylic alcohol substrate is connected through a metal–alcoholate bond (transition state **G**, Fig. 1), for these homogeneous oxidation catalysts $A^{1,2}$ strain controls the *erythro* selectivity for vanadium (dihedral angle < 50°) and $A^{1,3}$ strain the *threo* selectivity for titanium (dihedral angle > 50°). Consequently, such stereochemical criteria cannot be employed to asses whether in the heterogeneous titanium catalysts metal–alcoholate bonding of the allylic alcohol operates. In fact, the heterogeneous oxidants resemble most closely the homogeneous $Ti(OiPr)_4/TBHP$ system in that *threo* selectivity (except for substrate **1b**) predominates and for the homogeneous case unquestionably titanium-alcoholate bonding applies. The small difference in the diastereoselectivity for substrate **1b** ($A^{1,2}$ strain only), i.e. a slight *threo* for the heterogeneous but a definite *erythro* preference for the homogeneous titanium catalyst, is in the proper direction to argue against direct attachment of the allylic alcohol to the metal site through a Ti–O bond in the heterogeneous cases. Additionally, for steric reasons we speculate that the space

around the titanium site in the zeolite lattice is too encumbered to accommodate the oxygen acceptor (allylic alcohol) through direct Ti–O bonding as well as the activated oxygen donor (H_2O_2), as portrayed in the transition state structure **F** (Fig. 1) for the oxygen transfer. For this structure, three additional coordination sites are required and it is questionable whether the congested titanium site in the zeolite lattice can provide these. Moreover, inspection of models for the transition state **F** implies severe steric congestion in an attempt to align the double bond of the bound allylic alcohol and the activated peroxide bond for the stereochemically controlled S_N2 attack, i.e. along the required linear (180°) coordinate [22]. Thus, although this query cannot be answered satisfactorily at this stage, we favor transition state **D** (only hydrogen bonding by the allylic hydroxy functionality) rather than structure **F** (full metal–alcoholate bonding).

In summary, all oxidants examined herein (except $VO(acac)_2$/TBHP) show moderate to excellent *threo* selectivity when $A^{1,3}$ strain is present in the allylic alcohol. On account of the diastereomeric ratios similar to the peracids (Table 1), we propose the peracid-like species **C** for the titanium-containing zeolites as the active oxidant with the transition state geometry **D** (Fig. 1) for the oxygen transfer. The substrate is coordinated by hydrogen bonding to the metal site, for which a dihedral angle of 120° is advantageous, and not by a metal–alcoholate bond (structure **F**). Comparison of the stereochemical data (Table 1) for dimethyldioxirane, and more appropriately the diperoxo metal complex of MTO speak against the titanium peroxo species **B** for the oxygen transfer.

3. Experimental

3.1. Materials

The TS-1 catalyst (Si/Ti ratio of 29) was prepared from silicium tetraethoxide, titanium tetrabutoxide, tetrapropylammonium hydroxide and water according to the literature procedure [23]. The MFI structure was proven by X ray analysis and the absence of any amorphous material by scanning electron micrography. The particle size of the cuboid-shaped crystallites ranged from 0.2 to 0.3 μm and the IR spectrum showed the characteristic absorption at 960 cm^{-1}. Some selected substrates were also epoxidized with a TS-1 batch prepared by a different procedure [24]. The results correspond within the error limit. The Ti-beta catalyst (4 wt% TiO_2, Si/Al = 140) was also obtained according to literature [25] and checked by the above-mentioned physical and spectroscopic methods. The allylic alcohols were prepared according to literature-known procedures [21].

3.2. General procedure for the TS-1 catalyzed epoxidations

A solution of 200 mg (2.00 mmol) of the allylic alcohol in 10 mL acetone was added dropwise to a suspension of 184 mg (2.00 mmol) UHP and 100 mg (50 wt%) TS-1 in 10 mL acetone at room temperature (ca. 20°C). The mixture was held at reflux for 20 h, the solids removed by filtration at room temperature through a glass filter, the residue was washed with acetone (2 × 10 mL), and the solvent was rotoevaporated (35°C, 20 Torr). The crude product was analyzed by NMR spectroscopy.

The Ti-beta-catalyzed epoxidations were carried out analogously in acetonitrile. The hydrogen peroxide was employed as 85% aqueous solution and the reaction temperature was ca. 25°C. For the experimental details on the MTO-catalyzed reactions [19] and the DMD oxidations [21] see the original literature.

Acknowledgements

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