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ARTICLE TYPE

Selective sulfoxidation with hydrogen peroxide catalysed by a titanium catalyst

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A moisture tolerant cyclopentadienyl-silsesquioxane titanium complex efficiently catalyses the selective oxidation of various types of sulfides to either sulfoxides (TOFs up to 32.530 h^{-1}) or sulfones with H_2O_2 (30% in water), under mild conditions.

Introduction

The development of highly efficient catalytic systems for the oxidation of sulfides is of much current interest because the final products, sulfoxides and sulfones, are important intermediates for the synthesis of chemically and biologically significant molecules,[1] and also in the context of desulfurisation of fuels.[2]

The use of an environmentally benign oxidant like H_2O_2, represents an important goal in oxidation reactions, since it is not toxic, cheap and forms water as the only by-product.[3] Furthermore, the selective synthesis of sulfoxides over the fully oxidised sulfones represents another important challenge.

In recent years, some homogeneous H_2O_2-based catalytic systems mediated by transition metals for the oxidation of sulfides have been reported in the literature.[4,5] However, most of them present disadvantages, such as the use of excess of oxidant, low chemoselectivity, and limited applicability. Noteworthy are the efficient catalytic systems based on Ti,[6] V,[7] and Fe[8] using equimolecular amount of H_2O_2.

Recently, we disclosed the excellent performance of robust titanium cyclopentadienyl-silsesquioxanes in olefin epoxidation using H_2O_2 as oxidant.[9] For the first time, we demonstrated the applicability of H_2O_2 as oxidant in reactions catalysed by titanium-silsequioxanes. Encouraged by these exciting results, we decided to explore further their catalytic activity in oxidation processes. Herein, we report an efficient method for the selective oxidation of sulfides to either sulfoxides or sulfones under green conditions, using H_2O_2 as oxidant and methanol as solvent, with the titanium complex $[Ti\{\eta^5\text{-}C_5H_4SiMe_2OPh_7Si_7O_{11}\text{-}\kappa^2O_2\}Cl]$ **1** (Figure 1). To the best of our knowledge, this is the first report on the oxidation of sulfides by titanium silsesquioxane complexes using aqueous H_2O_2 as the primary oxidant. So far, the use of titanium silsesquioxanes in oxidation reactions has been limited to catalytic epoxidation of olefins.[10-14]

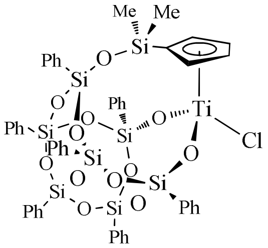


Figure 1 Titanium cyclopentadienyl-silsesquioxane complex **1**

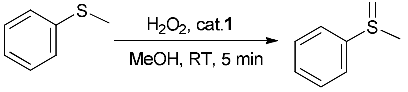
Results and discussion

We first investigated the oxidation of methylphenylsulfide (thioanisole) as a model substrate to explore the potential of **1** as sulfoxidation catalyst and optimise reaction conditions. Such oxidation was initially performed in methanol using a 0.5 mol% **1** loading, and 1 equiv of H_2O_2 (30% in water) at ambient temperature. We were pleased to find that thioanisole was quantitatively and chemoselectively oxidised to methylphenylsulfoxide in 5 min (Table 1, entry 1). The reaction mixture was examined after 24 h, confirming that no over oxidation process to the corresponding sulfone occurred. In addition, blank experiments confirmed that no reaction took place in the absence of catalyst.

The catalyst loading could be lowered to 0.01 mol% (Table 1, entry 4) without appreciable deterioration of the effectiveness of the catalyst, achieving turnover frequency (TOF) values up to 32530 h^{-1}. These TOF numbers represent among the highest reported for titanium catalysed reactions.[6]

We investigated the reuse and the selectivity of the catalyst by adding to the reaction mixture, new charges of substrate and oxidant in a ratio 1:1. Interestingly, the catalyst was reused for up to fourteen cycles without any loss in its activity and selectivity. The total turnover attained was 2800. No sulfone was present in the reaction mixture after being stirred for ca. 6 h, indicating the remarkable chemoselectivity and stability of our catalyst under the reaction conditions.

Table 1. Selective sulfoxidation of thioanisole to methylphenylsulfoxide catalysed by **1**[a]

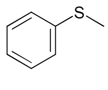
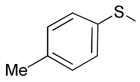
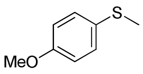
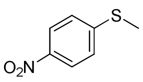
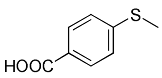
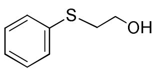
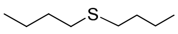
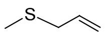
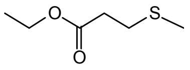


Entry	Cat. (mol%)	%Yield[b]	TOF[c]
1	0.5	>99	2385
2	0.25	>99	4771
3	0.1	58	6987
4	0.01	27	32530

[a]All reactions were carried out with 0.54 mmol of thioanisole and 1 equiv. of H_2O_2 (30% aqueous solution) in MeOH at ambient temperature in 5 min.[b]Yield determined by ^{1}H NMR spectroscopy using mesitylene (0.26 mmol) as internal standard.[c]TOFs (turnover frequencies) calculated at 5 min of reaction.

To explore the scope of **1** as sulfoxidation catalyst, we studied the oxidation of a wide variety of substrates with aqueous hydrogen peroxide, under the optimised reaction conditions found for thioanisole (0.25 mol% of **1**, 1 equiv. of H_2O_2, in methanol, and at room temperature). As summarised in Table 2, various aryl-alky (Table 2, entries 1-6) and dialkyl sulfides (Table 2, entries 7-9) were selectively oxidised in excellent yields (98-85%) within short reaction times (5-60 min). It is worthy to emphasise, the high tolerance displayed by **1** toward sensitive functional groups such as C=C, OH, OMe, N_2O, COOEt or COOH. However, when using this protocol for oxidation of thiophene derivatives (benzothiophene and dibenzothiophene), the corresponding sulfones were formed along with the sulfoxides almost simultaneously. The low selectivity observed with diaryl sulfides is a general behaviour in electrophilic oxidations.[15]

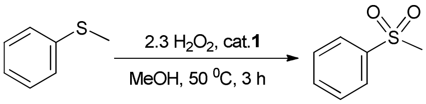
Table 2. Selective oxidation of sulfides to sulfoxides catalysed by **1**[a]

Entry	Substrate	t (min)	%Yield[b]
1		5	98
2		5	87
3		5	88
4		60	98
5		30	88
6		30	97
7		5	98
8		15	85
9		15	87

[a]All reactions were carried out with 0.54 mmol of substrate and 1 equiv. of H_2O_2 (30% aqueous solution) in MeOH at ambient temperature using 0.25 mol% of catalyst.[b]Isolated yields.

Based on these results, we decided to pursue the oxidation of sulfides to sulfones by increasing the substrate:oxidant molar ratio. Thus, when the oxidation of thioanisole was performed in methanol using 0.5 mol% **1** loading, and 2 equiv of H_2O_2 (30% in water) at room temperature, a mixture of the sulfoxide and sulfone was observed. Nevertheless, we were delighted to find that a slight increment of oxidant amount and reaction temperature, up to 2.3 equiv. and 50 ºC respectively, led to quantitative oxidation of thioanisole to methylphenylsulfone in a reasonable short reaction time (>99% yield in 3 h, Table 3, entry 1). Remarkably, a quasi-equivalent amount of H_2O_2 oxidant was sufficient to achieve the 99% yield of sulfone, indicating the high efficiency of the oxidation. The effect of catalyst amount on reaction rate was evaluated in methanol; decreasing the amount of catalyst to 0.25 and 0.1 mol% significantly slowed down the oxidation process (Table 3, entries 2 and 3, respectively). The oxidation in different solvents under the optimal reaction conditions was also investigated. As shown in Table 3, methanol and acetonitrile yielded quantitative methylphenylsulfone in 3 h, while lower yields were obtained in dichloromethane and acetone (Table 3, entries 1, 4, 5, and 6, respectively).

Table 3. Optimisation of reaction conditions for oxidation of thioanisole to methylphenylsulfone catalysed by **1**[a]

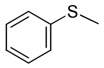
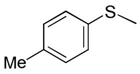
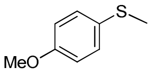
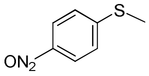
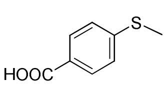
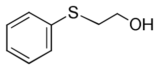
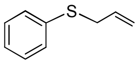
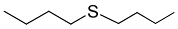
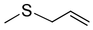
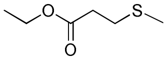
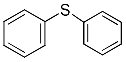
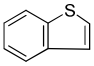
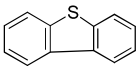


Entry	Cat. (mol%)	%Yield[b]	Solvent
1	0.5	>99	MeOH
2	0.25	76	MeOH
3	0.1	53	MeOH
4	0.5	>99	NCMe
5[c]	0.5	56	CH_2Cl_2
6[c]	0.5	60	acetone

[a]All reactions were carried out with 0.54 mmol of thioanisole and 2.3 equiv. of H_2O_2 (30% aqueous solution) in MeOH in 3 h at 50 ºC.[b]Yield determined by ^{1}H NMR spectroscopy using mesitylene (0.26 mmol) as internal standard.[c]Reaction time 5 h.

Further we explored the scope of the oxidation of sulfides to sulfones with a wide variety of substrates under the optimised reaction conditions, using 0.5 mol% of catalyst **1** and 2.3 equiv. of H_2O_2 in methanol at 50 °C. Various alkyl-aryl (Table 4, entries 1-7) dialkyl (Table 4, entries 8-10), and diaryl (Table 4, entries 11-13) sulfides were oxidised to the corresponding sulfones with high efficiency, quantitatively within relatively short periods of time. Results are summarised in Table 4. Significantly, challenging compounds such as benzothiophene (BTP) and dibenzothiophene (DBT) were also oxidised to the corresponding sulfones in quantitative yields (Table 4, entries 12 and 13), although higher amount of catalyst was required for these substrates (2 mol% of **1**).

Table 4. Selective oxidation of sulfides to sulfones catalysed by **1**[a]

Entry	Substrate	t (h)	%Yield[b]
1		3	>99(98)
2		3	>99(70)
3		3	>99(85)
4		5	>99(84)
5		3	>99(85)
6		0.5	>99(95)
7		3	>99(72)
8		3	>99(98)
9		3	>99(97)
10		3	>99(91)
11		5	>99(60)[c]
12		5	>99(56)[c]
13		5	>99(70)[c]

[a]All reactions were carried out with 0.54 mmol of substrate and 2.3 equiv. of H_2O_2 (30% aqueous solution) with 0.5 mol% of catalyst **1** in MeOH at 50 ºC.[b]Yield determined by ^1H NMR spectroscopy using mesitylene (0.26 mmol) as internal standard; the numbers in parentheses are isolated yields.[c]Yield determined by GC analysis, reactions done with 2 mol% of catalyst **1**. The numbers in parentheses are isolated yields.

The general accepted mechanism for titanium-based oxidation catalysts involves the formation of a peroxo-titanium active species, in which the peroxo group is η^2 coordinated to the metal centre.[6] In order to get an insight into the species formed during the course of the reaction, catalyst **1** was treated with a 10-fold excess of H_2O_2 (30% in water) in acetonitrile at ambient temperature, and the reaction was followed by MS-ESI. The MS-ESI spectrum of **1** displays an intense peak at *m/z* 1096.8 corresponding to the titanium ion $[C_{49}H_{45}O_{12}Si_8Ti]^+$, $[M\text{-}Cl]^+$. Immediately after addition of H_2O_2, a new intense peak at *m/z* 1146.9 appeared in the mass spectrum while the peak at 1096.8 completely disappeared from the spectrum. The peak at *m/z* 1146.9 displayed the characteristic pattern arising from the natural abundance of titanium isotopes and it was assigned to the aquo peroxo-titanium species $[M(O\text{-}O)(H_2O)]^+$, which might be the catalytic active species. The MS-ESI experiments were performed in acetonitrile instead of methanol (the solvent used in the catalytic essays) because the poor solubility of the titanium species in methanol. Recently, Licini and Zonta have reported an elegant mechanistic study of the oxidation of sulfides with H_2O_2 in methanol using a titanium(IV) aminotriphenolate complex.[16] Based on kinetic experiments and theoretical calculations, they proved the fundamental role of methanol in the activation of H_2O_2 in sulfoxidations. In order to clarify if MeOH could coordinate to the titanium centre of **1**, we decided to study the stability of **1** in methanol by preparing a solution of **1** in deuterated chloroform, adding some drops of methanol, and monitoring the sample by NMR spectroscopy. We observed that complex **1** was maintained intact after 24 h in methanol at room temperature. Complex **1** exhibited also remarkably stability towards water; wet methanol solutions of **1** could be kept for 48 h without noticing any decomposition. These observations corroborate that methanol does not coordinate to complex **1**. The use of methanol does not seem to accelerate the oxidation reaction, since similar activity of catalyst **1** was found when the reactions were performed in acetonitrile (Table 3, entries 1 and 4).

Conclusions

In summary, the titanium complex **1** acts as a highly efficient catalyst for the chemoselective oxidation of sulfides either to sulfoxides or sulfones, with near stoichiometric amount of aqueous H_2O_2. This method represents the first example of a titanium-silsesquioxane complex catalysing the oxidation of sulfides under environmentally friendly (H_2O_2/methanol) and mild conditions. Noteworthy, catalyst **1** showed remarkably stability towards water, being reused for up to fourteen cycles without appreciable lost in its activity. We are currently investigating the potential of this kind of catalysts in other oxidation processes with hydrogen peroxide.

Experimental Section

Materials and methods

Compound $Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3$ was synthesised according to the method described in the literature.[17] All other reagents were used as received from commercial suppliers without further purification. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques and solvents were purified from appropriate drying agents. Deuterated solvents were degassed and stored over molecular sieves. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker Avance III 400 MHz. Electrospray mass spectra (ESIMS) were recorded on a Micromass Quatro LC instrument; nitrogen was employed as drying and nebulising gas.

Synthesis of $Ti(\eta^5\text{-}C_5H_4SiMe_2OPh_7Si_7O_{11}\text{-}\kappa^2O_2)Cl$, 1. A solution of NEt_3 (0.40 mL, 2.88 mmol) in CH_2Cl_2 (25 mL) was added to a mixture of $Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3$ (0.3 g, 0.96 mmol) and $Ph_7Si_7O_9(OH)_3$ (0.89 g, 0.96 mmol), finely mashed. The reaction mixture was heated at 70 ºC and stirred for 3 days. The resultant suspension was cooled down to room temperature and the ammonium salt removed by filtration. The filtrate was concentrated under vacuum and the residue was extracted into toluene (5 x 15 mL). The toluene solution was concentrated (35 mL) and cooled at -20 °C to give **1** as a pale yellow solid. Yield: 1.03 g (95%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.43 (s, 6H; $SiMe_2O$), 6.89, 6.97 (m, 2 x 2H; C_5H_4), 7.33, 7.41, 7.66 (m, 14H, 7H, 14H; Ph). ^{13}C NMR ($CDCl_3$): δ 0.9 ($SiMe_2O$), 123.8, 124.1, 125.8, 125.9, 126.6, 126.9, 127.7, 127.8, 127.9, 128.0, 128.2, 128.5, 128.9, 129.1, 130.2, 130.4, 130.43, 130.5, 130.6, 130.7, 131.6, 131.9 (C_5H_4 and C_6H_5). ^{29}Si NMR ($CDCl_3$): δ – 6.7 ($SiMe_2O$), – 70.3, – 69.4, – 67.3, – 66.5, – 65.8. Anal. Calc for $C_{49}H_{45}ClO_{12}Si_8Ti$ (1133.92): C, 51.86; H, 3.97. Found: C, 51.83; H, 4.01. MS (ESI-TOF): *m/z* $[M\text{-}Cl]^+$ calcd for $C_{49}H_{45}O_{12}Si_8Ti$, 1097.0; found: 1096.8 $[M\text{-}Cl]^+$.

Catalytic oxidation of sulfides to sulfoxides. To a stirred mixture of catalyst, sulfide (0.54 mmol), and mesitylene (0.26 mmol, 37 µl) in MeOH (1.25 mL), was added 1 equiv of H_2O_2 (30% aqueous solution, 60µl). The course of the reaction was monitored by ^{1}H NMR or analyzed by GC. In the latter case, aliquots of 0.1 mL were taken at regular intervals, treated with of MnO_2 in 0.4 mL of CH_2Cl_2, and filtered over celite previously to be analysed. The products were characterized by ^{1}H and ^{13}C NMR spectroscopy.

Catalytic oxidation of sulfides to sulfones. A procedure similar to that described for sulfoxides was adopted, by using 2.3 equiv. of H_2O_2 (30% aqueous solution**,** 140µl) and heating to 50 °C.
To isolate the final sulfone o sulfoxide, the above-motioned reactions were performed without mesitylene and kept until completion of the reaction. The final mixture was treated with of MnO_2 in 2 mL CH_2Cl_2, filtered over a celite pad, and volatiles were removed under vacuum to afford the corresponding sulfone or sulfoxide. The data produced were identified by comparison of the NMR spectra with reported data.[18]

Acknowledgements

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Notes and references

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† Electronic Supplementary Information (ESI) available: NMR and MS-ESI spectra of coumpounds.

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