

Titanium-catalysed oxidation of thianthrene 5-oxide in heterogeneous (zeolites) versus homogeneous media: electrophilic versus template-mediated oxygen transfer

Waldemar Adam, Catherine M. Mitchell, Chantu R. Saha-Möller, Thangaraj Selvam, Oliver Weichold *

Institut für Organische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

Received 20 July 1999; received in revised form 13 September 1999; accepted 8 October 1999

Abstract

Large differences in the ratio of sulfide versus sulfoxide oxidation of thianthrene 5-oxide (SSO) have been observed for heterogeneous versus homogeneous Ti^{IV} catalysts; whereas the Ti-doped zeolites (heterogeneous) oxidise by means of an electrophilic species, sulfoxide coordination (template effect) for $\text{Ti}(\text{O}i\text{Pr})_4$ (homogeneous) masks the true electrophilic character of the metal oxidant. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Zeolites; Titanium; Thianthrene 5-oxide; Oxygen transfer; Sulfoxide coordination

1. Introduction

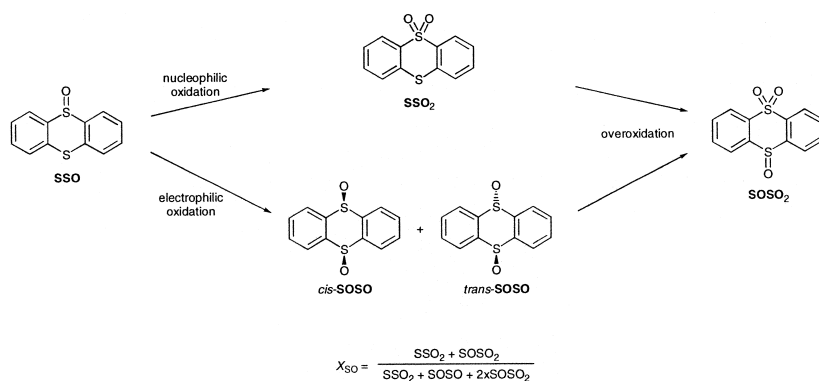
During the last decade, organic reactions within molecular sieves have attracted great interest [1]. Besides extensive use in industrial processes, zeolites have been employed in numerous laboratory-scale reactions, in particular, highly selective and efficient oxidations with H_2O_2 as oxygen donor. The redox molecular sieves TS-1 and Ti-beta are known to catalyse a variety of oxidations by H_2O_2 [2–4], whereas the mesoporous Ti-MCM-41 is advantageously used in combination with nonpolar, water-free solvents and *t*BuOOH as oxidant [5–7]. The

reactions studied so far include epoxidations, arene oxidations, C–H insertions, and sulfoxidations [8]. For both TS-1 and Ti-beta, peracid-type transition states have been proposed, based on the epoxidation of chiral allylic alcohols with H_2O_2 [2], while nothing is yet known for Ti-MCM-41.

Thianthrene 5-oxide (SSO) has been used as a mechanistic probe to assess the electronic character of oxidants (Scheme 1) [9]. Electrophilic oxidants predominantly attack diastereomeric bis-sulfoxides *cis*- and *trans*-SOSO ($X_{\text{SO}} \leq 0.3$), while nucleophilic ones attack SSO mainly at the sulfide sulfur to oxidise the SSO to the sulfone SSO_2 ($X_{\text{SO}} \geq 0.7$). Generally, the formation of *trans*-SOSO predominates over that of *cis*-SOSO due to the *peri*-hydrogen atoms, which encumber attack at the *cis* sulfide

* Corresponding author.

E-mail address: adam@chemie.uni-wuerzburg.de (O. Weichold).



Scheme 1. Electrophilic and nucleophilic oxidations of SSO.

lone pair. Since little is known on the electronic nature of the oxygen-transferring species in zeolite catalysts, it was of importance to employ the SSO probe for this purpose.

2. Experimental

The zeolites used in this study are from the following sources: the titanium-free zeolite Al-beta was provided by Dr. M. Sasidharan, St. Andrews (UK), as was the TS-1 zeolite (Si/Ti ratio is 44; pore size $5.3 \times 5.6 \text{ \AA}$) [10]. The Ti-beta (pore size $6.4 \times 7.6 \text{ \AA}$) [10] and Ti-beta (Al-free) zeolites (Ti content of 2 wt.% as TiO_2), and the microporous Ti-MCM-41 (pore size 32 \AA i.d.; 2 wt.% Ti as TiO_2 , no Al) were provided by Profs. A. Corma and H. García, Valencia (Spain). The Ti-beta-Na zeolite and the silylated Ti-MCM-41, denoted as Ti-MCM-41 (sil), were prepared according to literature procedures [11,12].

The oxidation of SSO to the *trans*-SOSO, *cis*-SOSO, and SSO₂ products was catalysed by the above-mentioned Ti-doped zeolites with H₂O₂ or *t*BuOOH as oxygen donors. The oxidation conditions were chosen in such a way as to minimise ($\leq 12\%$) the over-oxidation product SOSO₂. In a typical experiment, SSO (ca. 0.12 mmol) was dissolved in 10 ml of solvent, 1.0–2.0 equiv. of the oxygen donor (35% aq. H₂O₂ or 80% *t*BuOOH in *t*BuOO*t*Bu) was added while stirring, followed by 20 mg of the zeolite. The slurry was stirred for 12 h at 20–

40°C; subsequently, the zeolite was removed by means of a membrane filter (0.45 μm pore size), and washed with a 1:1 mixture of EtOH/CH₂Cl₂ (3 × ca. 1 ml). The product mixture was analysed by HPLC as previously described [9].

3. Results and discussion

Control experiments showed that no reaction occurred in the absence of zeolite (data not shown) nor when the titanium-free catalyst Al-beta was used (Table 1, entry 1). Thus, the titanium metal is essential for the activation of H₂O₂, and direct oxidation of the substrate by H₂O₂ does not take place. The oxidation of SSO occurring inside the zeolite channels or cavities and not on the outer surface was unequivocally shown in the case of TS-1 as catalyst (entry 2). With TS-1/35% H₂O₂, no conversion was observed, possibly because of the difficulty of the substrate to enter the channels of the zeolite. Semi-empirical AM1 calculations (the Vamp6.0 program for Iris Indigo work stations was used) revealed that the transannular distance between the two H atoms on the same aromatic ring of SSO is 5 Å, which is slightly smaller than the width of the channel. Thus, even if SSO were to enter the TS-1 zeolite, it would occupy the available space and it should be unlikely that the transition state for oxygen transfer be formed.

Table 1

Oxidation of thianthrene 5-oxide (SSO) to the corresponding sulfoxides and sulfones by titanium catalysts^a

Entry	Catalyst	Oxygen source ^b	T (°C)	M.b. ^{c,d} (%)	Conv ^d (%)	Product distribution (%)			X _{SO} ^e
						ΣSOSO ^f	SSO ₂ ^g	SOSO ₂ ^h	
1	Al-beta ⁱ	35% H ₂ O ₂ (2.0)	40	80	–	–	–	–	–
2	TS-1	35% H ₂ O ₂ (2.0)	40	92	–	–	–	–	–
3	Ti-beta ^j	35% H ₂ O ₂ (2.0)	40	93	36	93	0	7	0.07
4	Ti-beta ^k	35% H ₂ O ₂ (2.0)	40	≥ 95	32	88	3	9	0.11
5	Ti-beta-Na	35% H ₂ O ₂ (2.0)	40	≥ 95	16	88	4	8	0.11
6	Ti-beta (Al-free)	35% H ₂ O ₂ (2.0)	20	≥ 95	14	84	5	11	0.14
7	Ti-MCM-41	35% H ₂ O ₂ (1.0)	20	≥ 95	27	94	0	6	0.06
8	Ti-MCM-41 (sil)	35% H ₂ O ₂ (1.0)	20	82	43	83	6	11	0.15
9	Ti-beta (Al-free)	80% tBuOOH (2.0)	20	91	3	81	19	0	0.19
10	Ti-MCM-41	80% tBuOOH (1.0)	20	≥ 95	22	81	10	9	0.17
11	Ti-MCM-41 (sil)	80% tBuOOH (1.0)	20	89	51	80	12	8	0.18
12	Ti(OiPr) ₄	80% tBuOOH (0.5)	20	≥ 95	13	46	46	8	0.50

^aCH₃CN was used as solvent in entry 2, for all other entries, CH₂Cl₂ was employed; reaction time was 12 h for entries 1–11, and 20 min for entry 12; the amount of over-oxidation product SOSO₂ was kept low (ca. 10%), since correction for this would falsify the chemoselectivity.

^bEquivalents of oxidants are given in parentheses.

^cM.b. = mass balance.

^dMass balances, conversions, and product distributions were determined by HPLC analysis on an RP-18 column with H₂O/CH₃CN/CH₃OH (55:25:20) as eluent and 1-phenyl-1-penten-3-one as internal standard, detected at 254 nm, error ± 3% of the stated values.

^eX_{SO} = sulfoxide oxidation/total oxidation; calculated according to Ref. [9].

^fSum of *cis*- and *trans*-5,10-dioxides.

^g5,5-Dioxide.

^h5,5,10-Trioxides.

ⁱSi/Al ratio is 13.

^jSi/Al ratio is 125.

^kSi/Al ratio is 114.

^l5 mol% of Ti(OiPr)₄ was used.

For all titanium-doped catalysts, *trans*-SOSO was obtained predominantly (*trans*:*cis* ≤ 5.7), while the sulfone SSO₂ was only a minor product (≤ 12%). For instance, the oxidation system Ti-beta/35% H₂O₂ gave a product ratio (*trans*-SOSO/*cis*-SOSO/SSO₂/SOSO₂) of 68:25:0:7 (entry 3). No significant change in the product distribution was observed when the Si/Al ratio of the Ti-beta zeolite was varied (entries 3 and 4). Similar results were also obtained with the less Brønsted-acidic, Na-exchanged Ti-beta-Na and the less Lewis-acidic, Al-free Ti-beta with H₂O₂ as oxygen donors (entries 5 and 6). The X_{SO} values, which reflect the extent of oxidation at the SO site in SSO, lie between 0.07 and 0.14 for these transformations, which unequivocally indicates an electrophilic oxidant.

The selectivity data for the catalysts Ti-MCM-41 and Ti-MCM-41 (sil) with 35% H₂O₂ as oxidant are in a similar range to those with the Ti-beta zeolites (X_{SO} = 0.06 and 0.15; entries 7 and 8). For Ti-MCM-41 and Ti-MCM-41 (sil), H₂O₂ is not commonly used as oxygen donor, but rather *t*BuOOH (in contrast to Ti-beta) [5–7]. With *t*BuOOH (entries 9–11), the selectivity of SOSO versus SSO₂ with Al-free Ti-beta, Ti-MCM-41, and silylated Ti-MCM-41 is only slightly decreased compared to when H₂O₂ is employed (entries 6–8). The low X_{SO} values indicate that these oxidation systems act as electrophilic oxidants.

For comparison of these zeolite results with a homogeneous Ti^{IV} catalyst, the commonly used oxidant Ti(OiPr)₄/*t*BuOOH was employed (entry 12). It is mechanistically significant to note

that the selectivity of sulfoxide versus sulfide oxidation with this homogeneous system is in stark contrast to those observed with the heterogeneous oxidants. While all the heterogeneous catalysts give X_{SO} values < 0.20 (little sulfoxide oxidation), for the homogeneous $\text{Ti}(\text{O}i\text{Pr})_4/t\text{BuOOH}$, X_{SO} is 0.50 (appreciable sulfoxide oxidation). Thus, the spatial constraints in the zeolite interior significantly alter the chemoselectivity, particularly evident for entry 10 [Ti-MCM-41/ $t\text{BuOOH}$] and entry 12 [$\text{Ti}(\text{O}i\text{Pr})_4/t\text{BuOOH}$], for which the SOSO/SSO_2 selectivity drops from 89:11 to 50:50.

The larger amount of SSO_2 in the $\text{Ti}(\text{O}i\text{Pr})_4$ -catalysed process is attributed to the propensity of sulfoxides to coordinate to $\text{Ti}(\text{O}i\text{Pr})_4$. Such coordination of the sulfoxide oxygen to the titanium promotes oxygen transfer at the sulfoxide site through a template effect, that is, the simultaneous coordination to titanium of both the oxygen acceptor and the oxygen donor (Fig. 1, structure A). Notable evidence for such ligation of the sulfoxide to the Ti catalyst comes from studies on the sulfoxidation with $\text{Ti}(\text{O}i\text{Pr})_4$ and optically active hydroperoxides [13] as well as computational work [14]. Without such a template effect, an attack at the more electron-rich sulfide sulfur should be favoured and the genuine electrophilic nature of these transition-metal oxidants becomes apparent [13,15,16].

Previously, evidence for the coordination of sulfoxides to the titanium in the case of $\text{Ti}(\text{O}i\text{Pr})_4$ was provided by experiments conducted in the presence of additives, in which the latter suppress sulfur coordination and the template effect [13]. In our case for the zeolites, the addition of ligands such as water or DMSO did not cause any significant shift in the product distribution; therefore, we propose that such substrate coordination does not take place in zeolites.

The mode of attack, which we propose for the oxidation of SSO in zeolites (Fig. 1, structure B), occurs mainly at the lone pairs of the sulfide sulfur, as expected for an electrophilic oxidant. Presumably, steric constraints around the lattice-bound titanium in the zeolite interior shield the sulfoxide from coordination (Fig. 1, structure C) and, thus, no template effect operates to mask its true electrophilic nature. A similar argument also applies to the possible coordination of the sulfide functionality in SSO to the metal centre (the coordination of sulfides to titanium is known [17–19]). Besides these steric effects, ligand exchange inside zeolites occurs only with small, polar molecules like H_2O , H_2O_2 , and MeOH , in contrast to $\text{Ti}(\text{O}i\text{Pr})_4$, for which more bulky ligands, for example, isopropylate and *tert*-butylate, are readily exchanged [5]. For these reasons, the ligand exchange with the large SSO is encum-

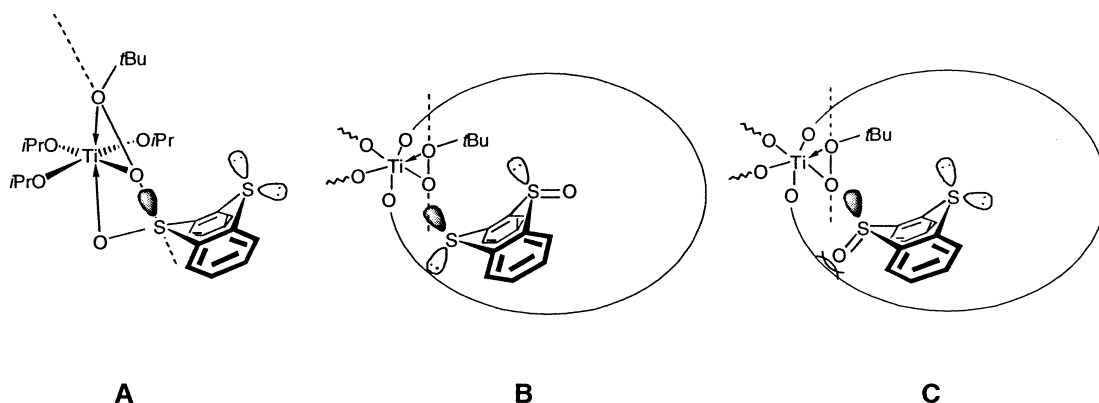


Fig. 1. Oxidation of SSO with $t\text{BuOOH}$ catalysed by $\text{Ti}(\text{O}i\text{Pr})_4$ (A) and Ti-MCM-41 zeolite (B,C). $\text{S}_{\text{N}}2$ attack of the lone pair takes place along the axis of the O–O-bond (dotted line).

bered even for the larger pore-sized Ti-MCM-41; additionally, the lattice-bound titanium atom is sufficiently shielded from coordination with the **SSO** substrate and predominantly **SOSO** is formed. The fact that the same chemoselectivity is observed for the much larger pore-sized Ti-MCM-41 and the Ti-beta zeolite implicates that the spatial constraints derive from the lattice-wall rather than cage-size effects (similar **SOSO/SSO₂** product ratios). This is further substantiated in that the reported reduction of the pore size and pore volume by trimethylsilylation of the inner surface was found not to alter the **SOSO/SSO₂** product ratio (entries 10 and 11).

4. Conclusion

It was demonstrated that the catalytic heterogeneous oxidation of **SSO** by H_2O_2 and *t*BuOOH in Ti-doped zeolites takes place inside the zeolite channels. Due to the steric constraints around the lattice-bound titanium atom, substrate coordination is obstructed and, thus, no template effect operates. This stands in stark contrast to the corresponding homogeneous catalytic oxidation with $\text{Ti}(\text{O}i\text{Pr})_4/t\text{BuOOH}$, for which such a template effect masks the true electrophilic nature of the metal oxidant.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (SFB 347 'Selektive Reaktionen Metall-

aktivierter Moleküle') and the Fonds der Chemischen Industrie for generous financial assistance. T.S. thanks the Alexander-von-Humboldt Foundation for a postdoctoral research fellowship (1998–1999).

References

- [1] I.W.C.E. Arends, R.A. Sheldon, M. Wallau, U. Schuchardt, *Angew. Chem., Int. Ed. Engl.* 36 (1997) 1144.
- [2] W. Adam, A. Corma, T.I. Reddy, M. Renz, *J. Org. Chem.* 62 (1997) 3631.
- [3] T.I. Reddy, R.S. Varma, *J. Chem. Soc., Chem. Commun.* (1997) 471.
- [4] V. Hulea, P. Moreau, F. Di Renzo, *Stud. Surf. Sci. Catal.* 108 (1997) 361.
- [5] L.Y. Cheng, G.K. Chuah, S. Jaenicke, *Catal. Lett.* 50 (1998) 107.
- [6] M.A. Cambor, A. Corma, P. Esteve, A. Martínez, S. Valencia, *J. Chem. Soc., Chem. Commun.* (1997) 795.
- [7] T. Blasco, A. Corma, M.T. Navarro, J. Pérez-Pariente, *J. Catal.* 156 (1995) 65.
- [8] A. Corma, *Chem. Rev.* 97 (1997) 2373.
- [9] W. Adam, D. Golsch, *Chem. Ber.* 127 (1994) 1111.
- [10] T. Blasco, M.A. Cambor, A. Corma, J. Pérez-Pariente, *J. Am. Chem. Soc.* 115 (1993) 11806.
- [11] A. Corma, P. Esteve, A. Martínez, *J. Catal.* 161 (1996) 11.
- [12] T. Tatsumi, K.A. Koyano, N. Igarashi, *J. Chem. Soc., Chem. Commun.* (1998) 325.
- [13] W. Adam, M.N. Korb, K.J. Roschmann, C.R. Saha-Möller, *J. Org. Chem.* 63 (1998) 3423.
- [14] M. Bonchio, S. Calloni, F. Di Furia, G. Licini, G. Modena, S. Moro, W.A. Nugent, *J. Am. Chem. Soc.* 119 (1997) 6935.
- [15] J.-M. Brunel, H.B. Kagan, *Synlett* (1996) 404.
- [16] J.-M. Brunel, H.B. Kagan, *Bull. Soc. Chim. Fr.* 133 (1996) 1109.
- [17] G.W.A. Fowles, D.A. Rice, J.D. Wilkins, *J. Chem. Soc. A* (1971) 1920.
- [18] O. Bortolini, C. Campello, F. Di Furia, G. Modena, *J. Mol. Catal.* 14 (1982) 63.
- [19] O. Bortolini, F. Di Furia, G. Modena, *J. Mol. Catal.* 16 (1982) 61.