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On the biocatalytic cleavage of silicon–oxygen bonds: A substrate structural approach to investigating the cleavage of protecting group silyl ethers by serine-triad hydrolases

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ABSTRACT

The biotransformation of compounds containing silicon has recently been a subject of much interest. In this study, a variety of commercially available serine hydrolases were tested for their ability to catalyse the hydrolysis of the silicon–ether bond in a variety of silyl ethers. The hydrolysis of trimethylethoxysilane in buffer was not found to be accelerated by the presence of trypsin, chymotrypsin, or a variety of other lipase and protease enzymes. Cleavage of a range of alternative silyl ether substrates, including a trimethylsilyl (TMS) ether, by these hydrolases was also not observed, but, interestingly, only two of the enzymes tested were able to cleave a *t*-butyl α,α,α-carboxylate that was approximately isosteric with the TMS-protected substrate. This suggests that the cleavage of Si–O bonds by serine hydrolases, such as the cathepsin homolog silicatein-α, may be in part limited by steric effects, as the reactive centre in the substrate is always, by analogy to C-centred substrates, tertiary, and thus inherently sterically demanding regardless of the putative catalytic competence of the enzymes.

1. Introduction

The biotransformation of compounds containing silicon has recently been a subject of much interest [1,2]. In addition to reports of biotransformations of organic substrates that contain silicon [3,4] and the resolution of Si-centred chiral molecules by lipases [5], the biocatalytic cleavage of the Si–O bond itself has been unearthed as an interesting biocatalytic reaction that is of emerging relevance. Much of this work has been prompted by an interest in the mechanisms by which siliaceous diatoms and marine sponges are able to sequester silicon from the marine environment and to biogenetically catalyse the polymerisation of silicates to yield complex and beautiful microscopic architectures, the precise dimensions of which exceed the current capabilities of human engineering [6]. Morse and co-workers were able to demonstrate that an enzyme, silicatein-α, isolated from the spicules of the marine sponge *Tethya aurantia* was able to catalyse the polymerisation of silicates, *in vitro*, using the xenobiotic alkoxysilane tetraethoxysilane, as a substrate, *via* cleavage of the Si–O bond of the molecule [7]. Mutation experiments on the silicatein-α of *T. aurantia* have demonstrated that Si–O bond cleavage by this enzyme is catalysed by a classical serine hydrolase triad, that features in a protein whose sequence is somewhat related to that of mammalian cathepsins (Fig. 1) [8].

Other experiments have also demonstrated Si–O bond cleavage in microorganisms. Semprini and co-workers described the enrichment, in a chemostat, of a microbial consortium that was able to degrade tetraethoxysilane by apparent cleavage of the Si–O bond [9] and Fattakhova et al. demonstrated that the yeast *Rhodotorula mucilaginosa* produced a substrate-inducible esterase that catalysed the cleavage of the Si–O bond in a range of silatrane substrates [10,11]. Most recently, Bassindale et al. have shown that serine hydrolases such as trypsin and chymotrypsin appear to catalyse the formation of siloxane bonds at the active sites of the enzymes, yet the hydrolytic reaction, whilst accelerated in the presence of the protein, is promoted only by non-specific interactions with the enzyme in use [12].

Our interest was prompted by the possibility of using enzymes in the context of applied biocatalysis in organic synthesis. The use of silyl ether protecting groups in synthesis is widespread [13],

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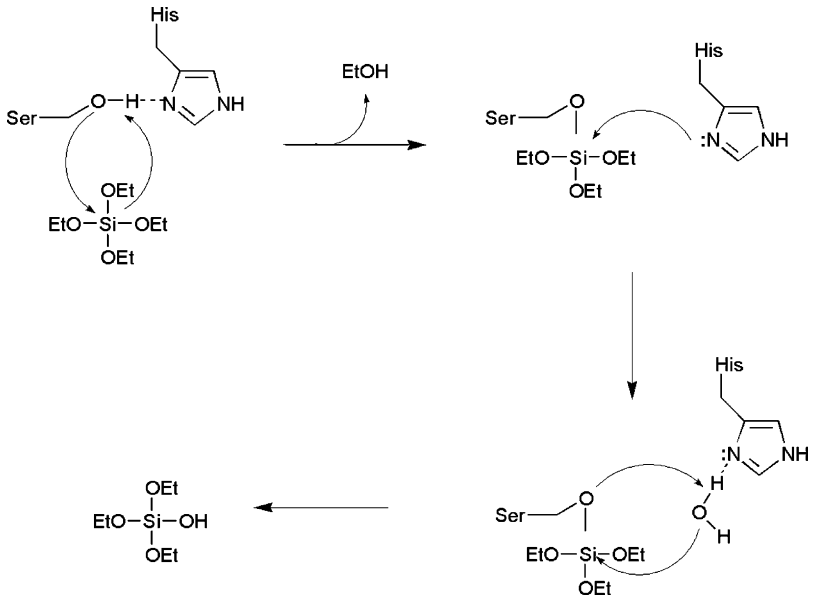


Fig. 1. Proposed mechanism of silyl ether cleavage by serine of catalytic triad in silicatein-α as proposed by Zhou et al. [8].

and many reports are published which demonstrate the regio- and chemoselective removal of silyl ether groups that are differentiated by, for example, the order of substitution (primary or secondary), their aromatic/aliphatic character or pattern of alkyl substitution at silicon itself [*tert*-butyldimethylsilyl (TBDMS), triethyl (TES)] [14]. Of additional interest are recent reports that detail the *chiral* functionalisation of an alcohol with silicon. Isobe et al. used modified guanidine bases to effect the partial resolution of racemic indanol using silanes [15], and Zhao and Snapper have recently demonstrated that a chiral tripeptide is able to effect the desymmetrisation of, for example, prochiral *cis*-cyclopentene-3,5-diol by silylation using chlorotertiarybutylsilane as a protecting group at low temperature [16]. The results of these latter studies seem to suggest that longer polypeptides such as enzymes may be competent for the selective transformation of silyl ethers, however, few studies of investigations of this particular aspect have been forthcoming.

Based on studies that demonstrated both the catalytic competence of serine-triad hydrolases for silicon–oxygen bond cleavage [8] and their successful application in the biotransformation of silyl ether substrates [12], we considered that a screen of commercially available serine-triad hydrolases for the removal of silyl ether protecting groups with a view to their possible application in preparative biocatalysis was merited and present our results herein. Although none of the enzymes showed the desired activity, it was found that commonly used silyl ether protecting groups may prove too sterically demanding for enzymatic reaction at the silicon atom, if acting according to the mechanisms suggested.

2. Experimental

2.1. Chemicals

Commodity chemicals and solvents were purchased from either Sigma–Aldrich or Fluka. Enzymes were purchased from a variety of sources as listed in Table 1.

2.2. Synthesis of substrates

Silyl ethers **2**, **3**, **4**, **5**, and **8** were synthesised from the relevant alcohols and chlorosilanes (TBDMS–Cl or TMS–Cl) using imidazole in either dichloromethane or dimethylformamide as solvent. Ether **10** was synthesised from 2-phenylethanol and the relevant alkyl bromide in the presence of sodium hydride. Phenylethylpivalate **9** was synthesised from 2-phenylethanol and pivalic acid anhydride using zinc perchlorate hexahydrate as catalyst.

2.2.1. *tert*-Butyldimethyl-(2-phenylethoxy)-silane (**3**)

^{1}H NMR: 0.00 (s, 6H, H_9); 0.89 (s, 9H, H_{11}); 2.84 (t, 7.1 Hz, 2H, H_2); 3.82 (t, 7.1 Hz, 2H, H_1); 7.18–7.33 (m, 5H, H Arom.); ^{13}C NMR: −5.4 (C_9); 18.3 (C_{10}); 25.9 (C_{11}); 39.6 (C_2); 64.5 (C_1); 126.1 (C_6); 128.2; 129.1 (C_4, C_5, C_7, C_8); 139.1 (C_3).

2.2.2. *tert*-Butyldimethyl-(1-phenylethoxy)-silane (**4**)

^{1}H NMR: 0.00 (s, 3H, H_7); 0.01 (s, 3H, H_7); 0.94 (s, 9H, H_9); 1.44 (d, 6.4 Hz, 3H, H_1); 4.90 (q, 6.4 Hz, 1H, H_2); 7.22–7.38 (m, 5H, H Arom.); ^{13}C NMR: −4.8 (C_7); 18.3 (C_8); 25.9 (C_9); 27.3 (C_1); 70.78 (C_2); 125.2; 128.0 (C_4, C_5); 126.6 (C_6); 146.9 (C_3).

2.2.3. *tert*-Butyl-(hex-2-yloxy)-dimethyl silane (**5**)

^{1}H NMR: 0.04 (s, 6H, H_7); 0.82–0.92 (m, 12H, H_9, H_6); 1.11 (d, 6.4 Hz, 3H, H_1); 1.20–1.45 (m, 6H, H_3, H_4, H_5); 3.70–3.82 (m, 1H, H_2); ^{13}C NMR: −4.7; −4.4 (C_7); 14.1 (C_6); 18.2 (C_8); 22.7; 23.8; 28.0; 39.4 (C_1, C_3, C_4, C_5); 25.9 (C_9); 68.6 (C_2).

2.2.4. Trimethyl(phenylethoxy)silane (**8**)

^{1}H NMR: 0.00 (s, 9H, $SiCH_3$); 2,77 (t, 7.1 Hz, 2H, CH_2Ph); 3.71 (t, 7.1 Hz, 2H, CH_2O); 7.09–7.26 (m, 5H, H Arom.); ^{13}C NMR: −0.6 (C–Si); 39.5 (CH_2Ph); 63.9 (CH_2O); 126.1; 128.3; 129.0 (CH Arom.); 139.9 (Cq Arom.).

2.2.5. Phenyl ethyl pivalate (**9**)

^{1}H NMR: 1.08 (s, 9H, H_9); 2.85 (t, 7.2 Hz, 2H, H_2); 4.19 (t, 7.2 Hz, 2H, H_1); 7.07–7.26 (m, 5H, H Arom.); ^{13}C NMR: 27.1 (C_9); 35.1 (C_2); 38.6 (C_8); 64.8 (C_1); 126.4 (C_6); 128.3; 128.9 (C_4, C_5); 137.9 (C_3); 178.4 (C_7).

2.2.6. 2-Phenylethylethylether (**10**)

^{1}H NMR: 1.13 (t, 7.1 Hz, 3H, H_8); 2.82 (t, 7.4 Hz, H_2); 3.43 (q, 7.1 Hz, 2H, H_7); 3.55 (t, 7.4 Hz, 2H, H_1); 7.09–7.25 (m, 5H, H Arom.);

Table 1
Enzymes used in study, including names of relevant suppliers, activity, and amounts applied to obtain an activity of at least 10 U against the respective standard substrates

Enzyme	Supplier	Amount (mg)	Activity (U/mg)
Porcine liver esterase	ASA Spezialenzyme (Wolfenbüttel)	10	1
Aspergillus lipase	Fluka (Neu-Ulm)	20	0.5
Aspergillus niger lipase	Fluka (Neu-Ulm)	2.9	3.41
Aspergillus oryzae lipase	Fluka (Neu-Ulm)	0.2	50
Candida antarctica lipase	Fluka (Neu-Ulm)	3.3	3
C. antarctica lipase A	Novozymes (Bagsvaerd – Dänemark)	1	10
C. antarctica lipase B	Roche (Mannheim)	1.1	9.2
Candida lipolytica lipase	Fluka (Neu-Ulm)	10	1
Candida rugosa lipase	Sigma (Steinheim)	8.5	1.18
Chromobacterium viscosum lipoprotein lipase	Fluka (Neu-Ulm)	0.1	1300
Hog pancreas lipase	Fluka (Neu-Ulm)	0.4	25
Mucor javanicus lipase	Fluka (Neu-Ulm)	2	5
Penecillium roquefortii lipase	Fluka (Neu-Ulm)	5.3	1.9
Pseudomonas cepacia lipase	Fluka (Neu-Ulm)	0.2	50
Pseudomonas fluorescens lipase	Sigma – Amano AK (Steinheim)	0.3	31.5
Pseudomonas sp. lipoprotein lipase	Fluka (Neu-Ulm)	0.1	1500
Pseudomonas sp. lipoprotein lipase B	Fluka (Neu-Ulm)	0.1	160
Pseudomonas stutzeri lipase	Jülich Fine Chemicals (Jülich)	0.3	30
Rhizomucor miehei lipase	Sigma (Steinheim)	20	0.5
Rhizopus arrhizus lipase	Fluka (Neu-Ulm)	1	10
Rhizopus niveus lipase	Fluka (Neu-Ulm)	6.7	1,5
Thermomyces lanuginosa lipase	Roche (Mannheim)	0.1	830
Wheat germ lipase	Fluka (Neu-Ulm)	50	0.1
Papain	Serva (Steinheim)	25	0.4
A. oryzae protease	Sigma (Steinheim)	2.7	3.7
Bacillus licheniformis protease	Sigma (Steinheim)	0.8	13.1
Bacillus polymyxa protease IX	Sigma (Steinheim)	8.3	1.2
Bacillus sp. protease	Sigma (Steinheim)	0.6	16
Trypsin	Fluka (Neu-Ulm)	0.1	10735

^{13}C NMR: 15.1 (C_8); 36.4 (C_2); 66.2; 71.5 (C_1, C_7); 126.1 (C_6); 128.3, 128.8 (C_4, C_5); 138.9 (C_3).

2.3. Assays

Prior to reaction, 2 mL glass vials were rinsed with acetone and ethanol, dried and silylated with hexamethyldisilazane in the presence of acetic acid for 30 min at room temperature. Afterwards, the vials were rinsed with ethanol and dried in a high-vacuum with heating.

2.3.1. Hydrolysis of TMEOS

The reactions were performed in a total volume of 1 mL in 50 mM Tris/HCl buffer at pH 7. 130 mM Trimethylethoxysilane (TMEOS) was added and the hydrolysis was monitored by quantitative GC analysis sampling at every 10 min over a 3-h period at room temperature. In a second trial, 10 mg of trypsin (from bovine pancreas) were added to the samples. 1-Butanol (20 mM) was used as the internal standard. For analysis a HP5890 GC equipped with a flame ionisation detector and a FFLP column (30 m × 0.25 mm, 0.1 μm film) which tolerates water as solvent was used. Helium was used as carrier gas with a pre-column pressure of 7.5 psi and a split of 100:1. The temperature program was as follows: 50 °C (30 s) → 90 °C (1.37 min) at 10 °C/min. Temperatures of the injector and detector were both set at 150 °C. Typical retention times of the substrate and the products were TMEOS (1.85 min), ethanol (1.36 min), and hexamethyldisiloxane (2.27 min).

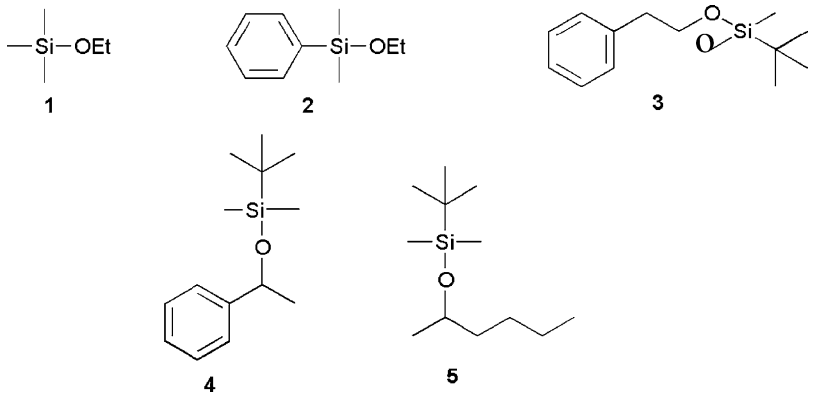
2.3.2. Screening of commercially available lipases

The reactions were conducted in a two-phase system of buffer and either hexane or MTBE as solvent. This was done because of the known enhancement of lipase activity in the presence of interfaces and the better solubility of substrates in hexane or MTBE, respectively, than in water. Buffer and solvent were at a ratio of 1:5 buffer:solvent. The final volume was 3 mL. Enzymes (10 U, or 10–20 mg; see Table 1) were dissolved in a 50 mM Tris/HCl buffer (pH 7 and 8), and silyl ether substrates (100 mM) were dissolved in the organic phase with 20 mM decane as internal standard. The samples were stirred for 24 h at room temperature, centrifuged for phase separation, and samples drawn from the organic phase were analysed by GC. Samples containing the different esters and ethers as substrates followed the same procedure.

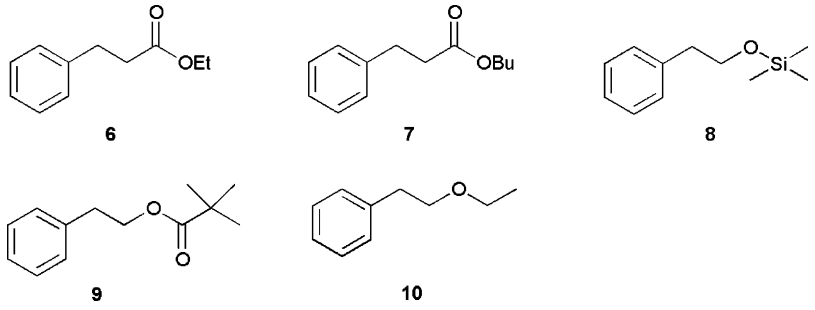
Analysis was performed by a HP5890 GC equipped with a flame ionisation detector and a FS Supreme 5 column (30 m × 0.25 mm,

Table 2
Temperature programs for GC analysis of compounds used in this study

Substrate	T_{Inj} (°C)	T_{Det} (°C)	P_C (psi)	T_{ini} (°C)	Gradient (°C/min)	$T_{meantime}$ (°C)	Gradient (°C/min)	T_{end} (°C)
1	250	260	7.5	50 (30 s)	2	56	40	250
2	220	220	15	100 (30 s)	30	–	–	200
3	250	275	15	100 (30 s)	30	–	–	250
4	250	275	15	100 (30 s)	30	–	–	250
5	250	260	7.5	50 (30 s)	2	58	40	250 (42 s)
8	250	275	15	100 (30 s)	30	–	–	250
6	220	220	15	100 (30 s)	30	–	–	200
7	250	275	15	100 (30 s)	30	–	–	250
10	250	275	15	100 (30 s)	30	–	–	250
9	250	275	15	100 (30 s)	30	–	–	250



Scheme 1.



Scheme 2.

0.1 μm). Nitrogen served as carrier gas and the split was set at 100:1. Temperature programs are given in Table 2. Typical retention times of the substrates are **1** (3.77 min), **2** (2.85 min), **3** (3.97 min), **4** (4.45 min), **5** (9.52 min), **8** (3.31 min), **6** (3.47 min), **7** (4.4 min), **10** (3.88 min) and **9** (4.42 min).

3. Results and discussion

A number of silane substrates were used in this study to investigate the general ability of commercial serine hydrolases to accelerate the hydrolysis of silyl ethers (Scheme 1). In an initial experiment, trypsin was assayed for its ability to accelerate the hydrolysis of trimethylethoxysilane (TMEOS) **1** in water. These experiments were performed after Bassindale et al. [12] who had reported that trypsin was able to accelerate the hydrolysis of **1**, though the active site of trypsin was almost certainly not responsible for the catalysis. In our hands, however, the addition of trypsin did not give any rate acceleration over and above the reaction observed in water alone (Fig. 2). This could have been the result of the considerably faster auto-hydrolysis of **1** in our experimental set-up than reported by Bassindale et al. [12].

As a wide range of commercially available serine-triad hydrolases was available to use within the laboratory, a wider-ranging screen of enzymes was performed against **1** and also a range of silyl ether substrates that would test the ability of serine hydrolases to catalyse Si–O bond cleavage in organic solvent buffer mixtures at pH 7.0 or 8.0. The substrates, trimethylethoxysilane **1**, dimethylphenylethoxysilane **2**, *t*-butyldimethyl-(1-phenyl)-ethoxysilane **3**, *t*-butyldimethyl-(2-phenylethoxy)-silane **4** and *t*-butyl(hex-2-yloxy)silane **5** were incubated with a series of commercially available hydrolases: porcine liver esterase, lipases from *Aspergillus niger*, *Aspergillus oryzae*, *Candida antarctica* (lipases A and B), *Candida lipolytica*, *Candida rugosa*, porcine pancreas, *Mucor javanicus*, *Penicillium roquefortii*, *Pseudomonas cepacia*, *Pseudomonas fluorescens*, *Pseudomonas stutzeri*, *Rhizomucor miehei*, *Rhizopus arrhizus*, *Rhizopus niveus*, *Thermomyces lanuginosa*, and wheat germ, lipoprotein L from *Chromobacter viscosum*, trypsin, proteases from *A. oryzae*, *Bacillus licheniformis*, *Bacillus polymyxa* and the cysteine protease papain. Disappointingly, in this wider range screening of both substrates and enzymes, no evidence of enzyme catalysed silyl ether cleavage was observed. For some enzymes such as lipase from wheat germ, this could have been the consequence of a very low enzyme concentration in the assay due to the low overall activity of the commercial preparations (see Table 1). For the most part, however, it could be assumed that enzyme amounts and concentrations employed would be sufficient for the detection of catalytic activity if there was any to be observed.

It was therefore necessary to re-examine the behaviour of the chosen catalysts with a feasible biotransformation that would validate the reaction conditions, and indeed the activity of the catalysts themselves. A selection thereof, including lipases from *P. stutzeri*, *T. lanuginosa*, *C. rugosa*, *P. fluorescens*, *R. miehei* and

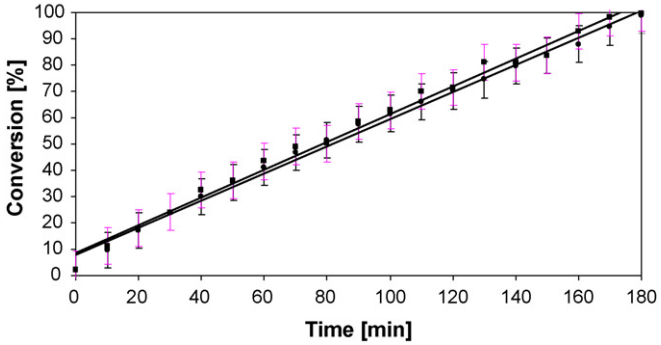


Fig. 2. Relative rates of hydrolysis of trimethylethoxysilane (130 mM) in water (■) or in water with trypsin (●) during a reaction time of 3 h.

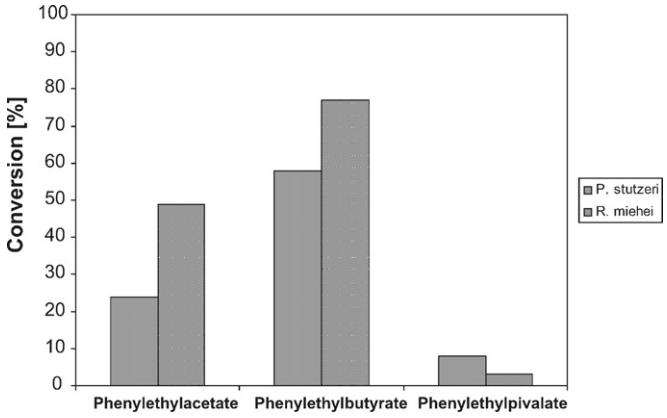


Fig. 3. Comparison of the conversion levels of substrates **6**, **7** and **9** by the lipases of *P. stutzeri* and *R. miehei* used in this study with a substrate concentration of 100 mM and a reaction time of 24 h.

C. antarctica (lipase B) was able to hydrolyse the simple esters, phenylethylacetate 6 and phenylethylbutyrate **7** (Scheme 2) with varying efficiency at both pH 7.0 and 8.0 using equivalent conditions to those described for the silyl ether experiments. Having confirmed the viability of the catalysts, each was then challenged with (a) trimethylphenylethoxysilane **8** and (b) phenylethylpivalate **9** the latter of which was thought to be the closest ester isostere of the simple silyl ether. The results were instructive in respect of the use of serine hydrolases in the envisaged applications. Of the six biocatalysts above, only lipases from *P. stutzeri* and *R. miehei* were competent for the hydrolysis of **9** after 24 h. Comparison of conversions of these substrates (Fig. 3) shows that conversion levels of the *tertiary* α,α,α-carboxylate **9** were much lower than for **6** and **7**.

In an additional control experiment, enzymes were challenged with the carbon ether **10**, yet, unsurprisingly, no cleavage of the ether moiety was observed. Given the known efficiency of enzymes such as lipase B from *C. antarctica* for the cleavage of esters and the validation of the relevant catalyst samples used in this study, it is apparent that the tertiary substitution on the carboxylate moiety of the ester provides a steric challenge to the majority of the enzymes under study. The consequence of this is that, even if serine triad hydrolases were to be chemically and *catalytically* competent for the hydrolysis of silyl ethers as suggested previously, that steric constraints may often preclude the utility of these enzymes for application in the transformation of synthetically useful molecules.

An investigation of serine-triad hydrolases that might be useful for the hydrolysis of tertiary alcohols revealed that such enzymes that were able to recognize tertiary substitutions at the alcohol for effective hydrolysis were restricted to those that possessed a GGGX motif within the active site that allowed accommodation of the larger tertiary moiety [17]. The hydrolysis of α,α,α-trisubstituted carboxylates has also only rarely been described, although the protease from *A. oryzae* has been shown to catalyse the hydrolysis of such challenging substrates in buffered solution [18]. Whilst we have demonstrated that commercial hydrolases appear not to be useful for the hydrolysis of synthetically relevant silyl ether groups such as might be applied in (de)protection strategies, the identification of the lipase from *P. stutzeri* as being useful in the hydrolysis of sterically demanding α,α,α-carboxylates may be a candidate for further study in this context.

4. Conclusion

In summary, we have screened a range of commercially available serine-triad hydrolase enzymes for their potential use as catalysts for the cleavage of silicon–oxygen bonds in commonly used silyl ether protecting groups. Although at the outset, the potential of these enzymes for the cleavage of Si–O bonds appeared to be reinforced by both a sound theoretical mechanistic background and some activity precedent in the literature, no positive results for the transformation sought were obtained. However, validation experiments using isosteric ester and ether compounds related to the relevant silyl ether substrates suggest that steric factors may play a significant role in the inactivity of the catalysts, and hence the catalytic potential of the classical serine-based hydrolytic triad for the cleavage of Si–O bonds cannot be ruled out at this stage.

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