

Palladium-catalyzed hydroesterification of styrene derivatives in the presence of ionic liquids

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Abstract

The palladium-catalyzed hydroesterification of olefins occurs efficiently in a range of ionic liquid media. Selectivities ranging from 5–7:1 for the linear ester were obtained with styrene in a range of IL solvents. The use of ILs allowed the catalyst to be easily separated from the organic product by either extraction or distillation. The $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ precatalyst could be recovered unchanged from the ionic liquid phase. The IL/catalyst phase could be recycled five times with an average yield of 68%.

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1. Introduction

Ionic liquids (ILs) have seen increased use in many types of reactions catalyzed by transition metal centers [1–4]. The proper selection of ILs (Fig. 1) allows for stabilization of charged metal centers due to their low coordinating ability and similar polarities to polar organic solvents [5–10]. These characteristics, in addition to their non-volatility and tunable properties, make ILs promising solvents for catalytic cycles, in which recycling of the catalyst is desirable [11–14].

The hydroesterification of vinyl aromatics is an important reaction for the synthesis of anti-inflammatory agents used in the pharmaceutical industry [15]. The regioselectivity of the hydroesterification reaction is dependent on the reaction conditions [16], with higher linear to branched product ratios found when the catalyst contains weakly coordinating anions and the reac-

tion is run at high temperature and low CO pressures [17,18]. The palladium-catalyzed hydroesterification of styrene and other derivatives in a biphasic IL medium composed of 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_4\text{mim}][\text{BF}_4]$), isopropanol, and cyclohexane has been previously reported [19]; however, $[\text{C}_4\text{mim}][\text{BF}_4]$ was the only IL studied and recycling of the catalyst was not achieved. Additionally, the palladium-catalyzed hydroesterification of aryl halides and *tert*-butyl alcohol in ILs to give the corresponding esters has been reported [20,21]. Our group, and others, recently reported the palladium-catalyzed co-polymerization of styrene and CO in ILs [22–24] where the polymerization occurs with catalysts supported by chelating ligands.

Here, we report a homogeneous system for the hydroesterification of styrene, and other alkenes, in the presence of ILs and methanol catalyzed by $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ (Eq. (1)). The products were extracted from the IL-methanol phase using hexane with reaction yields monitored by gas chromatography (GC), and the IL-catalyst solution was recycled for subsequent runs.

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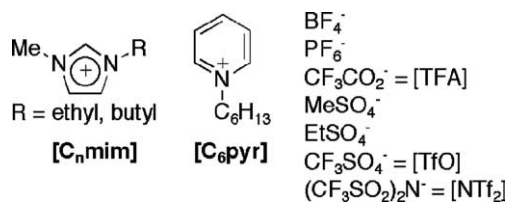
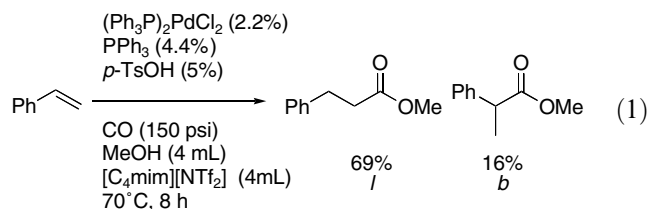


Fig. 1. Typical ionic liquid cations and anions.



2. Experimental

2.1. Materials

All reactions were run in a Parr pressure reactor with electronic temperature control and mechanical stirring. $[\text{C}_4\text{mim}][\text{Cl}]$, $[\text{C}_4\text{mim}][\text{PF}_6]$, $[\text{C}_4\text{mim}][\text{TfO}]$, $[\text{C}_4\text{mim}][\text{TFA}]$, $[\text{C}_2\text{mim}][\text{EtSO}_4]$, $[\text{C}_4\text{mim}][\text{MeSO}_4]$, $[\text{C}_4\text{mim}][\text{BF}_4]$, $[\text{C}_4\text{mim}][\text{NTf}_2]$, $[\text{C}_6\text{pyr}][\text{NTf}_2]$, $[\text{C}_6\text{pyr}][\text{MeSO}_4]$, and $[\text{C}_6\text{pyr}][\text{Cl}]$ were prepared following literature procedures [25–28]. $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ was prepared as described in the literature [29]. CO was C.P. grade and was used as received. All other materials were obtained from Aldrich, Milwaukee, WI and used as received.

2.2. Typical hydroesterification procedure

$(\text{Ph}_3\text{P})_2\text{PdCl}_2$ (34.8 mg, 0.05 mmol), PPh_3 (26.2 mg, 0.10 mmol), and p -toluenesulfonic acid (23.75 mg, 0.125 mmol) were weighed out and transferred to the high-pressure Parr reactor. Styrene (0.25 mL, 2.17 mmol), MeOH (4 mL), and IL (4 mL) were added. Tetradecane (0.3 mL) was then added to the reactor to serve as an internal standard. The reactor was purged twice with 150 psi of CO. The third pressurization was to the desired pressure of CO. The reaction was heated to the reaction temperature and allowed to proceed at a stir speed of 400 rpm.

Upon reaction completion, the reactor was allowed to cool to room temperature and then degassed. The IL mixture was transferred to a separatory funnel where it was then extracted with hexane to remove unreacted styrene, tetradecane and the reaction products. The hexane phase was reduced in volume by rotoevaporation and analyzed by GC. Products were identified by comparison to authentic materials. GC yields were determined relative to the internal standard using

calibration data obtained from authentic samples of styrene and the product esters. Alternatively, reaction products were obtained by direct distillation of the crude product from the reaction mixture under vacuum (0.1 mm Hg). Volatile materials were collected in an ice-cooled receiver flask. The product distribution was then determined by ^1H NMR spectroscopy.

2.3. Catalyst solution recycling experiments

The hexane immiscible catalyst/IL/methanol phase was recovered, extracted and added directly back to the Parr reactor. To this, PPh_3 (0.10 mmol), p -toluenesulfonic acid (0.125 mmol), and styrene (2.17 mmol) were again added. CO pressure, temperature, and reaction time were adjusted accordingly.

2.4. Measurement of solvent parameters for $[\text{C}_2\text{mim}][\text{EtSO}_4]$

Solutions of p -nitroaniline and N,N -diethyl p -nitroaniline in $[\text{C}_2\text{mim}][\text{EtSO}_4]$ with an approximate concentration of 0.1 mM were prepared and analyzed by UV–Vis spectroscopy. The absorption maxima were found to be 385 nm for p -nitroaniline and 415 nm for N,N -diethyl p -nitroaniline. Using the equations reported by Kamlet and Taft [30], the β parameter was determined to be 0.411. Attempts to determine the E_T^N [31], π^* [32], and α [33] were unsuccessful because Reichardt's dye was rapidly decolorized upon addition to the IL. Presumably the phenoxide of the betaine is alkylated, as a similar bleaching was seen with methyl sulfate ILs.

3. Results

Reaction parameters were varied in an effort to determine optimum reaction conditions. Excess PPh_3 ligand was necessary to prevent catalyst decomposition. The best results were achieved when two equivalents of ligand, relative to $(\text{Ph}_3\text{P})_2\text{PdCl}_2$, were added for all experiments. The catalytic system was found to be pressure and temperature dependent with 200 psi of CO and 90°C proving to be optimal (Table 1). In addition, the methanol and IL volumes were found to play a role. Lower amounts of methanol gave markedly lower yields. When IL was added to the system, higher linear to branched ester product ratios were observed. An increased product yield was obtained using lower catalyst concentrations (entries 7 and 10). A similar effect has been seen in styrene/CO co-polymerizations in ILs, although the exact nature of this effect is unclear [22,23].

Upon optimization of the reaction parameters, various ILs were screened to determine both cation and anion effects (Table 2). Hydroesterification regioselectivity has been shown to be strongly dependent on the anion

Table 1
Optimization of hydroesterification of styrene and carbon monoxide^a

Entry	IL (mL)	MeOH (mL)	Time (h)	T (°C)	P _{CO} (psi)	Yield ^b (%)	<i>l:b</i> ^c
1	2.0	4.0	6	50	150	2	5.2
2	2.0	4.0	6	70	150	36	4.4
3	2.0	4.0	6	90	150	80	5.0
4	2.0	4.0	6	70	100	37	4.6
5	2.0	4.0	6	70	200	52	4.3
6	2.0	1.0	6	70	150	5	–
7	2.0	2.0	6	70	150	12	10.0
8	0.0	4.0	6	70	150	>99	3.3
9	1.0	4.0	6	70	150	76	3.9
10	4.0	4.0	6	70	150	36	5.1

^a IL = [C₄mim][NTf₂], styrene (0.25 mL), (Ph₃P)₂PdCl₂ (2.3 mol%), Ph₃P (4.6 mol%), *t* = 6 h.

^b Yields and *l:b* ratio were determined by GC.

^c *l:b* = linear to branched product ratio.

Table 2
Solvent screening for palladium-catalyzed hydroesterification of styrene^a

IL	Yield ^b (%)	<i>l:b</i> ^c
[C ₆ pyr][NTf ₂]	51	5.0
[C ₆ pyr][MeSO ₄]	48	4.5
[C ₂ mim][EtSO ₄]	70	6.8
[C ₄ mim][PF ₆]	13	5.4
[C ₄ mim][TfO]	50	5.5
[C ₄ mim][BF ₄]	51	5.7
[C ₄ mim][MeSO ₄]	50	5.6
[C ₄ mim][TFA]	0	NA
[C ₄ mim][NTf ₂]	60	5.0
[C ₄ mim][NTf ₂] ^d	22	5.2

^a 4 mL IL, 4 mL methanol, 90 °C, 200 psi CO, styrene (0.50 mL), (Ph₃P)₂PdCl₂ (1.2 mol%), Ph₃P (2.3 mol%), *t* = 3 h.

^b Yields were determined by GC.

^c *l:b* = linear to branched product ratio, NA = not applicable.

^d Addition of 0.5 wt% [C₄mim][Cl] relative to [C₄mim][NTf₂].

of the catalytic species [18], so we explored whether the *l:b* ratio could be affected by the choice of IL anion. Recently, Seddon et al. [34] reported that product regioselectivity in the nitration of toluene was dependent on choice of IL. Reactions, in this study, were run under conditions where complete conversion was not expected, to magnify differences in catalyst activity in the different ILs. However, the IL and anion were found to play little role in controlling which isomer formed.

Table 2 shows the yield of ester product with the corresponding linear to branched product ratios. In most cases, there was little effect of the choice of anion and cation on product yield (50–60%) and linear selectivity (4.5–5.5). [C₂mim][EtSO₄] gave somewhat higher yields (70%) and linear selectivity (6.8) than the other ILs. The [PF₆][−] and [TFA][−] anions significantly depressed the yield of ester, although there was no effect on the linear selectivity in the case of [PF₆][−].

Addition of 0.5 wt% chloride in the form of [C₄mim][Cl] to reactions run in [C₄mim][Tf₂N], showed little effect on the *l:b* ratio, but the overall yield was de-

creased by nearly 40%. When the hydroesterification was performed in pure [C₆mim][Cl], the reaction yields dropped to 3% and the *l:b* ratio dropped to 1.3. Changing the cation structure from the imidazolium ring to the pyridinium ring showed essentially no effect on catalyst performance. The formation of a Pd:carbene complex with the C2 position of the imidazolium cation has been seen in some catalytic processes [35], but this does not occur since yields with pyridinium and imidazolium ILs were similar.

Using the optimum conditions (90 °C, 200 psi CO), styrene derivatives and 1-octene were hydroesterified. Due to the negligible vapor pressure of the ILs, it was possible to recover the volatile ester products by vacuum distillation directly from the crude reaction mixture. Product selectivity was found to be dependent on the electronic nature of the alkene (Table 3). Good yields of ester products were obtained with styrene and 4-chlorostyrene (65–75%). The more electron rich 4-*t*-butylstyrene gave a significantly lower yield, however (30%). Styrene and 4-chlorostyrene gave comparable *l:b* ratios, while 4-*t*-butylstyrene gave a somewhat lower preference for the branched ester product. In each case, the reactions went to completion, as no starting material was found in the crude reaction product, although it is pos-

Table 3
Hydroesterification of various alkenes under optimum conditions^a

Alkene	Yield ^b (%)			<i>l:b</i> ^b
	m.a. ^c	l.e. ^d	b.e. ^e	
4-Chlorostyrene	3	50	14	3.5
Styrene	n.d.	60	16	3.7
4- <i>t</i> -Butylstyrene	32	22	8	2.5
1-Octene	n.d.	52	12	4.3

^a 4 mL [C₄mim][NTf₂], 4 mL methanol, 90 °C, 200 psi CO, *t* = 3 h.

^b Product distribution determined from ¹H NMR spectra of the distilled product mixtures. n.d., none detected.

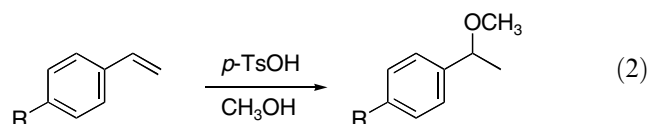
^c Methanol addition product.

^d Linear ester.

^e Branched ester.

sible that small amounts of residual starting material could have been lost in the distillation process. 1-Octene gave a 4.3:1 ratio of linear to branched product which is somewhat higher than that typically seen for this catalyst system in alcohol solvents (2–3:1) [17].

A side reaction that occurred in these reactions was the acid-catalyzed addition of methanol to the alkene (Eq. (2)). Methanol addition was a minor side product for styrene and 4-chlorostyrene (<5%), but became a major competitive pathway with 4-*t*-butylstyrene. Due to the increased electron density, the alkene in 4-*t*-butylstyrene would be more susceptible to protonation than styrene. In the case of 1-octene, no methanol addition was observed.



Separation of the products from the catalyst-IL-methanol phase was easily accomplished by hexane extraction, with the catalyst being retained within the IL-methanol phase. The hexane extracts were colorless and showed no catalyst by ^{31}P NMR. Approximately one third of the added phosphine was extracted (24% as PPh_3 and 8% as PPh_3O), however. Upon concentration of the IL-MeOH solution remaining after hexane extraction, a yellow crystalline precipitate formed, which was identified as *trans*-(Ph_3P) $_2$ PdCl_2 . Isolation of this solid from the residual IL solution showed recovery of $\approx 55\%$ of the original catalyst. In contrast, extensive catalyst leaching was observed when pure methanol was used as the solvent and the IL is omitted.

The ease of separation and ability to recover unchanged a large fraction of the catalyst precursor encouraged us to explore the recyclability of the IL/catalyst solution. Recycling experiments were carried out at 70 °C (Table 4) rather than 90 °C, since catalyst decomposition was more prevalent at higher temperatures. After each run, the ester products were removed by hex-

ane extraction. The IL solution was returned to the reactor with fresh reagents. Additional triphenylphosphine was added in each cycle to account for leaching losses. Polystyrene production, which occurred when recycling studies were carried out at 90 °C, was nearly totally suppressed at 70 °C. Ester yields remained constant through the first two runs with near complete conversion of styrene followed by a gradual decline in product yields. Yields remained greater than 50% until the sixth cycle. The catalyst solution remained yellow throughout the recycling, suggesting the catalyst remains intact. Mechanical loss during the extraction likely accounts for some of the loss of activity, as the IL volume decreased from 2 to 1 mL during the recycling study. Interestingly, the *l:b* ratio increased from 4.3 to 9.8 from the first to sixth run. This increase may reflect an increased amount of phosphine in the system.

4. Discussion

ILs are effective solvents for the palladium-catalyzed hydroesterification of alkenes. The $\text{PPh}_3/\text{Pd}/\text{TsOH}$ system used by us and Dupont [19] is known to give modest linear selectivities (1.5:1 *l:b*) in methanol under similar reaction conditions to this work. In IL solvents, the $\text{PPh}_3/\text{Pd}/\text{TsOH}$ catalyst system gave high linear to branched ratios (3–5) that were relatively independent of reaction conditions. Typically, the regioselectivity of hydroesterification catalysts with weakly coordinating anions is strongly dependent on the reaction conditions. For example, the $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{CH}_3\text{CN})_2]^{2+}$ catalyst system gave a *l:b* ratio of 2.7 with 75 psi CO at 80 °C, while the *l:b* ratio was 0.11 using 300 psi CO at 50 °C [17]. In contrast, our results showed little change in the *l:b* ratio (3–5) when both the temperature and CO pressure were varied, although product yields were significantly affected by these changes. Thus, it appears that under our conditions, the IL induces a linear preference that is insensitive to the reaction conditions.

Claver and co-workers [36] have proposed that catalysts with high branched selectivity proceed through a neutral catalytic cycle, while those with a linear preference follow a cationic catalytic cycle (Scheme 1). In the neutral catalytic cycle, styrene displaces a phosphine to give a neutral Pd-styrene complex. Since the (monophosphine)Pd-styrene complex is relatively unhindered, migratory insertion preferentially occurs to give the electronically favored benzylic-Pd species. CO insertion and methanolysis gives the branched product. In the cationic pathway, styrene displaces chloride to give a cationic Pd-styrene complex. Because the (diphosphine)Pd center is more sterically crowded than the monophosphine complex of the neutral pathway, insertion to give the primary Pd-alkyl is preferred leading to the linear ester. The preferred pathway can be influenced by choice of

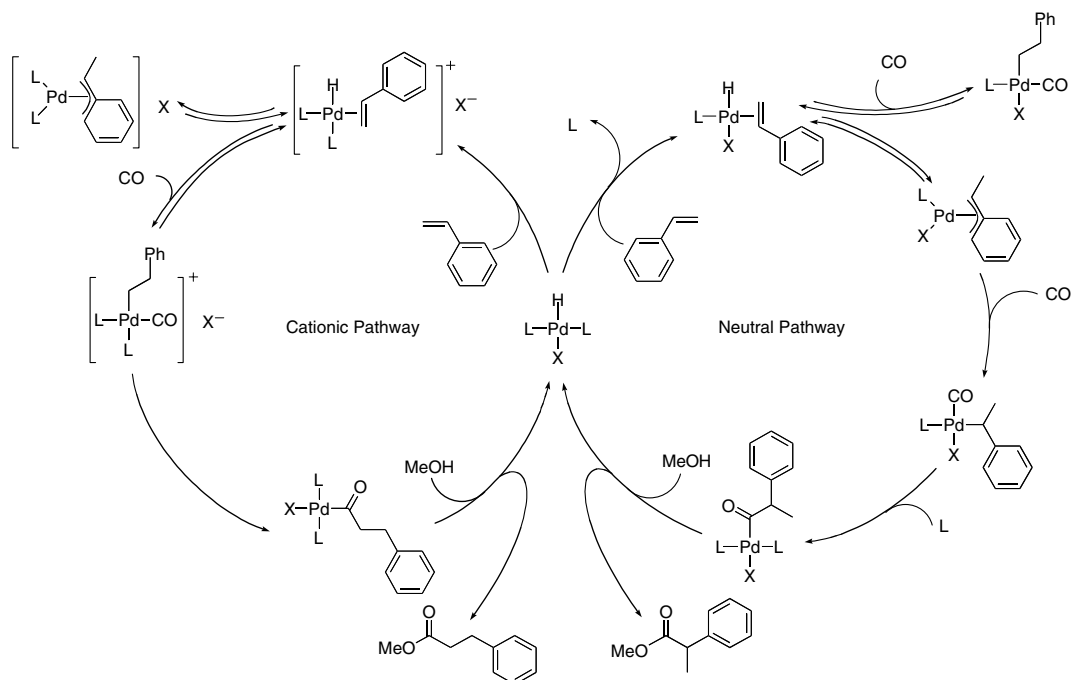
Table 4
Recycling of IL-catalyst solution used in the hydroesterification of styrene^a

Run	Yield ^b (%)	<i>l:b</i> ^c
1	85	4.3
2	83	5.0
3	64	5.6
4	50	7.2
5	60	6.8
6	30	9.8

^a 4 mL $[\text{C}_4\text{mim}][\text{NTf}_2]$ IL, 4 mL methanol, 70 °C, 200 psi CO, 0.25 mL styrene. Runs 2–6 used IL/catalyst solution recovered from the previous run.

^b Determined by GC.

^c *l:b* = linear to branched product ratio determined by GC.



Scheme 1. Competing neutral and cationic catalytic cycles showing major product expected for each pathway.

ligand (chelating diphosphines have a strong preference for the cationic pathway) or palladium counter ion (weakly coordinating anions should favor the cationic pathway). In addition, solvents that stabilize the charge separated species in the cationic cycle should lead to linear products.

Ionic liquids are expected to be able to stabilize charge separated species because of their polarity and good hydrogen bond donor character. ILs have been shown to promote the ligand displacement of anionic ligands by neutral ligands in d^8 square planar metal complexes [37]. In this study, we saw a stronger than expected preference for formation of the linear ester that was largely unaffected by reaction conditions. These results suggest that the IL solvent caused a stronger preference for the cationic pathway, leading to predominantly linear ester products. When the IL anion was replaced by a more strongly coordinating anion, such as chloride, we see a significant decrease in the linear selectivity ($l:b = 1.3$) as well as catalytic activity. In the presence of a high concentration of chloride, the displacement of chloride by styrene would undoubtedly be less favorable.

Interestingly, the results described here have shown a distinctly different regiochemical preference for the hydroesterification of styrene to that reported by Dupont and co-workers [19], despite using a similar catalyst system. Using similar CO pressures and reaction temperatures, Dupont reported an 80% preference for the branched product when triphenylphosphine was used as ligand, while we see 75–80% linear ester. Using a

more sterically demanding and electron rich ligand, neomenthylidiphenylphosphine, nearly complete branched selectivity was obtained. Dupont's results were obtained in a solvent system made up of $[C_4mim][BF_4]$ /cyclohexane/isopropanol (1:3:2), while the work described here uses a 1:1 mixture of IL/methanol. It is possible that the presence of the non-polar cyclohexane solvent made the neutral pathway more favorable, thus, resulting in a preference for the branched ester product. While the exact nature of this difference in regioselectivity is unclear, it does point to the fact that the IL solvent can have a significant effect on the regioselectivity of this reaction.

In general, there was little effect on ester yield or selectivity as the IL cation and anion were changed, although low yields were obtained with the $[PF_6]^-$ and $[TFA]^-$ anions, while $[C_2mim][EtSO_4]$ gave somewhat higher yields and selectivity. The solvent properties of imidazolium ionic liquids as measured by solvatochromic studies fall in a fairly small range, particularly when compared to organic solvents [31]. The ILs in this study had E_T^N values ranging from 0.63 to 0.673 (Table 5), which are comparable to ethanol ($E_T^N = 0.66$). $[C_4mim][TFA]$ had the lowest E_T^N value of the ILs used and was the only IL where no ester was formed. The difference in the E_T^N values is comparable to the difference between ethanol and 1-propanol, so it seems unlikely that there would be such a dramatic solvent effect due to this small difference in solvent polarity.

Similarly, the hydrogen bond acidity (α) and polarizability (π^*) Kamlet–Taft parameters are very similar for each of the ILs used in this study [38]. The hydrogen

Table 5
Solvent properties of ionic liquids

IL	E_T^{Na}	π^{*b}	α^c	β^d	[CO] (mM) ^e
[C ₄ mim][PF ₆]	0.667	1.032	0.634	0.207	1.47
[C ₄ mim][TfO]	0.667	1.006	0.625	0.464	–
[C ₄ mim][BF ₄]	0.673	1.047	0.627	0.376	1.59
[C ₂ mim][EtSO ₄]	–	–	–	0.411 ^f	–
[C ₄ mim][TFA]	0.630	–	–	–	2.49
[C ₄ mim][NTf ₂]	0.642	0.984	0.617	0.243	3.60

^a Literature value determined from Reichardt's dye [31].

^b Kamlet–Taft polarizability parameter (literature values) [38].

^c Kamlet–Taft hydrogen bond acidity parameter (literature values) [38].

^d Kamlet–Taft hydrogen bond basicity parameter (literature values) [38].

^e Calculated solubility of CO at 1 bar using Henry's constant (literature values) [39].

^f Measured using solvatochromic dyes *p*-nitroaniline and *N,N*-diethyl *p*-nitroaniline by the method of Kamlet and Taft [30].

bond basicity (β), does vary with the basicity of the anion, ranging from 0.207 for [PF₆][−] to 0.464 for [TfO][−] in the [C₄mim]⁺ series. There was no clear correlation between the β parameter and ester yield or selectivity, however. [C₄mim][PF₆] did have the lowest β value of the ILs used, which could correlate with the low yield obtained in this IL. The β value of [C₄mim][NTf₂] is also quite low, yet it gave comparable ester yields and selectivities to ILs that were better hydrogen bond acceptors. Similarly, the β parameter for [C₂mim][EtSO₄] is relatively high, due to the more basic sulfate anion. The high yields and selectivity obtained in this IL cannot be solely ascribed to the increased basicity of the IL, as [C₄mim][TfO] has a higher β parameter, yet gave a lower yield and selectivity than [C₂mim][EtSO₄].

Another solvent property that could affect the efficiency of the catalytic process is the solubility of CO in the ILs. As seen in Table 5, the solubility of CO ranges from 1.47 to 3.60 mM for those ILs where it has been measured [39]. In the series [C₄mim][PF₆], [C₄mim][BF₄], and [C₄mim][NTf₂], there is a correlation between increasing CO solubility and increasing ester yield. The fact that [C₄mim][TFA] has a relatively high CO solubility, yet completely inhibited the esterification reaction shows that the correlation does not apply in all cases. It is likely that each of these solvent properties plays a role in determining both the activity and selectivity of the catalyst system.

5. Conclusions

The palladium-catalyzed hydroesterification of styrene in the presence of various ILs and methanol has been successfully demonstrated. Interestingly, high selectivity for linear products was observed with both styrene derivatives and 1-alkenes, in contrast to Dupont's results [19]. Promising catalyst recycling results were obtained suggesting the IL can effectively sequester the active species. The type of IL was found to have little

effect on catalytic activity or product selectivity in most cases, although certain ILs either promoted or inhibited the esterification reaction. Further studies with a broader range of solvents and a better understanding of IL solvent properties will be needed to more fully understand IL solvent effects on this catalytic process.

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