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Comparative behavior of various lipases in benign water and ionic liquids solvents

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Abstract

Lipases were shown to catalyze acylation of various sulfonamides using water or ionic liquids (ILs) as solvents. Ionic liquids that were used include [bmim][PF_6], [bmim][$N(Tf)_2$], and [bmim][BF_4] (where bmim = 1-butyl-3-methylimidazolium, PF_6 = hexafluorophosphate, $N(Tf)_2$ = bis(trifluoromethylsulfonyl)imide, and BF_4 = tetrafluoroborate). As a function of the lipase nature the ionic liquid can be or not a suitable solvent for this reaction. Therefore, it may be stated that an optimization of the process implies a molar ratio of 1:3, the use of lipase *PS Amano* as catalyst and the use of [bmim][$N(Tf)_2$] ionic liquid as solvent. A comparison of the systems shows that the reactivity of the enzyme in [bmim][$N(Tf)_2$] ionic liquid was generally lower than in water but the selectivity to monoacylated sulfonamide was always 100%.

Keywords: Biocatalysis; Ionic liquids; Acylation; Sulfonamides

1. Introduction

A major problem in the fine chemistry industry is the use of solvents as environmental legislation and governmental regulations have severely curtailed the use of dangerous and pollutant ones. The best solvent is no solvent, and if a solvent is needed, it should preferably be water, which is nontoxic, noninflammable, inexpensive, and abundantly available [1]. On the other hand non-aqueous biocatalysis provides a useful component of methodology in organic synthesis [2]. Recently ionic liquids (ILs), organic salts liquid at or near room temperature, have emerged as alternative green media for biotransformations, using both whole cell systems and isolated enzymes. The use of ionic liquids in biocatalysis has showed many advantages, such as better enzyme stability, substrate and/or product selectivity, and suppression of side reaction [3]. The rule for enzyme activity in ionic liquids seems to be "there is no rule", since the performance in a particular ionic liquid appears to vary significantly from enzyme to enzyme. Ionic liquids probably affect enzymatic activity in the same way as the commonly used solvents do [3]. Regarding stability in ionic liquids, it appears that when enzymes actually dissolve in an ionic liquid they are totally inactivated [4]. To remain active in ionic liquids, enzymes must remain in a powder suspension, so that the system can be classified as a heterogeneous one. Ionic liquids do not inactivate enzymes as hydrophilic solvents do, which makes it possible to use ionic liquids for the synthesis of compounds that involve polar substrates, such as glucose, maltose or ascorbic acid [4]. However, the IL-counter-ion can also affect the enzymes stability. Although the majority of enzymes reported to be active in ILs are lipases [5] the presence of methylsulfate, nitrate or lactate counter-anions seem to render the enzyme inactive [3].

Acylations are still a current topic in synthetic organic chemistry. This route provides important intermediates in a very wide field of chemistry, including pharmaceuticals, cosmetics, dyes, fragrances and agrochemicals, such as fungicides, herbicides and insecticides. The acylation is usually carried out using acid anhydrides or acyl chlorides, as acylating agents, in the presence of stoichiometric amounts of amine bases (as tertiary amines, 4-(dimethylamino)pyridine, 4-pyrrolidinopyridine, tributylphosphine) [6,7]. Many of the industrial processes still use homogeneous catalysts as HF or $AlCl_3$, producing high amounts of contaminating wastes. Furthermore, "classical" chemistry under a variety of conditions does not work very selectively. The development of cleaner methods of chemical production, which minimizes waste and avoids toxic reagents, is based on the principles of atom efficiency and catalysis [8–10]. In view of the requirements of

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low-cost production in line with environmental responsibility, catalytic methods including enzyme-mediated transformations are preferred tools to meet such necessities. In particular, in drug synthesis the *N*-acylsulfonamide moiety has emerged as an important feature for biological activity. Several recently developed drugs, including therapeutic agents for Alzheimer's disease [11] and prostaglandin F1 (sulfonamides for the potential treatment of osteoporosis) [12] incorporate this moiety. As for the case of the other substrates, this acylation has been initially made using basic reaction media [13–15]. Another preparation way involves the use of concentrated H_2SO_4 in the carboxylic acid anhydride itself taken as a solvent [16] or the use of concentrated H_2SO_4 in acetonitrile solvent [17].

We report here a quite unusual route to generate acylated sulfonamides. Although there are reports indicating that lipases can catalyze the regioselective acylation of some substrates [18], these enzymes are typical catalysts for deacylation via a hydrolysis route. Serine proteases catalyze the hydrolysis of amide bonds of their protein and peptide substrates according to a three-step mechanism. In the first step, substrate and enzyme combine to form the Michaelis complex. From within this complex, the hydroxyl of the active site serine attacks the carbonyl carbon of the amide bond of the substrate to generate an acyl-enzyme intermediate and liberate the first product (Scheme 4). Finally, hydrolysis of the acyl-enzyme produces the reaction's second product and regenerates free enzyme [19–21].

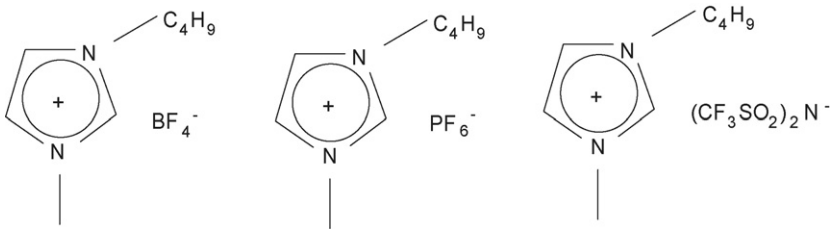
Here we present another example in which the acylation of different benzenesulfonamides was carried out in the presence of lipases. These experiments were carried out using as solvent both water and ILs.

2. Experimental

In a typical procedure, 1 mmol of benzenesulfonamide derivative (benzenesulfonamide, *p*-nitrobenzenesulfonamide, *p*-methoxybenzensulfonamide) was dissolved in 8 ml of solvent (water or ionic liquids) in a glass vial of 10 ml. As ionic liquids were used [bmim][PF_6], [bmim][$N(Tf)_2$], and [bmim][BF_4] (where bmim = 1-butyl-3-methylimidazolium, PF_6 = hexafluorophosphate, $N(Tf)_2$ = bis(trifluoromethylsulfonyl)imide, and BF_4 = tetrafluoroborate) (Scheme 1). The acylating agent (maleic anhydride, in a substrate:acylating agent molar ratio of 1:1–3:1) and the catalyst (15 mg of *Pancreatic lipase* – PL from Sigma; lipase from *Candida cylindracea* – CaCL from Sigma or lipase *PS Amano* – PSAL, from Amano Enzyme Ltd.) were added to the above mixture. Buffer salts, Suc-Phe-pNA, and PNAA were from Sigma Chemical Co. The reaction mixture was vigorously stirred for 18 h at room temperature.

Since the acylated products were practically insoluble in water, their separation from the reaction medium (lipase, water and unreacted sulfonamide) was done very easily through a simple centrifugation. The reaction carried out in ILs was stopped by filtration of the enzyme. After that the residual sulfonamide was extracted with hexane (6 × 5 ml), and then the acylated sulfonamide was separated by extraction with ethyl ether (6 × 5 ml). After extraction the solvent was removed under the vacuum.

The separated product was redissolved in methanol and was subject to the chromatographic analysis. The conversion and selectivity were determined from analytic data collected using a Knauer HPLC with UV–vis detection system in the following conditions: column: GROM-SIL 80 ODS-2 FE, eluent: MeOH:H_2O = 40:60; flow rate: 0.5 ml/min; wavelength: 235 nm; volume sample:15 μl. The products were identified with the aid of pure compounds (standards) separated by thin layer chromatography, and extracted in methanol. The purity of these compounds was checked by ^{1}H NMR and ^{13}C NMR spectroscopy using a Varian Gemini 300BB instrument, operated at 300 MHz for ^{1}H and 75.5 MHz for ^{13}C. The structures of the compounds was tentatively assigned on the basis of ^{1}H and ^{13}C NMR analyses: benzenesulfonamide (^{1}H NMR (300 MHz, DMSO-d_6): δ 7.36 (1H, s, Ph), 7.51 (2H, dd, 2 × CHC*H*, Ph), 7.85 (2H, dd, 2 × SCC*H*, Ph) ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 126.0, 129.6, 132.0, 141.8); monoacylated benzenesulfonamide (^{1}H NMR (300 MHz, DMSO-d_6): δ 6.25 (1H, dd, C*H*COOH), 6.36 (1H, dd, NHCOC*H*) 7.36 (1H, s, Ph), 7.51 (2H, dd, 2 × CHC*H*, Ph), 7.85 (2H, dd, 2 × SCC*H*, Ph); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 126.1, 129.1, 130.9, 132.0, 144.3, 166.3, 167.3); diacylated benzenesulfonamide (^{1}H NMR (300 MHz, DMSO-d_6): δ 7.37 (1H, s, Ph), 7.45 (2H, s, CH), 7.52 (2H, dd, 2 × CHC*H*, Ph), 7.87 (2H, dd, 2 × SCC*H*, Ph); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 124.8, 129.6, 132.0, 149.8, 157.9); *p*-methoxybenzenesulfonamide (^{1}H NMR (300 MHz, DMSO-d_6): δ 3.80 (3H, s, OCH_3), 7.1 (2H, dd, OCC*H*, Ph), 7.76 (2H, dd, SCC*H*, Ph); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 56.1, 114.6, 128.2, 136.5, 162.2); acylated *p*-methoxybenzenesulfonamide (^{1}H NMR (300 MHz, DMSO-d_6): δ 3.80 (3H, s, OCH_3) 6.26 (1H, dd, C*H*COOH), 6.36 (1H, dd, NHCOC*H*), 7.10 (2H, dd, 2 × OCC*H*, Ph), 7.76 (2H, dd, 2 × SCC*H*, Ph); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 55.1, 114.6, 129.1, 131.9, 136.5, 162.2, 165.4, 167.3); diacylated *p*-methoxybenzenesulfonamide (^{1}H NMR (300 MHz, DMSO-d_6): δ 3.81 (3H, s, OCH_3), 7.10 (2H, dd, 2 × OCC*H*, Ph), 7.40 (2H, s, CH), 7.80 (2H, dd, 2 × SCC*H*, Ph); ^{13}C NMR



Scheme 1. Ionic liquids used in these experiments.

(75.5 MHz, DMSO-d_6): δ 55.9, 114.6, 129.0, 132.0, 134.3, 136.5, 165.2); *p*-nitrobenzenesulfonamide (^{1}H NMR (300 MHz, DMSO-d_6): δ 8.05 (2H, dd, 2 × SCC*H*, Ph), 8.48 (2H, dd, 2 × NO_2CCH, Ph); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 124.9, 127.7, 143.3, 149.8); acylated *p*-nitrobenzenesulfonamide (^{1}H NMR (300 MHz, DMSO-d_6): δ 6.25 (1H, dd, C*H*COOH), 6.37 (1H, dd, NHCOC*H*) 8.05 (2H, dd, 2 × SCC*H*, Ph), 8.48 (2H, dd, 2 × NO_2CCH, Ph); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 124.9, 127.7, 130.1, 138.2, 143.3, 165.3, 167.2); diacylated *p*-nitrobenzenesulfonamide (^{1}H NMR (300 MHz, DMSO-d_6): δ 7.38 (2H, dd, CH), 8.05 (2H, dd, 2 × SCC*H*, Ph), 8.48 (2H, dd, 2 × NO_2CCH, Ph); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 124.9, 127.7, 134.0, 143.2, 149.7, 162.1).

The activity of the catalysts was expressed in terms of conversion for all the cases.

3. Results and discussion

Scheme 2 describes the reactions of the investigated sulfonamides with maleic anhydride. The reaction can occur selectively to monoacylated compounds or non-selectively to both monoacylated and di-acylated sulfonamide-derivatives. Very surprisingly, all the enzymes catalyzed the acylation of these substrates in the first step, while more expected was the hydrolysis of the sulfonamide into maleic acid and sulfonamide.

In water, the investigated enzymes behave differently as a function of the substrate and substrate:acylation agent ratio. Fig. 1 presents the results for the acylation of benzenesulfonamide in the presence of the investigated lipases. For this substrate, except two experiments, the conversion was essentially the same irrespective of the substrate:acylation agent ratio. The two exceptions corresponded to the substrate:acylation agent ratio of 1:2 ratio where CaCL led to the higher conversions, and to 1:3, where the best catalyst was PSAL. The reactivity of other substrates was different. Using *p*-methoxybenzenesulfonamide (Fig. 2), for a substrate:acylation agent ratio of 1:1 PL led to higher conversions than CaCL and PSAL. The decrease of this ratio at 1:2 was consistent with an important increase of the conversion of CaCL and PSAL, but with a decrease of the selectivity in monoacylated sulfonamide, while for 1:3 all the three enzymes led to a total conversion with a total selectivity in monoacylated sulfonamide. The analysis

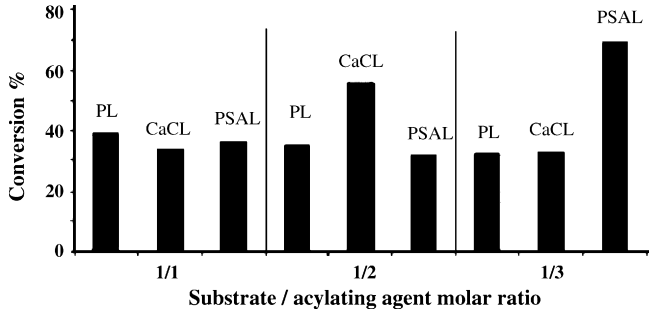


Fig. 1. The conversion of benzenesulfonamide as a function of the molar ratio and type of lipase (*Pancreatic lipase* – PL; lipase from *Candida cylindracea* – CaCL; lipase *PS Amano* – PSAL).

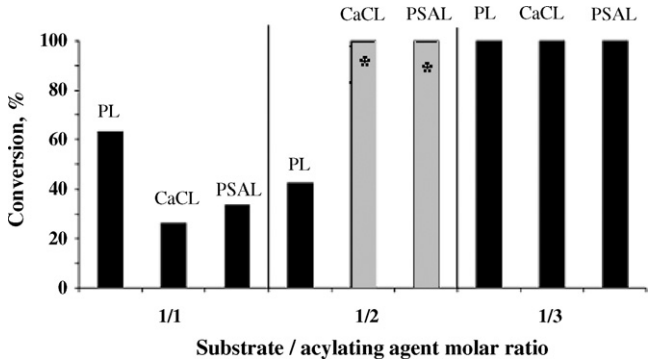
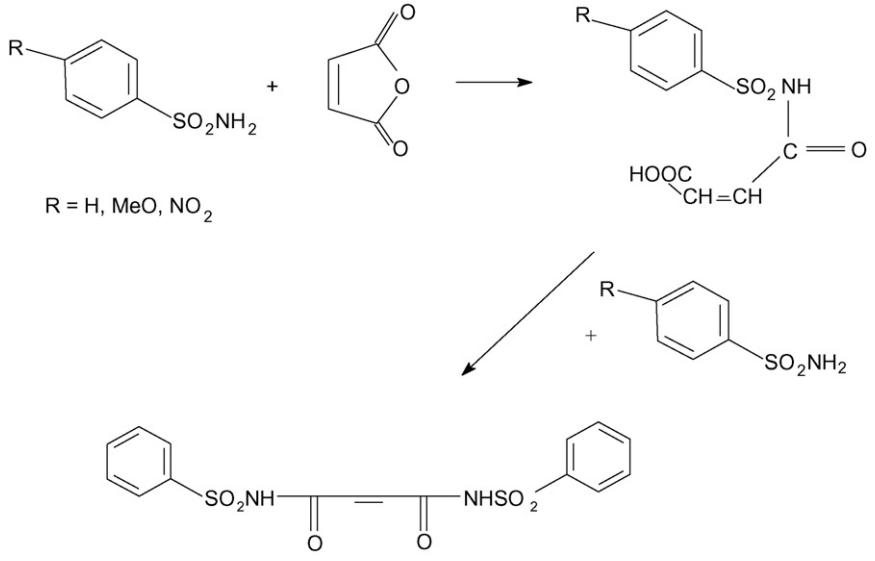


Fig. 2. The conversion of *p*-methoxybenzenesulfonamide as a function of the molar ratio and type of lipase (*Pancreatic lipase* – PL; lipase from *Candida cylindracea* – CaCL; lipase *PS Amano* – PSAL). *CaCL – selectivity to monoacylated product: 65.6%; *PSAL – selectivity to monoacylated product: 67.8%.



Scheme 2. Reactions involved in acylation of benzenesulfonamide derivatives.

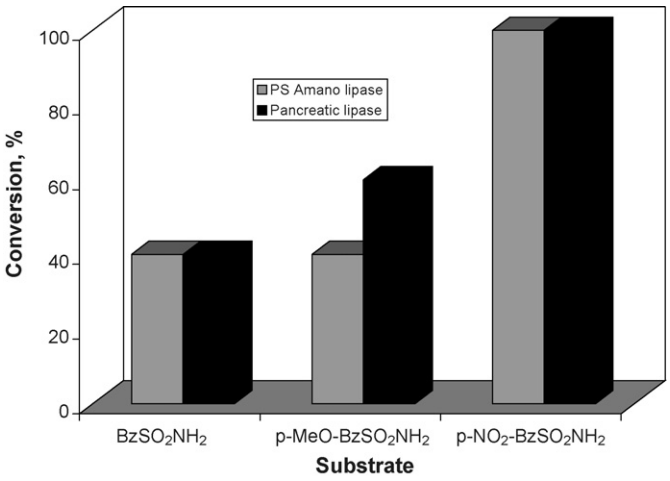


Fig. 3. The evolution of the conversion as a function of the substrate nature in the presence of lipase *PS Amano* and *Pancreatic lipase* (acylating agent/substrate molar ratio: 1/1).

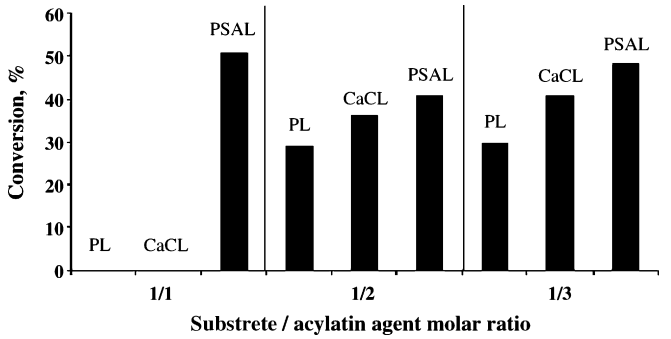
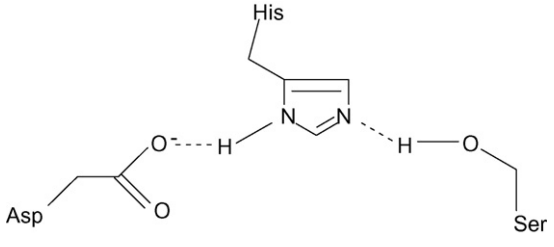


Fig. 4. The conversion of benzenesulfonamide as a function of the substrate:acylating agent molar ratio and type of lipase in [BMIm][NTf_2] (*Pancreatic lipase* – PL; lipase from *Candida cylindracea* – CaCL; lipase *PS Amano* – PSAL).

of di-acylated benzenesulfonamide (see Scheme 2) indicated a mixture of *E*- and *Z*-isomers.

Fig. 3 presents the effect of the substrate in this reaction. By comparing PSAL and PL, it results that the substituent exerts indeed an effect. *p*-Methoxy substituent has either a small (PL) or no effect on the lipase activity. On the contrary, *p*-nitro group exerts a positive role leading to a total conversion for both enzymes. For *p*-methoxy derivative the increase of the conversion paralleled the increase of the acylating agent/substrate molar ratio. However, like for benzenesulfonamide the behavior of *p*-nitro derivative was different. All the lipases catalyzed the transformation of this substrate efficiently with total conversion of the substrate into acylated sulfonamide. So neither the enzyme nature, nor the molar ratio influenced the conversion. It is worth to notice the fact that like for the other substrates investigated in this study, blank experiments without catalysts using both maleic anhydride and maleic acid led to conversion zero.

The catalytic effect the investigated enzymes in this reaction can be explained considering the general mechanism of the lipases. As mentioned above, lipases are known catalysts for hydrolysis of different substrates [22]. They have in their structure a series of three aminoacids: serine, histidine and aspartate, forming the as named "catalytic triad" (Scheme 3). The position of the catalytic residue at the end of a sharp turn allows histidine to gain access at one side and the substrate on the other. It was



Scheme 3. Catalytic triad in lipases.

stated that this special configuration of the nucleophyle in the active site is essential for the reaction of the substrate. So the active serine is activated by histidine and aspartate residues [22].

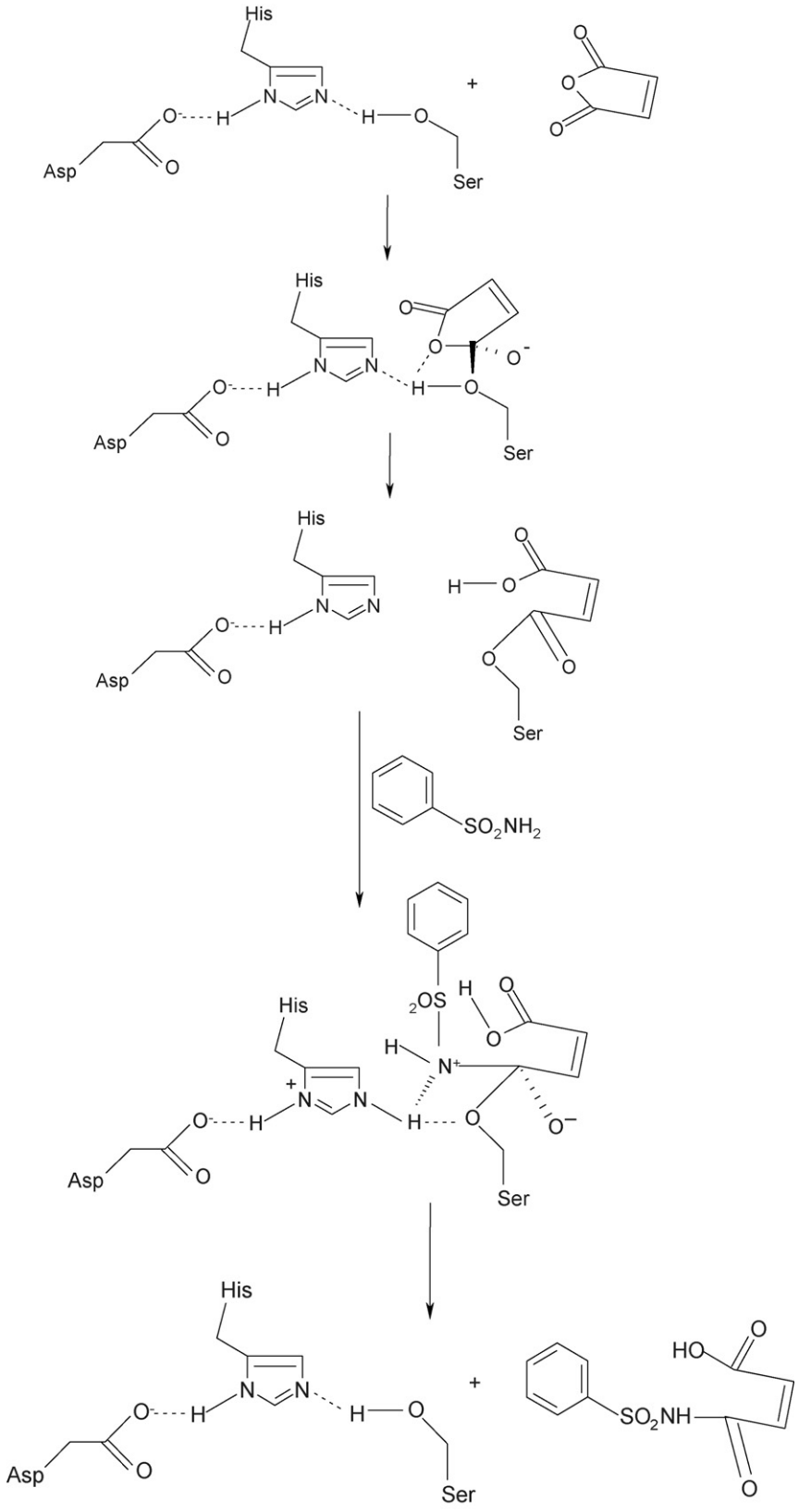
Based on this assumption we may speculate that for the case of benzenesulfonamide derivatives (Scheme 4), Ser-OH will react firstly with the acyl donor to give an acyl-enzyme intermediate (tetrahedral intermediate), which than will react with the substrate. The reaction will stop in this step.

The high conversions and selectivities in the acylated product for *p*-nitrobenzene-sulfonamide, in accordance with the same mechanism, can be explained by the high acidity induced by the presence of the nitro group on the aromatic ring. The data collected for the other two substrates (i.e. benzenesulfonamide and *p*-methoxybenzenesulfonamide) may be attributed to some staggering effects induced by the geometry of the enzymatic catalytic site.

Surprisingly, buffering these systems led to a complete deactivation of the enzymes.

The acylation of the same substrates using ILs as solvents led to the same products, but the effect of IL was evident. In [bmim][BF_4] and [bmim][PF_6] all lipases showed a very low activity leading to low conversions of sulfonamides to the corresponding *N*-acylsulfonamides (<5%). Fig. 4 shows the results obtained for the acylation of benzenesulfonamide in [bmim][NTf_2]. Excellent chemoselectivity was observed in all the cases. No side or monoacylated products were detected under these conditions. However, except for PSAL which showed also reaction for a substrate:acylating agent ratio of 1:1 the other enzymes required an excess of the acylating agent. The order of reactivity was preserved for all the substrate:acylating agent ratios: PSAL > CaCL > PL.

When using *p*-methoxybenzenesulfonamide or *p*-nitrobenzenesulfonamide, under the same experimental conditions, the conversion of the substrate was identified even for a substrate:acylating agent ratio of 1 (Figs. 5 and 6). The order of the reactivity was that found for benzenesulfonamide, i.e. PSAL > CaCL > PL. This order can be related to the stability of these enzymes in ILs. However, the order of the reactivity of the investigated substrates was different from that found in water. In ILs, *p*-nitrobenzenesulfonamide was less reactive. While in water this substrate was fully transformed in all the



Scheme 4. The acylation of sulfonamides with maleic anhydride catalyzed by lipases.

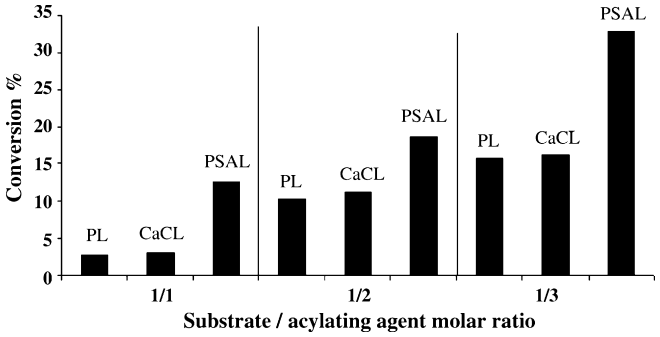


Fig. 5. The conversion of *p*-methoxybenzenesulfonamide as a function of the substrate:acylating agent molar ratio and type of lipase in [BMIm][NTf_2] (*Pancreatic lipase* – PL; lipase from *Candida cylindracea* – CaCL; lipase *PS Amano* – PSAL).

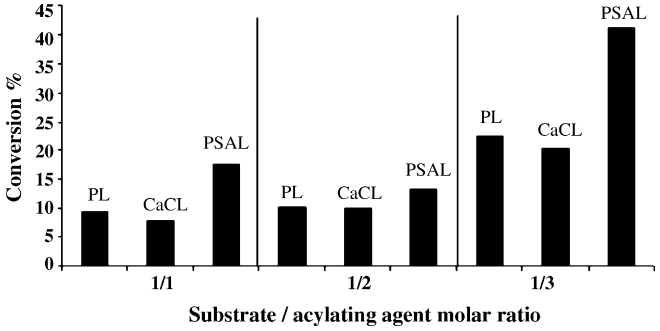


Fig. 6. The conversion of *p*-nitrobenzenesulfonamide as a function of the substrate:acylating agent molar ratio and type of lipase in [BMIm][NTf_2] (*Pancreatic lipase* – PL; lipase from *Candida cylindracea* – CaCL; lipase *PS Amano* – PSAL).

cases, in ILs its conversion varied between 13.4% and 22.4% as a function of the reaction conditions.

Acylations carried out in ILs show the fact that the anion had an important effect on the reaction rate. The conversions were very small in [bmim][BF_4] that is the most hydrophilic IL in this series. The ionic liquids [bmim][PF_6] and [bmim][$N(Tf)_2$], despite being polar, are hydrophobic. However, high reactivity differences were observed for the reactions carried out in these ILs. We assume that these differences are due to the viscosity effect, which is significantly different for [bmim][PF_6] and [bmim][$N(Tf)_2$] [23,24]. The increase in viscosity from [bmim][$N(Tf)_2$] to [bmim][PF_6] is a mass-transfer limiting parameter that appears to be responsible for the decrease of the enzymatic activity. Ionic liquids are, however, solvents characterized by a salt-like structure even in the liquid state. These salts, which cannot form ordered crystals, most probably contain voids that can accommodate small molecules. The different nature of the anion may affect the cation–anion interaction, and thus may determine the cavity size distribution and the diffusion of the molecules [25].

At the beginning of the reaction the pH was around 4 for all the investigated systems. Buffering or lowering the pH completely annihilated the reaction.

Comparing the results obtained in water with those in [bmim][$N(Tf)_2$] the differences in conversions obtained for benzenesulfonamide are not very high. However, the conversions for *p*-methoxybenzenesulfonamide and *p*-nitrobenzenesulfonamide were much smaller. These results were also connected with a more advanced deactivation of these enzymes in ionic liquids compared to water.

Although the reactivity of enzymes decreased when used in ionic liquids, their selectivity to the monoacylated sulfonamide was improved. All the reactions performed in ionic liquid proceeded with 100% selectivity. Another significant advantage of working in ILs is related on the catalyst separation. Because of their insolubility in ILs lipases can be easily separated and reused several times.

These results confirm previous reports showing that not all ILs are always suitable for biocatalysis, but many enzymes are active in ILs containing BF_4, PF_6, or $N(Tf)_2$ anions [26]. However, for the acylation of different benzenesulfonamides although the three investigated ILs had the same cation, they displayed quite different properties.

4. Conclusions

The results obtained in this study proved that fact that although lipases exhibit typical hydrolytic properties, they are able to catalyze the acylation of different benzenesulfonamide with maleic anhydride both in water and ILs. Acylation of these substrates occurred with very high conversions and selectivities, indicating the use of these catalysts as a promising route towards the synthesis of acylated benzenesulfonamides. No acylation was detected in blank experiments, namely, in the absence of enzymes.

Acylation of the investigated benzenesulfonamides was found to be sensitive to the ring substituents. In water the best results were obtained for *p*-nitrobenzenesulfonamide. Except for the substrate, in water, the lipases activity was also sensitive to the substrate:acylating agent molar ratio. Working in ILs corresponded to a decrease of the conversion. However, under these conditions the selectivity was always total, and the catalyst was easily to be recovered and recycled.

In conclusion, acylation of benzenesulfonamides in the investigated media occurred without the formation of any hazardous compound, as side products leading to valuable intermediates for the organic synthesis. Other studies are in progress to explain the effect of enzyme in such reactions.

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