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# Styrene oxidation by hydrogen peroxide in ionic liquids: the role of the solvent on the competition between two Pd-catalyzed processes, oxidation and dimerization<sup>†</sup>‡

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A series of hydrophilic *N*,*N*-dimethylpyrrolidinium- and *N*,*N*-dimethylpiperidinium-based ionic liquids (ILs) have been prepared and applied as reaction media in the Wacker oxidation of styrene by hydrogen peroxide using PdCl<sub>2</sub> as the catalyst. The efficiency of these ILs was compared with hydrophilic and hydrophobic imidazolium systems (including those with nitrile functionalities). The nature of the ionic liquid strongly influences the product distribution. In particular, in hydrophobic ILs, relevant amounts of 1,3-diphenyl-1-butene arising from styrene dimerization were detected, in addition to the expected phenylmethylketone. The formation of 1,3-diphenyl-1-butene may be attributed to the formation of Pd(0) species from "ClPdOH" (probably formed during the Wacker process) in a side-reaction. Consequently, the ability of the IL to favor or disfavor the reoxidation of "ClPdOH" to "ClPdOOH" by hydrogen peroxide, giving an homogeneous phase or a biphasic system, appears to be the main factor affecting selectivity.

## Introduction

The conversion of fossilized hydrocarbons to fuels and other chemical products is a basic technology that is mainly based on intensive oxidation processes.<sup>1</sup> Although it is important to consider a future switch to alternative material sources and technologies, such as the use of renewable feedstocks, the development of low temperature, selective and direct hydrocarbon oxidation processes will continue to be an important topic. Transition metal-based complexes are able to efficiently catalyze the oxidation of alkanes and alkenes.<sup>2</sup> An excellent example in this area is represented by the Wacker reaction for the conversion of ethylene to acetaldehyde in water using a  $PdCl_2$ -CuCl<sub>2</sub> catalyst system.<sup>3</sup>

 $RCH = CH_2 + PdCl_2 + H_2O \rightarrow RCOCH_3 + 2HCl + Pd(0)$ 

 $Pd(0) + 2CuCl_2 \rightarrow PdCl_2 + 2CuCl$ 

<sup>b</sup>Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015, Lausanne, Switzerland † Electronic supplementary information (ESI) available: NMR spectra of the ILs [mmpip][CF<sub>3</sub>CO<sub>2</sub>], [mmpip][CH<sub>3</sub>CO<sub>2</sub>], [mmpip][NO<sub>3</sub>], [mmpyrr][CF<sub>3</sub>CO<sub>2</sub>], [mmpyrr][HSO<sub>4</sub>] and [mmpyrr][HCO<sub>2</sub>]. See DOI: 10.1039/c0gc00945h

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The reaction mechanism proceeds via coordination of the olefin to the electrophilic Pd(II) center, followed by nucleophilic attack of water at the activated olefin ligand, which then releases the product and generates a Pd(0) species. The success of the catalytic cycle is assured by the ingenious in situ re-oxidation of Pd(0) to Pd(II) by a reaction with copper(II) chloride and oxygen (see the equations above). Nevertheless, the more general process, the oxidation of terminal olefins to methyl ketones (also known as the Wacker-Tsuji reaction), is a versatile reaction with broad application in synthetic chemistry, and is normally performed using a Pd(II) catalyst and molecular oxygen or excess hydrogen peroxide as the oxidant. Although the solvent of the original Wacker reaction is water containing HCl, due to the low solubility of many alkenes in water, low reaction rates and the formation of by-products are commonly observed, and consequently the reaction is generally conducted in mixtures of water and organic solvents (i.e. DMF, NMP and sulfolane) using an equimolar concentration of CuCl<sub>2</sub>.<sup>3</sup> The use of the PdCl<sub>2</sub>-CuCl<sub>2</sub> catalytic system has some limitations, including the formation of chlorinated compounds (CuCl<sub>2</sub> often promotes rearrangements followed by nucleophilic addition of chloride anion),3 the precipitation of metallic palladium and corrosion phenomena.

Recently, several attempts to improve the efficiency of the catalytic system have been proposed, such as avoiding the use of

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organic solvents or copper(II) salts. Surfactants, cyclodextrins, calixarenes, supported catalysts and alternative solvents such as fluorous phases, polyethylene glycols, supercritical  $CO_2$  and ionic liquids (ILs) have been used to reduce the main drawbacks of the Wacker oxidation process.<sup>4</sup> However, considering that ILs have attracted a lot of interest in the last decade as novel reaction media, and since they have been shown to be especially useful in metal-catalyzed processes,<sup>5</sup> it is surprising that there are only a few papers on ILs concerning the Wacker reaction. In 2002, the effect of catalytic amounts of ILs ([bmim][BF<sub>4</sub>] and [bmim][PF<sub>6</sub>], ca. 2.5 wt% of substrate) in the oxidation of styrene with  $H_2O_2$ in the presence of palladium chloride was described<sup>6</sup> for the first time, and subsequently a [bmim][BF<sub>4</sub>]-water mixture<sup>7</sup> was found to be an excellent solvent system for the Wacker oxidation of different olefins using the classical Pd/Cu catalyst under an oxygen atmosphere.

Herein, we report the oxidation of styrene with  $H_2O_2$  in the presence of palladium chloride in several ILs and show that the nature of the IL dramatically affects the selectivity and efficiency of the reaction, favoring, in some cases, the competitive process of styrene dimerization.

### **Results and discussion**

The oxidation of styrene with  $H_2O_2$  (35%) in the presence of palladium chloride was conducted in different 16 ILs (Scheme 1): hydrophobic ILs 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF<sub>6</sub>]), 1-ethyl-3-methylimidazolium bistriflimide ([emim][Tf<sub>2</sub>N]), 1-butyl-2,3-dimethylimidazolium bistriflimide ([bm<sub>2</sub>im][Tf<sub>2</sub>N]), 1-hexyl-3-methylimidazolium bistriflimide ([hmim][Tf<sub>2</sub>N]), 1-butylnitrile-3-methylimidazolium bistriflimide ([C<sub>3</sub>(CN)mim][Tf<sub>2</sub>N]) and butylnitrile pyridinium bistriflimide ( $[C_3(CN)py][Tf_2N]$ ), and hydrophilic ILs, including both the widely applied imidazolium salts 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF<sub>4</sub>]) and 1-ethyl-3-methylimidazolium dicyanamide ([emim][N(CN<sub>2</sub>)]) and the less investigated<sup>8</sup> cyclic onium salts, N,Ndimethylpiperidinium, and N,N-dimethylpyrrolidinium with nitrate, hydrogensulfate, formate and trifluoroacetate anions, were used.



Scheme 1 ILs evaluated as solvents in the Wacker reaction.

These new ILs were obtained through a simple twostep procedure starting from N-methylpyrrolidine and Nmethylpiperidine. Initially, N,N-dimethylpyrrolidinium- and N,N-dimethylpiperidinium-methylcarbonate were synthesized by alkylation of the corresponding tertiary amines with an excess of dimethyl carbonate (DMC) under reflux (Scheme 2).



Scheme 2 Synthetic strategy used to obtain *N*,*N*-dimethyl-pyrrolidinium- and *N*,*N*-dimethylpiperidinium-based ILs.

Both of these salts were subsequently transformed into the above mentioned ILs by the addition of an equivalent of the appropriate organic or inorganic acid.<sup>8</sup>

The oxidation of styrene (10 mmol) in the selected ILs (1 mL) were carried at 60 °C using a mole ratio of  $H_2O_2$  to styrene of 1.15 and 0.1 mmol PdCl<sub>2</sub>. To evaluate the efficiency of the ILs, reactions were stopped after 3 h prior to complete conversion, the products (see Scheme 3) extracted with diethyl ether, and analyzed by NMR and GC-MS. The results are summarized in Table 1.



Scheme 3 Isolated reaction products.

In hydrophilic ILs, phenylmethylketone (1) is the main oxidation product, accompanied by lower amounts of benzaldehyde (2) and benzoic acid (3). Only traces of aldehyde 4, the anti-Markovnikov Wacker product, were found in some reactions.

Table 1 Conversion and product distribution in the Wacker styrene oxidation in  $\mathrm{ILs}^a$ 

			Selectivity (%)			
	IL	Conversion (%)	1	2	3	5
1	[bmim][BF <sub>4</sub> ]	45	90	10		
2	$[\text{emim}][N(\text{CN})_2]$	<3				
3	[mmpip][AcO]	<3				
4	[mmpip][CF <sub>3</sub> CO <sub>2</sub> ]	85	92	8	_	_
5	[mmpip][NO <sub>3</sub> ]	42	90	8	2	_
6	[mmpyrr][NO <sub>3</sub> ]	80	95	5	_	_
7	[mmpyrr][HSO <sub>4</sub> ]	14	85	15	_	_
8	[mmpyrr][HCO <sub>2</sub> ]	13	100		_	_
9	[mmpyrr][ClO <sub>4</sub> ]	28	90	10	_	_
10	[mmpyrr][CF <sub>3</sub> CO <sub>2</sub> ]	80	93	7	_	_
11	[bmim][PF <sub>6</sub> ]	78	60	3	2	35
12	[emim][Tf <sub>2</sub> N]	90	30	3		67
13	$[bm_2im][Tf_2N]$	60	30	4		66
14	[hmim][Tf <sub>2</sub> N]	44	20	3		77
15	$[C_3(CN)py][Tf_2N]$	100	75	7	3	15
16	$[C_3(CN)mim][Tf_2N]$	100	62	3	5	30
17	$[C_3(CN)mim][BF_4]$	60	80	10	10	

" All products were characterized by GC-MS and NMR.

In contrast, the product distribution is significantly different in hydrophobic ILs, where, in addition to the oxidation products, the formation of relevant amounts of 1,3-diphenyl-1-butene (5) was always observed, sometimes accompanied by small amounts of (poly)styrenes.

1,3-Diphenyl-1-butene probably arose from the selective dimerization of styrene through a process that may be catalyzed by palladium species and generally requires the presence of a Lewis acid. However, the formation of 1,3-diphenyl-1-butene has been recently reported<sup>9</sup> in [bmim][PF<sub>6</sub>] using Pd(OAc)<sub>2</sub>–Cu(OTf)<sub>2</sub> and Pd(OAc)<sub>2</sub>–In(OTf)<sub>3</sub> as catalytic systems.

On the basis of the proposed mechanism (Scheme 4),<sup>9</sup> the dimerization of styrene should occur through nucleophilic attack of Pd(0)-styrene complex generated by the reduction of  $Pd(OAc)_2$  with the 1,3-dialkylimidazolium salt on the styrene double bond activated by complexation with copper triflate.



Scheme 4 Proposed mechanism for styrene dimerization.

Despite using a different palladium salt and with the absence of copper or indium salts, it is likely that an analogous mechanism is in operation in Tf<sub>2</sub>N-based ILs.<sup>9</sup> Nevertheless, the possibility that the IL cation, with acidic protons, can polarize the styrene double bond,<sup>10</sup> combined with the fact that Pd(0) may be formed under the reaction conditions, cannot be excluded. In molecular solvents, it has been reported that palladium-catalyzed olefin oxidations using hydrogen peroxide and PdX<sub>2</sub> salts occur through a palladium hydroperoxidic species ("XPdOOH"), probably formed by the addition of H<sub>2</sub>O<sub>2</sub> to the palladium salt (Scheme 5, X = Cl).<sup>11</sup> "XPdOOH" species may undergo oxygen transfer to the olefin through a pseudocyclic hydroperoxypalladation mechanism of the coordinated olefin, giving the corresponding ketone and "XPdOH".



**Scheme 5** Proposed mechanism for competitive palladium-catalyzed styrene oxidation and dimerization.

In the presence of an excess of  $H_2O_2$ , the hydroxyl species "XPdOH" is able to regenerate "XPdOOH". However, at low  $H_2O_2$  concentrations, hydroxypalladation of the olefin can take

place, affording the corresponding ketone and Pd(0), the latter usually precipitating as palladium black in molecular solvents but stabilized in ILs.

If the formation of Pd(0) in ILs competes with the regeneration of "XPdOOH" species, as in molecular solvents, one can hypothesize that oxidation and dimerization are two competitive processes having Pd(0) as a key intermediate (Scheme 5), and conditions that disfavor the regeneration of "XPdOOH" from "XPdOH" will result in increased levels of 5.

In agreement with this hypothesis, the formation of **5** was only observed in hydrophobic ILs, which afforded a biphasic system with the aqueous solution of  $H_2O_2$ . The biphasic nature of the system and the relatively high viscosity of these ILs probably reduces the re-oxidation rate of "CIPdOH" (due to mass transfer limitations). It is noteworthy that attempts to perform the dimerization process in the same ILs using exclusively PdCl<sub>2</sub> as catalyst gave significantly lower amounts of **5**, suggesting that a more efficient mechanism for Pd(0) formation is present during the oxidation process.

The formation of **5** in hydrophobic ILs makes these media unsuitable for the Wacker reaction. However, data reported in Table 1 show that hydrophilicity alone is not sufficient to ensure high yields and selectivities, and that the IL structure significantly affects product distribution and reaction rate. Low conversions (if any) are observed in ILs composed of basic anions or amphoteric anions (Table 1, entries 2, 3, 7 and 8), whereas high conversions and selectivities are obtained under comparable conditions in [mmpip][CF<sub>3</sub>CO<sub>2</sub>], [mmpyrr][CF<sub>3</sub>CO<sub>2</sub>] and [mmpyrr][NO<sub>3</sub>].

Since recent toxicity data<sup>12</sup> indicate that ammonium salts bearing short alkyl chains (including pyrrolidinium and piperidinium salts) are less toxic than most commonly-used ILs (mainly based imidazolium salts), and given that the procedure to prepare this class of ILs through the corresponding methylcarbonates is more environmentally benign and results in contaminant-free media, these ILs might have an important role as "green" media for oxidation reactions. However, since recycling of the solvent and catalyst is another vital parameter, the potential of these media to be reused was explored (Table 2).

In the recycling experiments, reactions were also stopped after 3 h. Generally, a progressive decrease in conversion was observed, which may be attributed to the progressive formation of palladium black, Pd(0), which was observed in most reactions performed in hydrophilic ILs. However, at least in the case of [mmpip][CF<sub>3</sub>CO<sub>2</sub>], it was possible to repeat the process four times, maintaining a satisfactory conversion and selectivity. Related to the problem of the formation of palladium black, it is noteworthy that this behaviour was not observed in nitrilecontaining ILs. In agreement with the previously observed<sup>13</sup> ability of these ILs to stabilize Pd(0) species (nanoparticles), high conversions were also obtained using [C<sub>3</sub>(CN)mim][Tf<sub>2</sub>N] after four recycles. Unfortunately, relevant amounts of 5 also were formed in the recycling experiments, reducing the possibility of using this IL as a solvent for the Wacker oxidation. It is noteworthy that the use of hydrophilic 1-butylnitrile-3methylimidazolium tetrafluoroborate ( $[C_3(CN)mim][BF_4]$ ) gave expected ketone 2 with a high selectivity (dimer 5 was not detected) and satisfactory conversion in the first cycle (Table 1,

Table 2 Recycling experiments<sup>a</sup>

	Recycle	Conversion (%)	Selectivity (%)			
IL			1	2	3	5
[mmpip][CF <sub>3</sub> CO <sub>2</sub> ]		85	92	8		
L FF1L 5 - 21	R1	80	91	6	3	
	R1	70	88	7	5	
	R3	75	85	7	8	
	R4	12	80	15	5	
[mmpyrr][NO <sub>3</sub> ]		80	95	5		
	R1	75	95	5		
	R2	55	60	27	13	
	R3	33	36	33	31	
	R4	<2				
[mmpyrr][CF <sub>3</sub> CO <sub>2</sub> ]		80	93	7		
	$\mathbf{R}_1$	65	91	9		
	$\mathbf{R}_{2}^{'}$	30	70	20	10	
	R3	18	70	30		
	R4					
[bmim][PF <sub>6</sub> ]		78	60	3	2	35
	R1	70	73	11	2	14
	R2	20	95	5		
	R3	10	95	5		
$[bm_2im][Tf_2N]$		60	30	4		66
	R1	50	52	11		37
	R2	18	62	8		30
$[C_3(CN)mim][Tf_2N]$		100	62	3	5	30
	R1	95	62		8	30
	R2	90	60	3	18	19
	R3	90	60	10	10	20
	R4	85	60	15	5	20
$[C_3(CN)mim][BF_4]$		60	80	10	10	
	R1	22	90	10		

<sup>a</sup> All products were characterized by GC-MS and NMR.

run 17), supporting the hypothesis that in  $[C_3(CN)mim][Tf_2N]$ , the biphasic system favors the formation of dimer **5**.

# Conclusions

In summary, the selectivity of the Wacker reaction of styrene towards the oxidation product has been shown to be high in hydrophilic ILs. In particular, high conversions and selectivities were obtained in [mmpip][CF<sub>3</sub>CO<sub>2</sub>], [mmpyrr][CF<sub>3</sub>CO<sub>2</sub>] and [mmpyrr][NO<sub>3</sub>]; three halogen-free ILs obtained through a relatively benign protocol (via pyrrolidinium and piperidinium methylcarbonates). In contrast, in hydrophobic ILs, significant amounts of 1,3-diphenyl-1-butene, arising from styrene dimerization, were formed in addition to the expected phenylmethylketone product. A plausible mechanistic explanation for the formation of this by-product involves the formation of Pd(0) via a side-process during the oxidation cycle. Therefore, the ability of the IL to favor or disfavor the re-oxidation of "CIPdOH" to "CIPdOOH" by reaction with hydrogen peroxide may be considered the main factor affecting the possibility of obtaining the expected ketone as the main (or practically only) product. In turn, the re-oxidation of "ClPdOH" or the reduction of the metal center to Pd(0) is strongly influenced by the 'accessibility' of  $H_2O_2$ . In hydrophilic ILs, the reaction mixture forms a single homogeneous phase and oxidation is favored, whereas in hydrophobic ILs, the aqueous solution of  $H_2O_2$  is immiscible, with the formation of a biphasic system, and the reduction of Pd(II) to Pd(0) becomes relevant.

# Experimental

# General

Reagents were of ACS grade and used as received. <sup>1</sup>H and <sup>13</sup>C NMR spectra of all the ILs were obtained on a Bruker 250 MHz spectrometer. Chemical shifts are reported downfield from TMS. GC-MS were performed by a gas chromatograph equipped with a DB-5 capillary column (30 m  $\times$  0.25 mm; coating thickness 0.25 mm) and an ion trap mass detector. Analytical conditions: injector and transfer line temperatures 220 and 240 °C, respectively; oven temperature programmed from 60 to 240 °C at 3 °C min<sup>-1</sup>; carrier gas helium at 1 mL min<sup>-1</sup>; injection of 0.2 mL (10% hexane solution); split ratio 1:30. Identification of the constituents was based on comparisons of the retention times with those of authentic samples, and matching against commercial (NIST 98 and ADAMS) and home-made mass spectra libraries built up from pure substances and MS literature data. Melting points were determined by differential scanning calorimetry (DSC) measurements under an inert atmosphere on 10 mg samples sealed in aluminium pans. Indium and tin were used for calibration. Samples were heated in the -30/250 °C temperature range at a 10 °C min<sup>-1</sup> heating and cooling rate.

1-Butyl-3-methylimidazolium hexafluorophosphate ([bmim]-[PF<sub>6</sub>]), 1-ethyl-3-methylimidazolium bistriflimide ([emim]-[Tf<sub>2</sub>N]), 1-butyl-2,3-dimethylimidazolium bistriflimide  $([bm_2im][Tf_2N]), 1-hexyl-3-methylimidazolium$ bistriflimide ([hmim][Tf<sub>2</sub>N]), 1-butylnitrile-3-methylimidazolium bistriflimide ( $[C_3(CN)mim][Tf_2N]$ ), butylnitrile pyridinium bistriflimide  $([C_3(CN)py][Tf_2N])$ , 1-butyl-3-methylimidazolium tetrafluoro-([bmim][BF<sub>4</sub>]), 1-ethyl-3-methylimidazolium borate dicvanamide  $([emim][N(CN_2)])$ and 1-butyInitrile-3methylimidazolium tetrafluoroborate  $([C_3(CN)mim][BF_4])$ were prepared from the corresponding chlorides by following a literature procedure.14

*N*,*N*-Dimethylpyrrolidinium methylcarbonate. A solution of *N*-methylpyrrolidine (10.0 mL, 94 mmol) in dimethylcarbonate (50 mL) was heated under reflux for 72 h; then, the excess of the unreacted substrate was removed under reduced pressure to give a highly hydroscopic solid. <sup>1</sup>H NMR (250 MHz, D<sub>2</sub>O):  $\delta = 2.18$  (m, 4H, CH<sub>2</sub>), 3.09 (s, 6H, CH<sub>3</sub>N), 3.29 (s, 3H, CH<sub>3</sub>O), 3.47 (m, 4H, CH<sub>2</sub>); <sup>13</sup>C NMR (62.9 MHz, D<sub>2</sub>O):  $\delta = 22.50$ , 49.74, 52.54, 66.72, 161. 27.

*N*,*N*-Dimethylpiperidinium methylcarbonate. A solution of *N*-methylpyperidine (10 mL, 81 mmol) in dimethylcarbonate (50 mL) was heated under reflux for 90 h; then, the excess of the unreacted substrate was removed under reduced pressure to give a highly hydroscopic solid. <sup>1</sup>H NMR (250 MHz, D<sub>2</sub>O):  $\delta = 1.61$  (q, *J* = 5 Hz, 2H, CH<sub>2</sub>), 1.84 (m, 4H, CH<sub>2</sub>), 3.05 (s, 6H, CH<sub>3</sub>), 3.30 (m, 4H, CH<sub>2</sub>), 3.49 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (62.9 MHz, D<sub>2</sub>O):  $\delta = 20.72$ , 21.25, 49.84, 52.40, 63.76, 161.24.

# General procedure for preparation of N,N-dimethylpyrrolidinium and N,N-dimethylpiperidinium acetate, trifluoroacetate, nitrate, perchlorate, hydrogensulfate and formate

To 20 mL of a 0.5 M aqueous solution of  $[mmpyrr][CH_3OCO_2]$  or  $[mmpip][CH_3OCO_2]$  was added dropwise an equivalent of

the proper acid dissolved in water (water solution 1 M) at room temperature. The mixture was stirred for an additional 24 h. The solvent and gaseous by-products were then removed on a rotary evaporator. All salts were checked for the presence of starting materials by NMR.

*N*,*N*-Dimethylpyrrolidinium nitrate. Hygroscopic white solid, m.p. = 220 °C (lit.<sup>8</sup> 220 °C). <sup>1</sup>H NMR (250 MHz, D<sub>2</sub>O):  $\delta$  = 2.18 (m, 4H, CH<sub>2</sub>), 3.07 (s, 6H, CH<sub>3</sub>N), 3.43 (m, 4H, CH<sub>2</sub>); <sup>13</sup>C NMR (62.9 MHz, D<sub>2</sub>O):  $\delta$  = 22.50, 52.48, 66.72.

*N*,*N*-Dimethylpyrrolidinium hydrogen sulfate. Hygroscopic white solid, m.p. = 204 °C. <sup>1</sup>H NMR (250 MHz, D<sub>2</sub>O):  $\delta$  = 2.06 (m, 4H, CH<sub>2</sub>), 2.97 (s, 6H, CH<sub>3</sub>N), 3.35 (m, 4H, CH<sub>2</sub>); <sup>13</sup>C NMR (62.9 MHz, D<sub>2</sub>O):  $\delta$  = 22.45, 52.54, 66.61.

*N*,*N*-Dimethylpyrrolidinium formate. Hygroscopic white solid, m.p. = 209 °C. <sup>1</sup>H NMR (250 MHz, D<sub>2</sub>O):  $\delta$  = 2.20 (m, 4H, CH<sub>2</sub>), 3.11 (s, 6H, CH<sub>3</sub>N), 3.49 (m, 4H, CH<sub>2</sub>), 8.40 (s, 1H HC); <sup>13</sup>C NMR (62.9 MHz, D<sub>2</sub>O):  $\delta$  = 22.50, 52.54, 66.72, 171.37.

*N,N*-Dimethylpyrrolidinium perchlorate. Hygroscopic white solid, m.p. = 280 °C (lit.<sup>8</sup> 280 °C). <sup>1</sup>H NMR (250 MHz, D<sub>2</sub>O):  $\delta$  = 2.18 (m, 4H, CH<sub>2</sub>), 3.09 (s, 6H, CH<sub>3</sub>N), 3.47 (m, 4H, CH<sub>2</sub>); <sup>13</sup>C NMR (62.9 MHz, D<sub>2</sub>O):  $\delta$  = 22.50, 52.54, 66.72.

*N*,*N*-Dimethylpyrrolidinium trifluoroacetate. Hygroscopic white solid, m.p. = 192 °C. <sup>1</sup>H NMR (250 MHz, D<sub>2</sub>O):  $\delta$  = 2.18 (m, 4H, CH<sub>2</sub>), 3.09 (s, 6H, CH<sub>3</sub>N), 3.47 (m, 4H, CH<sub>2</sub>); <sup>13</sup>C NMR (62.9 MHz, D<sub>2</sub>O):  $\delta$  = 22.50, 52.54, 66.72, 117.25 (q, 291 Hz).

*N*,*N*-Dimethylpiperidinium nitrate. Hygroscopic white solid, m.p. *ca.* 245 °C (melting point is very close to the decomposition temperature). <sup>1</sup>H NMR (250 MHz, D<sub>2</sub>O):  $\delta$  = 1.61 (q, *J* = 5.5 Hz, 2H, CH<sub>2</sub>), 1.84 (m, 4H, CH<sub>2</sub>), 3.05 (s, 6H, CH<sub>3</sub>), 3.30 (t, 4H, *J* = 5.5 Hz, CH<sub>2</sub>).<sup>13</sup>C NMR (62.9 MHz, D<sub>2</sub>O):  $\delta$  = 20.74, 21.28, 52.44, 63.76.

*N*,*N*-Dimethylpiperidinium acetate. Hygroscopic white solid, m.p. 164 °C. <sup>1</sup>H NMR (250 MHz, D<sub>2</sub>O):  $\delta$  = 1.59 (q, *J* = 5.5 Hz, 2H, CH<sub>2</sub>), 1.84 (m, 4H, CH<sub>2</sub>), 1.86 (s, 3H, CH<sub>3</sub>); 3.05 (s, 6H, CH<sub>3</sub>), 3.28 (t, *J* = 5.7, 4H, CH<sub>2</sub>); <sup>13</sup>C NMR (62.9 MHz, D<sub>2</sub>O):  $\delta$  = 20.72, 21.25, 24.00, 52.44, 63.76.

*N*,*N*-Dimethylpiperidinium trifluoroacetate. Hygroscopic white solid, m.p. *ca.* 201 °C (melting point is very close to the decomposition temperature). <sup>1</sup>H NMR (250 MHz, D<sub>2</sub>O):  $\delta$  = 1.61 (q, *J* = 5.5 Hz, 2H, CH<sub>2</sub>), 1.84 (m, 4H, CH<sub>2</sub>), 3.04 (s, 6H, CH<sub>3</sub>), 3.28 (t, *J* = 5.7, 4H, CH<sub>2</sub>); <sup>13</sup>C NMR (62.9 MHz, D<sub>2</sub>O):  $\delta$  = 20.70, 21.23, 52.40, 63.76, 117.25 (q, 291 Hz).

#### General procedure for the Wacker oxidation

Reactions were carried out in glass vials equipped with Teflon (R) screw caps under magnetic stirring using a parallel synthesizer. PdCl<sub>2</sub> (0.1 mmol) was added to the selected IL (1.0 mL), followed by  $H_2O_2$  (35%, 11.5 mmol) and styrene (10 mmol). The reaction mixtures were heated at 60 °C and stirred vigorously for 3 h.

Subsequently, the mixtures were cooled to room temperature and the products extracted with diethyl ether  $(3 \times 5 \text{ mL})$ . The combined extracts were then washed with water, dried with MgSO<sub>4</sub>, and analyzed by GC-MS and NMR spectroscopy.

#### **Recycling experiments**

After product extraction, the resulting mixtures were dried under vacuum before new reagents (styrene and  $H_2O_2$ ) were added. Reactions were stopped after 3 h and product extraction performed as described above.

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