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Design of phosphonium ionic liquids for lipase-catalyzed transesterification

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Abstract

Ionic liquids are now recognized as solvents for use in lipase-catalyzed reactions; however, there still remains a serious drawback in that the rate of reaction in an ionic liquid is slower than that in a conventional organic solvent. To overcome this problem, attempts have been made to evolve phosphonium ionic liquids appropriate for lipase-catalyzed reaction; several types of phosphonium salts have been prepared and their capability evaluated for use as solvent for the lipase-catalyzed reaction. Very rapid lipase PS-catalyzed transesterification of secondary alcohols was obtained when 2-methoxyethyl(tri-*n*-butyl)phosphonium bis(trifluoromethanesulfonyl)imide ([MEBu$_3$P][NTf$_2$]) was used as solvent, affording the first example of a reaction rate superior to that in diisopropyl ether.

Keywords: Ionic liquid; Phosphonium salt; Lipase; Transesterification; Rapid reaction

1. Introduction

Ionic liquids are now recognized as suitable for use in organic reactions and as providing potential for improvement in control of product distribution, enhanced reactivity, ease of product recovery, catalyst immobilization, and recycling [1–25]. We have been interested in the use of ionic liquids (ILs) in biochemical reactions [5–13]. One of the most important benefits of using an ionic liquid as the solvent is that it allows recyclable use of the catalyst. We developed two methodologies for the lipase recyclable use system in IL reaction media [6–14]: one is a lipase-catalyzed reaction under reduced pressure conditions [7,8], and the other is design of an ionic liquid appropriate for transesterification [9,10,12]. We further established a powerful means of activating lipase using an imidazolium PEG alkylsulfate ionic liquid coating [13,14], and showed that ionic liquid coated lipase can be used repeatedly in the ionic liquid solvent system (Fig. 1) [14]. However, there still remains a serious drawback of lipase-catalyzed transesterification in such a system. The rate of lipase-catalyzed reaction in an ionic liquid is significantly inferior to those in a conventional organic solvent like diisopropyl ether (i-Pr$_2$O) [5–25].

To obtain a hint toward overcoming this problem, we looked at ionic liquids that have been used as solvent for lipase-catalyzed reactions, because there have been many advances in this area over the past several years [5].

Various types of ionic liquids have been used as solvents for these reactions (Fig. 2), the most frequent being imidazolium salts (I) [1–25]. Although examples were limited, acceptable results were also obtained in non-imidazolium salts, such as ammonium salts (II) [15–18], pyrrolidinium salts (III) [15], alkylguanidinium salts (IV) [19], and pyridinium salts (V) [20]. On the other hand, only a poor enantioselective reaction was reported when lipase-catalyzed reaction was carried out in phosphonium salts (VI) ILs [26].

It has been established that lipase activity is significantly dependent on the anionic part of the IL [6,15]. According to the reported results of lipase-catalyzed reactions in ILs, four types of anions can be recommended as promising anionic parts of ILs: tetrafluoroborate (BF$_4$), hexafluorophosphate (PF$_6$), bis(trifluoromethanesulfonyl)imide (NTf$_2$) and

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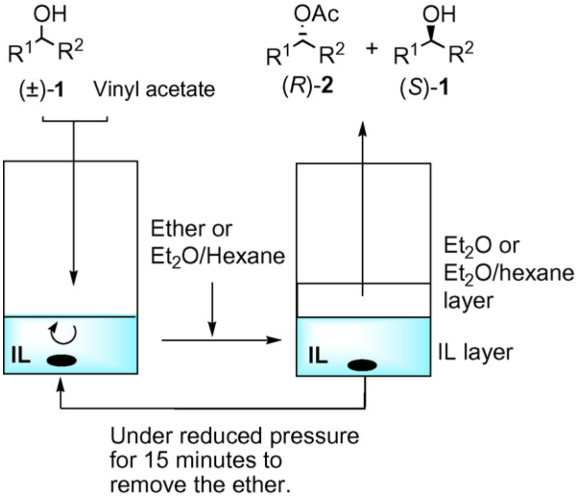


Fig. 1. Lipase recyclable use system using an ionic liquid solvent.

octafluoropentylsulfate (C5F8) [12,14]. Although PF_6 salts are the most frequently used ionic liquids, their use is no longer recommended because they have sometimes been hydrolyzed by moisture and produced hazardous hydrogen fluoride [27]. Reactions in BF_4 salts generally afford good results, but since the salts have a hydrophilic nature, serious trouble is occasionally encountered during performance of the workup process. Hydrophobic salts are far more preferable from the standpoint of realizing an easy workup process in organic reactions. Since NTf_2 salts or C5F8 [12] salts have hydrophobic property with no toxicity, they are now considered as a preferred anionic part of ionic liquids.

We anticipated that phosphonium salts may have potential to become good reaction media for biotransformation if an appropriate design were created, although poor enantioselectivity was reported for lipase-catalyzed reactions in the two phosphonium salt ILs, *n*-pentadecyl(tri-*n*-hexyl)phosphonium azide and methyl(tri-*n*-butyl)phosphonium tosylate [26]. Because the phosphonium salts moiety is commonly found in living creatures, it is assumed that the salts have good affinity with enzyme proteins and thus may provide a good environment for enzymes. Therefore, we attempted to design phosphonium NTf_2 type ILs appropriate for lipase-catalyzed reaction by evaluating the cationic part. We tested transesterification of some secondary alcohols in several phosphonium NTf_2 salts, and discovered that very rapid reaction was accomplished in 2-methoxyethyl(tri-*n*-butyl)phosphonium bis(trifluoromethanesulfonyl)imide ($[MEBu_3P][NTf_2]$) [28] with excellent enantioselectivity when (*E*)-4-phenylbut-3-en-2-ol was subjected to the lipase-catalyzed transesterification using vinyl acetate as an acyl donor. Here we report the detailed results that appropriately designed phosphonium ionic liquids are applicable to lipase-catalyzed transesterification as an efficient solvent.

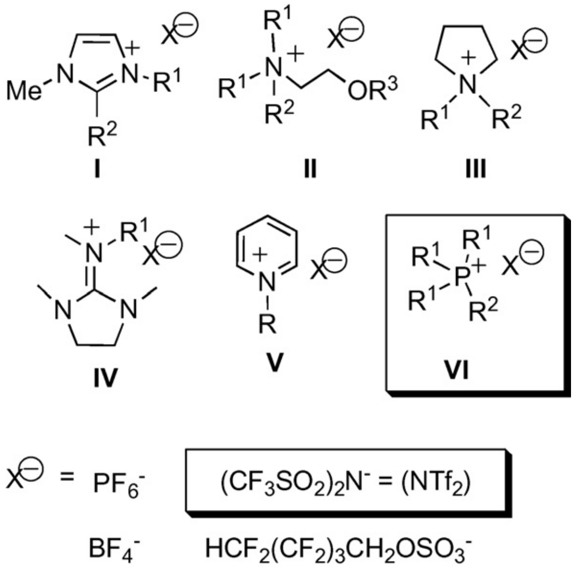


Fig. 2. List of ionic liquids compatible with enzymatic reactions.

2. Experimental

For the lipase, commercial Lipase PS (Amano) from *Burkholderia cepacia*, Novozym435 (*Candida antarctica*), and imidazolium alkyl-PEG sulfate ionic liquid coated lipase PS (IL1-PS) [13,14,31] were employed. IL1-PS was prepared by the reported method [14,31]. Ionic liquid [bmim][C5F8] was prepared by the reported method [12], and $[bmim][NTf_2]$ and $[bdmim][NTf_2]$ were purchased from Kanto Reagents Co., Ltd. Water content of an ionic liquids employed was determined by Karl Fischer moisture titrator. The values are listed as follows: $[Bu_3MeP][NTf_2]$ (Nippon Chemical Co., Ltd.): 145 ppm; $[Et_3(n\text{-Pent})P][NTf_2]$ (Nippon Chemical Co., Ltd.): 46 ppm; $[bmim][NTf_2]$(Kanto Reagents Co., Ltd.): 170 ppm; $[bdmim][NTf_2]$ (Kanto Reagents Co., Ltd.): 95 ppm.

2.1. Typical enzymatic reaction

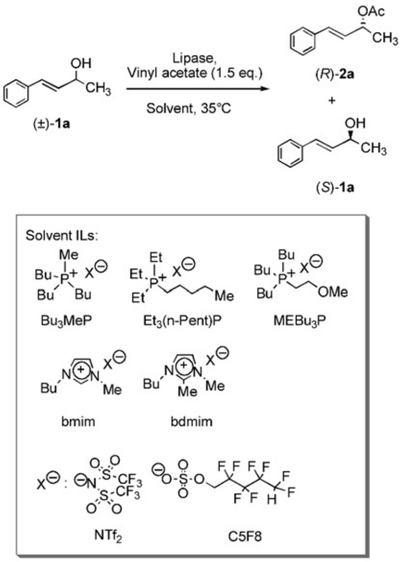
The reaction was typically carried out as follows [14]: To a mixture of 50 wt.% (based on the substrate) of Lipase PS, Novozym435 or 10 wt.% of IL1-PS in 1.0 mL of solvent was added (±)-**1a** (50 mg, 0.34 mmol) and vinyl acetate (1.5 equiv.) and the resulting mixture was stirred at 35 °C. To evaluate the initial reaction rate, the reaction was conducted in the presence of 0.5 mmol of hexadecane as an internal reference, an aliquot of the reaction mixture was sampled at 30 min of the reaction and extracted with a mixed solvent of diethyl ether and hexane (1:4) and the rate was determined by capillary GC analysis. The reaction course was monitored by silica gel thin layer chromatography (TLC) analysis and the product (*R*)-**2a** [14] and unreacted alcohol (*S*)-**1a** [14] were extracted with a mixed solvent of diethyl ether and hexane (1:4) when the spots became the same size and were purified by silica gel TLC. Since it is well recognized that water contents of the solvent influence the lipase performance, ionic liquids were dried under reduced pressure at 50 °C at 1 Torr for 3–5 h prior to the reaction.

2.2. Synthesis of 2-methoxyethyl(tri-n-butyl)phosphonium bis(trifluoro-methanesulfonyl)imide ([MEBu$_3$P][NTf$_2$]) [28]

To an ethanol (20 mL) solution of 1-bromo-2-methoxyethane (4.68 g, 40 mmol) was added tributylphosphine (7.5 g, 37 mmol) and the resulting mixture was stirred for 22 h at 80 °C. After being cooled to room temperature (rt), hexane was added to form a precipitate which was removed by filtration. The resulting filtrate was evaporated under vacuum to give the bromine salt (12.31 g, 36 mmol) in 97% yield. The salt was dissolved in ethanol (18 mL) and lithium bis(trifluoromethanesulfonyl)imide (11.37 g, 40 mmol) powder was added, then the mixture was stirred at rt for 17 h to form lithium bromide as a precipitate. The precipitate was removed by filtration, the filtrate was washed with hexane 3 times and the solvent removed using lyophilization. The resulting oil was dissolved in acetone and treated with active charcoal, and the charcoal was then removed by filtration. The filtrate was passed through active alumina (Type III) and dried under vacuum at 50 °C for 5 h to give [MEBu$_3$P][NTf$_2$] (19.15 g, 35 mmol) as colorless oil in 95% yield: ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.979 (9H, t, $J = 6.85$ Hz), 1.45–1.55 (12H, m), 2.10–2.20 (6H, m), 2.53 (2H, q, $J = 5.95$ Hz), 3.36 (3H, s), 3.75 (2H, dt, $J = 14.2$ Hz, $J = 5.95$ Hz); ^{13}C NMR (125 MHz, CDCl$_3$) δ 13.00, 19.16 (d, $J_{\text{C–P}} = 46.7$ Hz), 19.98 (d, $J_{\text{C–P}} = 46.7$ Hz), 23.24 (d, $J_{\text{C–P}} = 4.78$ Hz), 23.60 (d, $J_{\text{C–P}} = 16.2$ Hz), 58.82, 65.08 (d, $J_{\text{C–P}} = 7.64$ Hz), 119.80 (q, $J_{\text{C–F}} = 315.5$ Hz); ^{31}P NMR (202.46 MHz, CDCl$_3$) δ 39.08 (d, $J_{\text{P–C}} = 26.1$ Hz); ^{19}F NMR (170.6 MHz, CDCl$_3$, C$_6$F$_6$) δ 92.91; IR (neat) 2937, 2878, 1400, 1194, 1057, 738 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{34}OP$, 261.1670; found. 261.1666. Viscosity = 72 cP s at 25 °C (H$_2$O = 880 ppm), mp = 9.5 °C (DSC). Since it sometimes colored when [MEBu$_3$P][NTf$_2$] was dried at higher temperature, we usually dried the liquid at 50 °C at 1 Torr for 3–5 h and used it for the lipase-catalyzed reaction. However, it was possible to reduce the water content to 93 ppm when it was dried under reduced pressure at 5 Torr at 100 °C for 6 h.

3. Results and discussion

We initially evaluated the solvents using lipase-catalyzed enantioselective transesterification of (*E*)-4-phenylbut-3-en-2-ol ((±)-**1a**) [14,29,30] as a model reaction (Eq. (1)), and the results are shown in Table 1. For the lipase, we employed commercial Lipase PS, Novozym435, and imidazolium alkyl-PEG sulfate ionic liquid coated lipase PS (IL1-PS) [14,31]. Interestingly, although none of the enzymes we tested was soluble in the solvents employed and made only a sluggish mixture, the transesterification proceeded smoothly. As shown in Entries 1 and 2, both lipase PS and Novozym435 showed poor reactivity in diisopropyl ether (*i*-Pr$_2$O): acetate (*R*)-**2a** was obtained in 13% yield with 98% ee after 24 h reaction for Lipase PS, though acceptably high enantioselectivity was recorded because the *E* value [32] was calculated to be 148. Interestingly, although initially the rate was very poor for Novozym435, the reaction gradually proceeded and (*R*)-**2a** was obtained in 30% yield with 99% ee (Entry 2). On the other hand, IL1-PS displayed excellent reactivity: the reaction reached 47% conversion after just 1 h reaction with excellent enantioselectivity ($E > 200$) (Entry 3). We therefore decided to investigate further reactions using IL1-PS. Among the three organic solvents, *i*-Pr$_2$O, hexane, and toluene (Entries 3–5), the best result was obtained when the reaction was carried out in *i*-Pr$_2$O (Entry 3). We also tested several typical organic solvents: isooctane, THF, *t*-BuOMe, and dioxane.



(1)

Although the reaction proceeded, the rate was very poor and no solvent system superior to *i*-Pr$_2$O was found for the present model reaction using Lipase PS, Novozym435, or IL1-PS. Many types of phosphonium salt ionic liquids are now commercially available; however, we recognized that most commercial phosphonium ILs are not appropriate for use as solvent in the present lipase-catalyzed reaction because they have a long alkyl chain and thus show amphiphilic properties. We therefore tested the reaction using three original phosphonium NTf$_2$ ionic liquids, [Bu$_3$MeP][NTf$_2$] (Entry 6), [Et$_3$(*n*-Pent)P][NTf$_2$] (Entry 7), and [MEBu$_3$P][NTf$_2$] (Entry 8). To our delight, the enzymatic reaction proceeded with excellent enantioselectivity and reactions were much better than those in hexane and toluene in these solvent systems. In particular, the reaction in [MEBu$_3$P][NTf$_2$] proceeded very rapidly; the rate (1000 mM/mg enzyme, h^{-1}) was superior to that in *i*-Pr$_2$O (Entry 8). We carefully checked reliability of the reaction several times and confirmed that the reaction rate in [MEBu$_3$P][NTf$_2$] is indeed superior to that in *i*-Pr$_2$O. To the best of our knowledge, this is the first example that lipase-catalyzed reaction in an ionic liquid proceeded faster than in *i*-Pr$_2$O.

Since the viscosity of [MEBu$_3$P][NTf$_2$] (72 cP s at 25 °C, H$_2$O = 880 ppm) is much higher than that of *i*-Pr$_2$O (0.305 cP s at 32 °C) [33], the origin of this high reaction efficiency of lipase in the IL might not be due to the enhanced rate of mass transfer in the solvent system but to improved activity of the enzyme protein in [MEBu$_3$P][NTf$_2$]. Unfortunately, both lipase PS- and Novozym435-catalyzed reaction were poor even if the reactions were carried out in our phosphonium ionic liquid [MEBu$_3$P][NTf$_2$] (Entries 9 and 10) and enantioselectivity was reduced when Lipase PS was used as catalyst

Table 1
Results of lipase-catalyzed transesterification of (*E*)-4-phenylbut-3-en-2-ol in various solvent systems

Entry	Lipase	Solvent	Time (h)	% ee of (*R*)-**2a**[a] (%yield)[b]	% ee of (*S*)-**1a**[a] (%yield)[b]	Rate[c]	%conv.[d]	*E* value[d]
1	PS[e]	*i*-Pr_2O	24	98 (13)	25 (87)	3[f]	20	148
2	Novozym435[e]	*i*-Pr_2O	24	99 (30)	47 (60)	5[f]	32	>200
3	IL1-PS	*i*-Pr_2O	1	98 (35)	85 (38)	900	47	>200
4	IL1-PS	Hexane	26	86 (24)	34 (62)	120	28	19
5	IL1-PS	Toluene	24	97 (33)	72 (44)	250	43	138
6	IL1-PS	[Bu_3MeP][NTf_2]	11	98 (33)	72 (48)	560	44	62
7	IL1-PS	[Et_3(*n*-Pent)P][NTf_2]	22	93 (32)	53 (52)	380	36	44
8	IL1-PS	[$MEBu_3P$][NTf_2]	1	99 (35)	78 (44)	**1000**	44	**>200**
9	PS[e]	[$MEBu_3P$][NTf_2]	24	86 (11)	13 (70)	30[f]	13	15
10	Novozym435[e]	[$MEBu_3P$][NTf_2]	24	99 (30)	47 (63)	5[f]	32	>200
11	IL1-PS	[bmim][NTf_2]	4	93 (35)	75 (42)	520	45	60
12	IL1-PS	[bdmim][NTf_2]	24	99 (21)	46 (49)	290	32	>200
13	IL1-PS	[bmim][C5F8]	2.5	98 (32)	51 (62)	270	34	165

[a] Determined by HPLC (Chiralcel OB-H, hexane: *i*-PrOH = 20:1).

[b] Isolated yield.

[c] mM/mg enzyme, h^{-1}. The rate was determined by GC analysis at 30 min of reaction.

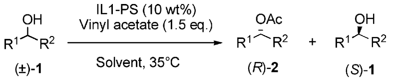
[d] Calculated by % ee of (*R*)-**2a** (eeP) and % ee of (*S*)-**1a** (eeS). $E = \ln[(1-c)(1+\text{eeP})]/\ln[(1-c)(1-\text{eeP})]$, here *c* means conv. which was calculated by the following formula: $c = \text{eeS}/(\text{eeP}+\text{eeS})$. See Ref. [32].

[e] 50 wt.% of enzyme was used.

[f] The rate was determined by GC analysis at 12 h of reaction because the reaction proceeded very slowly.

(Entry 9). Therefore, use of our novel phosphonium ionic liquid is particularly beneficial for the use of an ionic liquid coated enzyme. However, it was confirmed that lipase-catalyzed reaction in [$MEBu_3P$][NTf_2] was superior to those in the imidazolium ionic liquid solvents, [bmim][NTf_2], [bdmim][NTf_2], and [bmim][C5F8] (Entries 11–13). Since these ILs consist of the same anion, the results clearly show that the cationic part of the ILs has a certain impact on the reactivity of the lipase.

We further demonstrated the recyclable use of enzyme in this solvent system (Fig. 3). Surprisingly, the most rapid reaction was recorded after the enzyme had been used 5 times; the rate reached 1300 mM/mg enzyme, h^{-1} (11 fold that in hexane). We assume that this may be due to removal of a trace amount of impurity which may cause inhibition of the enzyme in the IL during repetition of the workup process. The rate remained at the similar level as that in *i*-Pr_2O even after 10 repetitions of the enzymatic reaction, though a slight drop of the E value was recorded.



(2)

We next tested reactions using three substrates (**1b**, **1c**, and **1d**) in two types of phosphonium ILs, [Bu_3MeP][NTf_2] and [$MEBu_3P$][NTf_2], and compared the results with those in *i*-Pr_2O (Eq. (2) and Table 2). As can be seen in Table 2, bet-

Table 2
Results of IL1-PS-catalyzed transesterification of secondary alcohols

Entry	R^1	R^2	Run	Solvent	Time (h)	% ee of (*R*)-**2**[a] (%Yield)[b]	% ee of (*S*)-**1**[a] (%Yield)[b]	Rate[c]	%conv.[d]	*E* value[d]
1	Ph	Me	1st	*i*-Pr_2O	1	>99 (34)	98 (40)	1800	50	>200
2	Ph	Me	1st	[Bu_3MeP][NTF_2]	1.5	99 (30)	85 (40)	1200	46	>200
3	Ph	Me	1st	[$MEBu_3P$][NTf_2]	1	99 (35)	72 (43)	1400	42	>200
4	Ph	Me	5th	[$MEBu_3P$][NTf_2]	1	>99 (30)	75 (41)	1200	43	>200
5	CH_2CN	Et	1st	*i*-Pr_2O	10 min	92 (32)	73 (42)	11000[e]	44	49
6	CH_2CN	Et	1st	[Bu_3MeP][NTF2]	30 min	80 (36)	27 (63)	8200[e]	29	2
7	CH_2CN	Et	1st	[$MEBu_3P$][NTf_2]	30 min	77 (27)	61 (51)	4300[e]	44	15
8	CH_2CN	Et	5th	[$MEBu_3P$][NTf_2]	30 min	88 (26)	33 (61)	3400[e]	28	21
9	CH_2CH_2Ph	$CH_2{=}CH–$	1st	*i*-Pr_2O	20	>99 (21)	22 (75)	60	18	>200
10	CH_2CH_2Ph	$CH_2{=}CH–$	1st	[Bu_3MeP][NTF2]	20	96 (16)	45 (71)	190	32	68
11	CH_2CH_2Ph	$CH_2{=}CH–$	1st	[$MEBu_3P$][NTf_2]	12	98 (34)	38 (63)	250	28	140

[a] % ee of 1-phenylethanol (**1b**) and acetate **2b**: HPLC (Chiralcel OB-H, hexane: *i*-PrOH = 20:1); % ee of 3-hydroxypentanenitrile (**1c**) was determined to be acetate **2c** by the capillary GC (Chiraldex G-Ta, 100 °C); % ee of 5-phenylpent-1-en-3-ol(**1d**): HPLC (Chiralcel OD-H, hexane: *i*-PrOH = 9:1); acetate **2d** HPLC (Chiralcel OJ-H, hexane: *i*-PrOH = 70:1).

[b] Isolated yield.

[c] mM/mg enzyme, h^{-1}, the rate was determined by GC analysis at 30 min of reaction.

[d] Calculated by % ee of (*R*)-**2** (eeP) and % ee of (*S*)-**1** (eeS). $E = \ln[(1-c)(1+\text{eeP})]/\ln[(1-c)(1-\text{eeP})]$, here *c* means conv. which was calculated by the following formula: $c = \text{eeS}/(\text{eeP}+\text{eeS})$. See Ref. [32].

[e] Since the reaction proceeded very rapidly for this substrate, the rate was determined at 10 min of the reaction by capillary GC analysis.

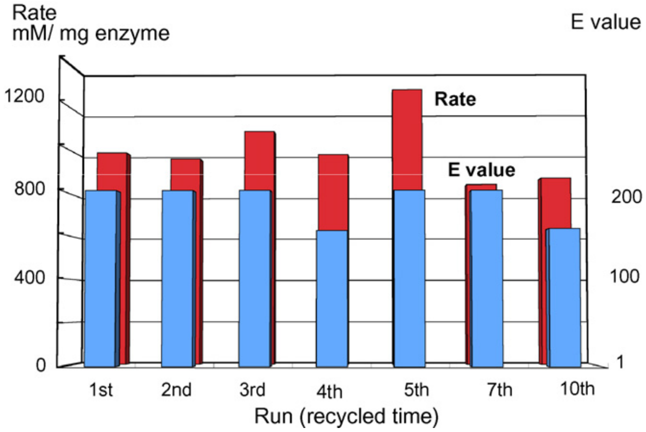


Fig. 3. Results of recyclable use of IL1-PS in the transesterification of (*E*)-4-phenylbut-3-en-2-ol using [$\mathrm{MEBu_3P}$][$\mathrm{NTf_2}$] solvent system.

ter results were always obtained in [$\mathrm{MEBu_3P}$][$\mathrm{NTf_2}$] than in [$\mathrm{Bu_3MeP}$][$\mathrm{NTf_2}$]. Interestingly, the solvent effect was dependent on the substrate. No significant change of lipase reactivity was observed for 1-phenylethanol (**1b**) (Entries 1–4). In contrast, reactivity of lipase depended on the solvent for **1c** (Entries 5–8) and 1d (Entries 9–11). A reduced reaction rate was recorded when 3-hydroxypentanenitrile (**1c**) was subjected to the IL1-PS-catalyzed reaction in phosphonium ILs (Entry 6 and 7), respectively. Particularly significant reduction of enantioselectivity was obtained in these phosphonium solvent systems. An improved reaction rate with reduced enantioselectivity was observed, in contrast, when 5-phenylpent-1-en-3-ol (**1d**) was used as a substrate in the phosphonium ILs (Entries 10 and 11). Although the results were not those desired, the phenomenon seems to provide evidence that the lipase reactivity is, in fact, dependent on the cationic part of the ionic liquid.

4. Conclusion

In conclusion, we established an excellent lipase-catalyzed reaction system using novel phosphonium ionic liquid [$\mathrm{MEBu_3P}$][$\mathrm{NTf_2}$] as a solvent. This is the first example of the reaction of lipase-catalyzed transesterification in an ionic liquid solvent system proceeding faster than in a conventional organic solvent such as *i*-$\mathrm{Pr_2O}$. Although both reaction rate and enantioselectivity depend on the substrate, it is obvious that [$\mathrm{MEBu_3P}$][$\mathrm{NTf_2}$] has a certain advantage over conventional organic solvents, because the solvent makes it possible to use the enzyme repeatedly and has less-volatile and less-flammable properties. We believe that further investigation of the scope and limitations of the reaction will make it even more beneficial.

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References

[1] P. Wasserscheid, T. Welton (Eds.), Ionic Liquids in Synthesis, Wiley-VCH Verlag, 2003.
[2] R.D. Rogers, K.R. Seddon (Eds.), Ionic Liquids as Green Solvents, ACS Symposium Series 818, American Chemical Society, 2002.
[3] N. Jain, A. Kumar, S. Chauhan, S.M.S. Chauhan, Tetrahedron 61 (2005) 1015–1060.
[4] S. Chowdhury, R.S. Mohan, J.L. Scott, Tetrahedron 63 (2007) 2363–2389.
[5] T. Itoh, in: T. Matsuda (Ed.), Future Directions in Biocatalysis, Elsevier, The Netherlands, 2007, pp. 3–20.
[6] T. Itoh, E. Akasaki, K. Kudo, S. Shirakami, Chem. Lett. (2001) 262–263.
[7] T. Itoh, E. Akasaki, Y. Nishimura, Chem. Lett. (2002) 154–155.
[8] T. Itoh, Y. Nishimura, M. Kashiwagi, M. Onaka, in: R.D. Rogers, K.R. Seddon (Eds.), Ionic Liquids as Green Solvents: Progress and Prospects, ACS Symposium Series 856, American Chemical Society, Washington DC, 2003, pp. 251–261 (Chapter 21).
[9] T. Itoh, Y. Nishimura, N. Ouchi, S. Hayase, J. Mol. Catal. B: Enzym. 26 (2003) 41–45.
[10] T. Itoh, N. Ouchi, S. Hayase, Y. Nishimura, Chem. Lett. 32 (2003) 654–655.
[11] T. Itoh, N. Ouchi, Y. Nishimura, S.-H. Han, N. Katada, M. Niwa, M. Onaka, Green Chem. 5 (2003) 494–496.
[12] Y. Tsukada, K. Iwamoto, H. Furutani, Y. Matsushita, Y. Abe, K. Matsumoto, K. Monda, S. Hayase, M. Kawatsura, T. Itoh, Tetrahedron Lett. 48 (2006) 1801–1804.
[13] T. Itoh, S.-H. Han, Y. Matsushita, S. Hayase, Green Chem. 6 (2004) 437–439.
[14] T. Itoh, Y. Matsushita, Y. Abe, S.-H. Han, S. Wada, S. Hayase, M. Kawatsura, S. Takai, M. Morimoto, Y. Hirose, Chem. Eur. J. 12 (2006) 9228–9237.
[15] J.L. Kaar, A.M. Jesionowski, J.A. Berberich, R. Moulton, A.J. Russell, J. Am. Chem. Soc. 125 (2003) 4125–4131.
[16] T.D. Diego, P. Lozano, S. Gmouh, M. Vaultier, J.L. Iborra, Biomacromolecules 6 (2005) 1457–1464.
[17] R.M. Lau, M.J. Sorgedrager, G. Carrea, F. van Rantwijk, F. Secundo, R.A. Sheldon, Green Chem. 6 (2004), 483–187.
[18] C. Chiappe, L. Neri, D. Pieraccini, Tetrahedron Lett. 47 (2006) 5089–5093.
[19] L. Zheng, S. Zhang, X. Yu, L. Zhao, G. Gao, X. Yang, H. Duan, S. Cao, J. Mol. Catal. B: Enzym. 38 (2006) 17–23.
[20] S.H. Schöfer, N. Karftzik, P. Wasserscheid, U. Kragl, Chem. Commun. (2001) 425–426.
[21] R.J. Kazlauskas, P. Kim, J. Org. Chem. 66 (2001) 8395–8401.
[22] H. Zhao, S.V. Malhotra, Biotechnol. Lett. 24 (2002) 1257–1260.
[23] H. Zhao, R.G. Luo, S.V. Malhotra, Biotechnol. Prog. 19 (2003) 1016–1018.
[24] S.V. Malhotra, H. Zhao, Chirality 17 (2005) S240–S242.
[25] H. Zhao, O. Olubajo, Z. Song, A.L. Sims, T.E. Person, R.A. Lawal, L.A. Holley, Bioorg. Chem. 34 (2006) 15–25.
[26] H. Yu, J. Wu, C.C. Bun, Chirality 17 (2004) 16–21.
[27] R.P. Swatloski, J.D. Holbrey, R.D. Rogers, Green Chem. 5 (2003) 361–363.
[28] T. Itoh, K. Kude, S. Hayase, M. Kawatsura, Tetrahedron Lett. 48 (2007) 7774–7777.
[29] A. Ghanem, V. Schurig, Tetrahedron: Asym. 14 (2003) 57–62.
[30] M.B. Onaran, C.T. Seto, J. Org. Chem. 68 (2003) 8136–8141.
[31] IL1-PS is commercially available from Tokyo Chemical Industry Co., LTD. Please contact Dr. Kenji Tahara of TCI: kenji.tahara@tokyokasei.co.jp, Tel.: +81 3 5640 8857, fax: +81 3 5640 8868.
[32] C.-S. Chen, Y. Fujimoto, G. Girdaukas, C.J. Sih, J. Am. Chem. Soc. 102 (1982) 7294–7298.
[33] For a recent example, see: K.V.N. Suresh Reddy, G. Sankara Reddy, A. Krishnaiah, Thermochim. Acta 440 (2006) 43–50.