Oxidation of thioethers and sulfoxides with hydrogen peroxide using TS-1 as catalyst

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A combined experimental and molecular simulation study of the oxidation of thioethers with hydrogen peroxide using Ti-containing zeolites as catalysts is described and discussed. Two aspects of reaction selectivity were explored. First, regioselectivity was studied for the oxidation of allyl methyl thioether with TS-1 as catalyst, and only products for the oxidation at sulfur, *i.e.*, the sulfoxide and sulfone, were observed. Second, shape-selective oxidation was studied using four isomeric butyl methyl thioethers. For *n*-, *iso*- and *sec*-butyl methyl thioethers the dominant product in the TS-1 catalysed reaction was the sulfone, but for *tert*-butyl methyl thioether, the dominant product was from partial oxidation to the sulfoxide. Molecular simulations were used to investigate the origin of this effect. For all substrates used in this study, the oxidation of the thioether to the sulfoxide was found to occur readily by a non-catalysed solution reaction and this was studied in detail. However, the oxidation of the sulfoxide to the sulfone was only observed in the catalysed reactions. It was observed that the non-catalysed reaction can be suppressed by carrying out the catalysed reaction in the presence of a base, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), that is too large to diffuse into the intracrystalline pore structure of TS-1. In the presence of DBU, the rate of reaction with TS-1 as catalyst was much lower and the relative ratios of the sulfoxide and sulfone products can be explained through a combination of intramolecular steric hindrance and the shape selectivity of the zeolite.

Introduction

Partial oxidation reactions are extensively used in industrial processes to functionalise hydrocarbon substrates, increasing their reactivity so that they can be utilised as intermediates in the chemical industry. The discovery of the titanium silicalite TS-1 by researchers at Enichem^{1,2} stimulated immense research interest into the partial oxidation of an extensive range of substrates under relatively mild reaction conditions using microporous and mesoporous materials containing cations known to be active for oxidation reactions,^{3,4} e.g., Ti,^{1,2} Cr⁵ and V.⁶ However, TS-1 remains the most widely studied material since, owing to the hydrophobic nature of its active sites, it can be used effectively with aqueous hydrogen peroxide. To date, TS-1 has been used for the oxidation of alkenes,⁷ alcohols,⁸⁻¹⁰ allylic alcohols,¹¹ phenols¹² and benzene.¹³ Recently, the intramolecular rearrangements of epoxides, that are typically a primary product for the oxidation of alkenes, have been studied.14 These previous investigations concentrated on oxidation at carbon centres, and relatively limited attention has been given to the oxidation at other atom centres, *e.g.*, sulfur in thioethers.¹⁵⁻¹⁸ The selective oxidation of thioethers, in particular dialkyl thioethers, has been studied by Hulea *et al.*¹⁹ and the oxidation of sulfoxides to sulfones has been studied by the same group using Ticontaining zeolites²⁰ to determine the effect of the solvent. In this paper, we present the results for the oxidation with hydrogen peroxide of a range of thioethers using TS-1 and Ti-zeolite β (Ti- β) as catalysts. A particular aspect of this study was to explore the possibility of shape-selective oxidation, a topic we previously highlighted for the epoxidation of allyl alcohol.²¹ Shape selectivity for the oxidation of thioethers was explored using four isomeric butyl methyl thioethers (n-, iso-, sec- and tert-butyl methyl thioether). In addition, the topic of regioselectivity was explored using allyl methyl thioether as substrate. For this molecule, two functional groups are available for oxidation by hydrogen peroxide, namely oxidation at the alkenyl double bond and oxidation at the sulfur atom. In addition, the study combined the results of the experimental studies with molecular simulations of the pore volume available to the substrates and products through the intracrystalline pore structure of TS-1 and Ti- β to confirm the origin of the observed shape selectivity effects.

Experimental

TS-1 (containing 2.4 mol% Ti) was prepared using a modified version of the method of Taramasso *et al.*¹ as described previously.^{11,22} The material was characterised using powder X-ray diffraction, infrared spectroscopy and scanning electron microscopy and was confirmed to be crystalline TS-1 with uniform orthorhombic crystallites 0.3 µm in diameter. Low Al Ti- β (containing 1.7 mol% Ti) was prepared following the method of Camblor *et al.*²³ The material was characterised using powder X-ray diffraction.

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Fig. 1 Oxidation of allyl methyl thioether with TS-1 at 21 °C. \blacklozenge , Thioether conversion with TS-1; \blacklozenge , sulfoxide selectivity with TS-1; \circlearrowright , sulfoxide selectivity with TS-1; \blacksquare , thioether conversion for non-catalysed reaction; \blacktriangle , sulfoxide selectivity for non-catalysed reaction; \bigtriangleup , sulfore selectivity for non-catalysed reaction.

Reactions of thioethers with hydrogen peroxide were carried out in a small scale batch reactor using standard conditions. In a typical reaction, the substrate (4.5 mmol), aqueous hydrogen peroxide (30%, 45 mmol), catalyst (0.015 g) and methanol (45 ml) were stirred together at 21 °C. Samples were removed at various times for analysis by gas chromatography (GC) and GC coupled with mass spectrometry (GC-MS).

Results

Oxidation of allyl methyl thioether using TS-1

The oxidation of allyl methyl thioether was investigated with TS-1 as catalyst using aqueous hydrogen peroxide. Allyl methyl thioether was selected for study as the molecule has two functional groups for oxidation, namely the carbon-carbon double bond and the sulfur atom. However, as can be seen from the representative results given in Fig. 1, no oxidation products of the carbon-carbon double bond were observed with TS-1 as catalyst. In the presence of TS-1, allyl methyl thioether is rapidly oxidised to the sulfoxide and sequentially to the sulfone. The oxidation of allyl methyl thioether in the absence of TS-1 catalyst was also investigated under the same experimental conditions. The results (Fig. 1) indicate that, again, no oxidation occurs at the carbon-carbon double bond but also, in the absence of the catalyst, the formation of the sulfone is significantly depressed.

Oxidation of butyl methyl thioethers using TS-1

The oxidation of the four isomeric butyl methyl thioethers was studied with TS-1 as catalyst to investigate the role of



Fig. 2 Oxidation of *n*-butyl methyl thioether with TS-1 at 21° C. Symbols as in Fig. 1.



Fig. 3 Oxidation of sec-butyl methyl thioether with TS-1 at 21 $^{\circ}$ C. Symbols as in Fig. 1.

shape selectivity in the catalysed process. The results for the catalysed and non-catalysed reactions are given in Fig. 2–5. As with allyl methyl thioether, the TS-1 catalysed reaction gave extensive formation of the sulfone, except for *tert*-butyl methyl thioether, for which selectivity to the sulfoxide was 100% after 1 h (Fig. 5) and only 7.6% conversion to the fully oxidised product was observed after reaction for 4 d. In contrast, in the absence of catalyst, the oxidation of the butyl methyl thioethers gave the sulfoxide almost exclusively and, even after several days of reaction, only 2–4% of the sulfone was formed.



Fig. 4 Oxidation of *iso*-butyl methyl thioether with TS-1 at $21 \degree$ C. Symbols as in Fig. 1.



Fig. 5 Oxidation of *tert*-butyl methyl thioether with TS-1 at 21 °C. Symbols as in Fig. 1.

Table 1 Oxidation of *tert*-butyl methyl thioether with TS-β at 21 °C

Time/	Conversion	Selectivity (%)		
min	(%)	Sulfoxide	Sulfone	
5	61.2	91.6	8.4	
15	86.5	81.2	18.8	
30	99.3	57.0	43.0	
60	100	43.8	56.2	
220	100	28.1	71.9	
300	100	19.7	80.3	
1440	100	0	100	

These results confirm that the oxidation of a thioether to a sulfoxide can proceed readily in the absence of a catalyst but the sequential oxidation of the sulfoxide to a sulfone requires an effective catalyst.

Oxidation of *tert*-butyl methyl thioether using Ti-β as catalyst

To investigate the oxidation of thioethers in a larger pore zeolite, *tert*-butyl methyl thioether was investigated with Ti- β and the results are given in Table 1. Ti- β has a pore structure with interlinking channels of cross-section 0.55×0.55 nm along the [011] direction and 0.76×0.64 nm along the [100] direction. It can, therefore, accommodate much larger molecules than can enter the pores of TS-1 (0.56×0.53 nm). In the more accessible pore volume of Ti- β , the sulfone is rapidly formed from sequential oxidation of the sulfoxide and so these results confirm the shape selectivity of the oxidation of *tert*-butyl methyl thioether with TS-1.

Oxidation of butyl methyl thioethers using TS-1 in the presence of 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU)

It is clear that oxidation of thioethers using H_2O_2 as oxidant with TS-1 or Ti- β as catalysts is complicated by a relatively rapid non-catalysed oxidation of the thioether to the sulfoxide. However, the sulfoxide is relatively stable with respect to non-catalysed oxidation. The non-catalysed reaction needs to be suppressed if the true effects of shape-selective oxidation using TS-1 are to be observed. This can be achieved if a strong base is incorporated in the reaction mixture, since this will deprotonate H₂O₂ leading to the production of the hydroperoxy anion, which is incapable of acting as an oxidant for these thioethers. Suitable strong bases include potassium carbonate and DBU.²⁴ Potassium carbonate was considered to be inappropriate for these TS-1 studies since the presence of potassium cations in solution could ion exchange the weak Brönsted site present in TS-1.²² DBU ($pK_a \approx 13$) is a very bulky molecule and molecular simulation calculations showed that DBU could not access the intracrystalline pore structure of TS-1. It is, therefore, an ideal base to suppress the noncatalysed reaction, since the shape-selective nature of TS-1 ensures that the active sites in the internal pores are not

affected by DBU. Unfortunately, equimolar amounts of DBU and hydrogen peroxide are required. In addition, it can be expected that the use of DBU may change the mechanism by which the oxidation proceeds since a different oxidising agent will be present. Hence the use of high pH and the different oxidising species can be expected to lead to a significant change in the rate of oxidation, and this is observed. However, the experiments with DBU were conducted to determine the relative selectivities of the catalysed reaction within the micropores of TS-1.

The oxidation of the butyl methyl thioethers in the absence of TS-1 in the presence of DBU (H_2O_2 : DBU = 1:1) was investigated under the same conditions as described above (Fig. 2–5). Even after a 24 h reaction time, no oxidation of the thioethers was observed. This confirms that DBU suppresses the non-catalysed oxidation of the thioether. The reactions were then carried out in the presence of TS-1 and the results are given in Table 2. The four butyl methyl thioethers all exhibit similar conversions in the presence of DBU (*ca.* 50% after 24 h of reaction), but there are significant differences in the selectivity to the sulfoxide and the sulfone. The selectivity to sulfone formation decreased in the order: n > iso - sec - sec - sec + tert-butyl methyl thioether.

Molecular simulations

To gain an improved understanding of the observed selectivity in the catalytic reaction, we carried out a series of calculations to assess the accessibility of the interior of the zeolite to the reactant molecules and the oxides produced. The structure of each molecule was initially optimised using MOPAC²⁵ with the PM3 Hamiltonian²⁶ using the eigenvector follower geometry optimiser. Structures were also obtained at the ab initio Hartree-Fock level using the GAMESS²⁷ program, with the standard double zeta plus polarisation (DZP)²⁸ basis functions. This provides a much richer basis for the description of the molecular orbitals compared with the MOPAC case, which is effectively a parameterised minimal basis set technique. In particular, the DZP basis provides d-functions on sulfur. The conformations used for each thioether are illustrated in Fig. 6 and the calculated geometry around the S atom for each molecule is given in Table 3. In general, the GAMESS-UK results give shorter S-C and S-O bonds although the maximum difference between the results from the two techniques for these molecules is only 0.05 Å for S-C and 0.06 Å for S-O. This indicates that even the simple semiempirical approach is able to give reasonable geometries for thioethers and their oxides. Test calculations using a DZ basis set in the ab initio calculation gave a general overestimation of the bonds to the sulfur atom by up to 0.2 Å compared with the results in Table 3. This indicates that polarisation basis functions are essential for obtaining reliable results from the ab initio approach. The semi-empirical method does give reasonable agreement with the higher level calculations and requires several orders of magnitude less computer time.

The occupiable pore volume for each molecule based on the GAMESS-UK DZP level molecular structures was calculated using the MSI Solids Characterise module within the InsightII package.²⁹ Only the pure silica frameworks were considered,

Table 2 Oxidation of butyl methyl thioethers with TS-1 in the presence of DBU at 21 °C for 24 h

	Conversion	Selectivity (%)		Product ratio
Substrate	(%)	Sulfoxide	Sulfone	sulfoxide : sulfone
<i>n</i> -Butyl methyl thioether <i>iso</i> -Butyl methyl thioether <i>sec</i> -Butyl methyl thioether	52.1 49.5 47.8	79.3 88.9 90.4 93.8	20.7 11.1 9.6	3.8 8.0 9.4



Fig. 6 Geometry optimised conformations from GAMESS-UK calculations on the isolated molecules: (a) *n*-butyl methyl thioether; (b) *sec*-butyl thioether; (c) *iso*-butyl methyl thioether; (d) allyl methyl thioether; (e) *tert*-butyl methyl thioether.



Fig. 7 Geometry optimised conformations from GAMESS-UK calculations on the oxidation products of (a) n-butyl methyl thioether and (b) *tert*-butyl methyl thioether. In each case the thioether is shown at the top of the diagram with the sulfoxide and sulfone below.

decrease in the accessible p at sulfur. This corresponds molecules as oxygen atom allyl methyl thioether a sm oxidation step but the oc both oxidation products.

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so the effect of extra framework cations on the available pore space was ignored, an approximation which should be valid for these low Al materials. Since the silica form is being used, we shall refer to the TS-1 structure by its generic structure type, MFI. We also used the pure achiral polymorph structure (polymorph B^{30}) for zeolite β . Both frameworks were taken from the MSI database. To calculate the occupiable volume, the unit cell of each zeolite was divided into a series of grid points with a separation of 0.5 Å. The probe molecule was then placed at each grid point in turn and rotated to attempt to find an orientation in which there was no steric conflict between the probe and the zeolite. The total number of grid points for which this is possible was then used to calculate the total volume of the unit cell that is occupiable by the adsorbate. The greater this volume, the easier it will be for the probe molecule to access the interior of the microporous material which contains the majority of the active sites. This method gives the volume of the framework which can be occupied by at least one molecular orientation. It differs from the idea of a kinetic diameter for a molecule, which is the pore diameter required to allow a molecule to occupy a location without significantly impeding its thermal motion. Neither method allows for the treatment of kinetic effects directly but simply gives an indication of the degree of restriction placed upon a molecule by the host. Full molecular dynamics calculations have been performed for relatively mobile alkane adsorbates in zeolites³¹ but the cost of such calculations for molecules whose dimensions are similar to the pore diameter is prohibitive.

The selectivity differences between these substrates for the catalysed reactions will arise from a combination of the electronic effect of differently branched butyl groups on sulfur, the effect of steric hinderance around sulfur due to substituent groups³² and the shape selectivity imposed by the pore. The pore access calculations can be used to assess the importance of the latter affect.

In the case of MFI, each C_4 substituted molecule shows a decrease in the accessible pore volume on successive oxidation at sulfur. This corresponds to the increasing steric bulk of the molecules as oxygen atoms are added (Fig. 7). In the case of allyl methyl thioether a small increase is observed for the first oxidation step but the occupiable volume remains high for both oxidation products. This indicates that the smallest probe molecule would not be strongly affected by the shape

Table 3 Geometries of thioethers and their oxides from MOPAC and GAMESS calculations⁴

Molecule		R–SMe/Å	RS–Me/Å	S–O/Å	C–S–C (°)
<i>n</i> -Butyl methyl thioether	М	1.826	1.801		101.7
	G	1.820	1.812	_	101.3
n-Butyl methyl sulfoxide	М	1.846	1.819	1.557	98.8
	G	1.812	1.803	1.500	98.9
<i>n</i> -Butyl methyl sulfone	Μ	1.828	1.794	1.468	99.1
	G	1.789	1.779	1.447	104.6
sec-Butyl methyl thioether	М	1.847	1.801	_	102.6
	G	1.835	1.813	_	103.4
sec-Butyl methyl sulfoxide	М	1.872	1.818	1.558	99.8
	G	1.831	1.804	1.501	101.5
sec-Butyl methyl sulfone	М	1.846	1.795	1.469	100.0
	G	1.800	1.782	1.448	106.9
iso-Butyl methyl thioether	М	1.824	1.801	_	103.9
	G	1.826	1.812	_	101.3
iso-Butyl methyl sulfoxide	М	1.854	1.819	1.560	99.6
	G	1.811	1.804	1.500	98.5
iso-Butyl methyl sulfone	М	1.827	1.797	1.469	98.0
	G	1.791	1.781	1.447	103.5
tert-Butyl methyl thioether	М	1.863	1.801	_	104.9
	G	1.846	1.815	_	103.9
tert-Butyl methyl sulfoxide	М	1.898	1.820	1.559	100.4
	G	1.847	1.805	1.502	102.1
tert-Butyl methyl sulfone	М	1.875	1.795	1.471	98.0
	G	1.824	1.785	1.449	108.8
Allyl methyl thioether	М	1.828	1.801	_	101.6
	G	1.820	1.810	_	99.5
Allyl methyl sulfoxide	М	1.851	1.819	1.556	98.5
	G	1.821	1.802	1.498	98.6
Allyl methyl sulfone	М	1.824	1.795	1.466	98.8
- *	G	1.788	1.782	1.445	103.2

^a M indicates MOPAC results, G indicates GAMESS-UK results, for the dioxides the two S=O bond lengths were always found to be equivalent to within 0.002 Å or less and so only a single value is quoted.

restrictions imposed by the microporous host during the oxidation process. The occupiable pore volume data (Table 4) also indicates that *n*- and *sec*-butyl methyl thioether have similar occupiable volumes for their sulfoxide and sulfones again suggesting that no shape selectivity should be expected in these cases. Only iso- and tert-butyl thioethers show significantly smaller occupiable volumes for the sulfone compared with the sulfoxide. This suggests that in these cases the pore shape of MFI will tend to prevent the creation of the bulky sulfone product and so influence the product selectivities. In the case of zeolite β all substrates show roughly equivalent occupiable volumes for the two oxide products, suggesting that no shape selectivity should be expected in this case.

Discussion

Oxidation of thioethers using hydrogen peroxide

Thioethers in the absence of TS-1 are oxidised by hydrogen peroxide to form the sulfoxide via a rapid non-catalysed reaction. The non-catalysed sequential oxidation of the sulfoxide

to the sulfone is not observed. In the presence of TS-1, oxidation to both the sulfoxide and sulfone is typically observed. The reactions were carried out with a reactant ratio of thioether to hydrogen peroxide of 1:10 and hence it is considered that the oxidation to the sulfoxide and sulfone can be represented by two sequential pseudo-first-order reactions:

thioether $\xrightarrow{k_1}$ sulfoxide $\xrightarrow{k_2}$ sulfone

The calculated rate constants for the non-catalysed and TS-1-catalysed reactions are given in Table 5. Since the catalysed and non-catalysed reactions are carried out under identical conditions except for the addition of the catalyst, the total observed rate constant (k_1) for the catalysed reaction can be considered to be a composite of the rate constant for the catalysed reaction $[k_1(cat)]$ and the non-catalysed reaction $[k_1(\text{non-cat})].$

$k_1 = k_1$ (non-cat) + k_1 (cat)

The non-catalysed reaction data gives the first of these terms directly and can then be used along with the catalysed

Table 4 Pore access results

	Cell	Available pore volume/Å ³ {% of total}			Ratio of %
R	Å ³	Thioether	Sulfoxide	Sulfone	sulfoxide: sulfone
MFI structure	5332				
<i>n</i> -Butyl methyl		1584{29.7}	1526{28.6}	1512{28.4}	1.007
sec-Butyl methyl		1449{27.2}	1212{22.7}	1174{22.0}	1.032
iso-Butyl methyl		1496{28.1}	1261{23.6}	967{18.1}	1.304
tert-Butyl methyl		820{15.4}	713{13.4}	590{11.1}	1.207
Allyl methyl		1617{30.3}	1622{30.4}	1574{29.5}	0.970
Zeolite β structure	4096	()	()	()	
<i>n</i> -Butyl methyl		1739{42.5}	1649{40.3}	1637{40.0}	1.008
sec-Butyl methyl		1665{40.6}	1665{40.6}	1512{36.9}	1.100
iso-Butyl methyl		1650{40.3}	1553{37.9}	1554{37.9}	1.000
tert-Butyl methyl		1591{38.8}	1266{30.9}	1177{28.7}	1.077
Allyl methyl		1689{41.2}	1715{41.9}	1727{42.2}	0.993

Table 5 Rate constants for TS-1 catalysed and non-catalysed oxidation of thioethers at 21 °C

Substrate	$k_1(\text{cat})/\text{s}^{-1}$	k_1 (non-cat)/s ⁻¹	k_2/s^{-1}
Allyl methyl thioether n-Butyl methyl thioether iso-Butyl methyl thioether sec-Butyl methyl thioether tert-Butyl methyl thioether	$9.0 \times 10^{-4} 13.3 \times 10^{-4} 2.2 \times 10^{-4} 0.15 \times 10^{-4} 5.8 \times 10^{-4}$	$5.2 \times 10^{-4} \\ 8.8 \times 10^{-4} \\ 4.8 \times 10^{-4} \\ 4.5 \times 10^{-4} \\ 16.0 \times 10^{-4}$	$\begin{array}{c} 1.6 \times 10^{-4} \\ 4.2 \times 10^{-4} \\ 0.6 \times 10^{-4} \\ 0.36 \times 10^{-4} \\ \underline{}_{a}^{a} \end{array}$
Not determined, rate negligible.			

reaction data to obtain the second term. Values of k_1 (non-cat) and k_1 (cat) for the reactions reported here are given in Table 5. Since sulfoxide oxidation is only observed for the catalytic reaction, the rate constant k_2 does not require compensation in this manner.

It is apparent that the order of reactivity for the catalytic formation of the sulfoxide from the butyl methyl thioether is n > tert - > iso - > sec-butyl methyl thioether. For the non-catalysed oxidation, *tert*-butyl methyl thioether is observed to be the most reactive for sulfoxide formation and, indeed, apart from *n*-butyl methyl thioether, the non-catalysed oxidation is the dominant process. The reactivity of the oxidation of the sulfoxide to the sulfone is very similar for the butyl methyl thioethers apart from *tert*-butyl methyl thioether, for which no sulfone is observed.

In the presence of DBU, the non-catalysed oxidation is totally suppressed and now the four butyl thioethers investigated have similar reactivities. The reaction rate is much lower than in the absence of DBU since, even after 24 h, only *ca.* 50% conversion was observed (Table 2). This lower reactivity is considered to be due to the high pH used which is known to deactivate TS-1.¹¹ It is clear that the hydroperoxy anion (OOH⁻) is much less reactive as an oxidant for the TS-1 catalysed reaction than the electrophilic HOOH species. However, these experiments are useful in demonstrating the selectivity of the oxidation processes occurring wholly within the micropores of TS-1.

Comments on regio- and shape selectivity

For the oxidation of allyl methyl thioether, only the products from the oxidation at sulfur are observed and, hence, the reaction is a clear example of regioselectivity. No oxidation of the carbon–carbon bond is observed. This is in contrast to the oxidation of allyl alcohol with TS-1,^{11,22} when it is found that glycidol can be formed with 100% selectivity and 20% yield under comparable reaction conditions. The pseudo-first-order rate constants for the formation of glycidol from allyl alcohol (21 °C, methanol as solvent, 10 : 1 hydrogen peroxide-to-substrate ratio) is $2.3 \times 10^{-4} \text{ s}^{-1}$. This is not significantly lower than the pseudo-first-order rate constant for the oxidation of allyl methyl thioether to the sulfoxide under the same conditions (9.0 × 10⁻⁴ s⁻¹). In view of this, it is clear that the sulfur deactivates the carbon–carbon double bond towards oxidation by the electrophilic oxidant hydrogen peroxide.

The presence of a heteroatom allylic to the carbon–carbon double bond is known to deactivate the substrate for TS-1 catalysed oxidation. For example, non-substituted alkenes react several orders of magnitude more rapidly than allylic alcohols.^{11,22} The relative ease with which sulfur is oxidised in thioethers can be expected as the sulfur lone pair electrons are more nucleophilic than the π electrons of the carbon–carbon double bond. This is well known from the non-catalysed oxidation of sulfides using monochloroperbenzoic acid as stoichiometric oxidant.³³ It is, however, interesting that, even when the sulfone is formed, no oxidation at the double bond is observed.

The pore access calculations suggest that the occupiable volumes for *tert*-butyl methyl thioether, sulfoxide and sulfone

in the MFI structure of TS-1 are less than for the other three butyl isomers (Fig. 7). In addition the space available to the sulfoxide is 1.2 times greater than to the sulfone which will be the most restricted of all the molecules studied. In the presence of DBU, oxidation will only take place in the pore space of the zeolite and we observe a high product ratio of sulfoxide to sulfone (Table 2) for tert-butyl methyl thioether compared with the other substrates. From the calculated occupiable volumes we suggest that this is due to the shape selectivity of the TS-1 catalyst which prevents the formation of the sulfone of the tert-butyl isomer. In the absence of DBU we have established that the non-catalysed reaction only proceeds as far as sulfoxide, and sulfone is only obtained as the major product in the presence of TS-1 catalyst. In the case of tertbutyl methyl thioether with TS-1 as catalyst, the second oxidation step is again prevented by the shape selectivity of the catalyst.

For Ti- β all the molecules studied have a much larger fractional pore occupiable volume than in TS-1 and the sulfoxideto-sulfone ratios are all near to unity. This suggests that, even for *tert*-butyl methyl thioether, no shape selectivity effects would be expected. In the presence of Ti- β we find that the conversion to sulfone for *tert*-butyl methyl thioether is observed from the beginning of the experiment and is complete after a 1 d reaction time (Table 1), confirming that shape selectivity is not present in the larger pore system.

In the case of *iso*-butyl methyl thioether with TS-1, the calculations indicate a ratio of 1.3 between the occupiable volumes of the sulfoxide and sulfone, although the individual occupiable volumes are larger than for the corresponding *tert*butyl isomers. In this case, too, then, we expect the shape selectivity of TS-1 to contribute to the observed selectivity toward the sulfoxide and it is interesting to note that the larger occupiable volumes for the two products correspond to a lower product ratio in Table 2.

The experimentally observed sulfoxide-to-sulfone product ratio for the sec-butyl methyl thioether case is actually higher than for the iso-butyl case and yet the occupiable volume calculations suggest that the two oxide products would have similar pore volumes available to them. In this case we would not expect, then, the pore size to restrict the second oxidation step. However, since the Ti catalytic centre in these materials is incorporated into the framework, it is possible that local steric interactions at the catalytic centre will influence reaction rate.³² Here the methyl group α to the sulfur atom in the secbutyl isomers will be more likely to inhibit reaction than the β -methyl of the *iso*-butyl molecules, particularly in the second oxidation for which the catalytic site will also have to accommodate the sulfoxide group. This may explain the lower k_2 rate constant (Table 5) for sec-butyl methyl sulfoxide compared with iso-butyl methyl sulfoxide despite the shape selectivity expected in the latter case.

Conclusions

We have demonstrated that regioselectivity to oxidation at sulfur is 100% for allyl methyl thioether. By a comparison of experimental product ratios and calculated occupiable volumes, we find that shape selectivity for *tert*-butyl and *iso*-butyl methyl sulfoxide reactions in TS-1 inhibits the formation

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