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Heterogeneous dehalogenation of arylhalides in the presence of ionic liquids

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Dehydrohalogenation of haloaromatics in ionic liquids derived from ethylmethylimidazolium or similar salts has been performed using Pd–C, Pd(OAc)$_2$ and other catalysts using formate salts as a hydrogen source. In the ionic liquid [emim][BF$_4$], chlorobenzene was dehalogenated by up to 40%, bromobenzene up to 25% and iodobenzene up to 41% in 2 h. Reactions in the absence of the ionic liquid were also performed. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: dehalogenation; ionic liquids; molten salts; haloaromatics; palladium

INTRODUCTION

Organohalides are often non-flammable and biocidal. These properties have led to the application of this type of compounds as flame-retardants, e.g. as poly(vinyl chloride) (PVC), and insecticides, e.g. polyhalogenated biphenyls (PCBs).[1] Their biocidal activity can, however, be a drawback since it is linked with resistance towards biological degradation and a tendency to accumulate in animal tissue. It is thus of considerable interest to develop efficient methods for the dehalogenation of recovered waste materials. These processes should also fulfil the requirements of 'green' chemistry, given the nature of the reaction.

The dehalogenation process has been studied in some detail in aqueous systems comprising water-soluble palladium(II) or ruthenium(II) catalysts. Allylic chlorides have been dehydrohalogenated in heptane–water solvent mixtures with [PdCl$_2$L$_2$] catalysts (L = sulfonated phosphines).[2] [RuCl$_2$(TPPMS)$_2$]$_2$ [TPPMS = PPh$_2$(3-C$_6$H$_4$SO$_3$Na)] and [Ru(H$_2$O)$_3$(PTA)$_3$]$_2^+$ (PTA = 1,3,5-triaza-7-phosphaadamantane) have proved effective catalysts in the hydrogenolysis of a variety of organic halides, such as CCl$_4$, CHCl$_3$, 1-hexyl and cyclohexyl halides, and benzyl chloride.[3] The reaction can be carried out at 80 °C with sodium formate as the hydrogen source with turnovers up to 1000 h^{-1}. Heterogeneous catalysts such as Pd–C,[4] Pt–C[5] or Raney–Ni[6] afford efficient dehydrohalogenation of aromatic halides under 1 bar of hydrogen pressure and mild conditions (50 °C) in multiphasic isooctane–aqueous medium in the presence of phase-transfer agents or surfactants. Cyclodextrines have been used as phase-transfer agenta in the aqueous reduction of bromoanisoles with sodium formate.[7]

A disadvantage with the use of water is the low solubility of many common organohalides in this particular solvent, thus necessitating the inclusion of a second, organic phase such as heptane or isooctane or a phase-transfer agent, as mentioned above. This is an aspect which ionic liquids can help to solve. Being of similar polarity to, for example, dichloromethane, they are able to dissolve both catalyst and substrate. Their negligible vapour pressure is also advantageous in that gaseous products, typically HCl, can be removed *in vacuo* together with the organic product. The water miscibility and polarity of the ionic liquid can also be tuned, allowing for a wide range of methods of product recovery and

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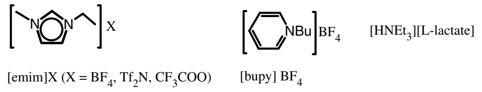


Figure 1. Ionic liquids studied.

catalyst recycling and the ionic liquid–catalyst phase can then be recharged with substrate and/or re-pressurised with hydrogen gas and reused.[8–14]

To date, two reports on the dehalogenation of organic substrates in ionic liquids have been published, one detailing the palladium phosphine catalysed hydrogenation of chloro- and bromoarylic substrates by reaction with sodium borohydride in the presence of tetramethylethylenediamine in carborane ionic liquids,[15] and the other concerned with the heterogeneous dehalogenation of functionalised arylhalides in Aliquat 336 under hydrogen gas using as catalysts Pd–C, Pt–C and Raney–Ni.[16]

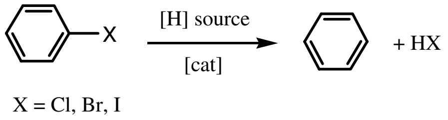
Here we describe the dehalogenation of mono- and dihaloaromatics X-C_6H_4-Y (X = Cl, Br, I; Y = H, Cl, Br) in a variety of ionic liquids [emim]X (X = BF_4, Tf_2N, CF_3COO) [bupy]BF_4 and [$HNEt_3$][L-lactate] (Fig. 1), hydrogen sources (H_2 gas, *iso*-propanol and formate salts) and using metal-based catalyst precursors.

RESULTS AND DISCUSSION

Initially, since H_2 solubility in ionic liquids is low, and relatively high pressures are therefore required,[17] the study was focused primarily on the use of non-gaseous hydrogen sources, such as *iso*-propanol and formate salts, the dehalogenation reaction of chlorobenzene to benzene (Scheme 1) was studied. Very poor results were obtained when *i*-propanol–KOH was used as hydrogen source. Whereas $RuCl_2(PPh_3)_3$ and its dppe-analogue[18] did react with tetramethylammonium formate to yield ruthenium hydride species, no subsequent dehalogenation of either chlorobenzene or bromobenzene was observed. However, both palladium(II) salts and palladium dispersed on carbon were found to be active in the dehalogenation of chlorobenzene using different formate salts as the hydrogen source, such palladium compounds are known to catalyse other reactions, involving the activation of aryl halides in ionic liquids.[19–23] This type of system was thus investigated in more detail (see Table 1).

For the dehalogenation of chlorobenzene to benzene, Pd–C and $Pd(OAc)_2$ were found to be more effective catalyst than either of the Pd(II) complexes investigated, [$PdCl_2(PPh_3)_2$] and [$PdCl_2$(dppp)], using [emim]BF_4 as ionic liquid and [$N(CH_3)_4$][OOCH] as hydrogen source (entries 1–4, Table 1). With Pd–C (5%) as catalyst, 33% of conversion in 4 h can be achieved with a TOF 52 h^{-1} (averaged value measured after 1 h).

H_2, sodium–, ammonium–, tetramethylammonium– and triethylammonium formate were all investigated as hydrogen



Scheme 1. Dehalogenation of haloaromatics.

Table 1. Dehydrogenation of chlorobenzene using palladium catalysts[a]

Entry	Ionic liquid	Catalyst	H source	Conv (%)
1	[emim][BF_4]	[$PdCl_2(PPh_3)_2$][b]	[$N(CH_3)_4$][OOCH]	0.3
2	[emim][BF_4]	[$Pd(OOCCH_3)_2$][c]	[$N(CH_3)_4$][OOCH]	6
3	[emim][BF_4]	[$PdCl_2$(dppp)][d]	[$N(CH_3)_4$][OOCH]	0.3
4	[emim][BF_4]	Pd/C (5%)	[$N(CH_3)_4$][OOCH]	20 (33, 4 h)
5	[emim][BF_4]	Pd–C (5%)	Na[OOCH]	7
6	[emim][BF_4]	Pd–C (5%)	Na[OOCH] (5M aq)	10
7	[emim][BF_4]	Pd–C (5%)	H_2[e]	6
8	[emim][BF_4]	Pd–C (5%)	[NH_4][OOCH]	4
9	[emim][BF_4]	Pd–C (5%)	[NEt_3H][OOCH]	5
10	[emim][Tf_2N]	Pd–C (5%)	[$N(CH_3)_4$][OOCH]	41
11	[emim][$OOCCF_3$]	Pd–C (5%)	[$N(CH_3)_4$][OOCH]	36
12	[bupy][BF_4]	Pd–C (5%)	[$N(CH_3)_4$][OOCH]	0
13	[$HNEt_3$][L-lactate]	Pd–C (5%)	[$N(CH_3)_4$][OOCH]	50
14	[emim][Tf_2N][f]	Pd–C (5%)	[$N(CH_3)_4$][OOCH]	6
15	[emim][Tf_2N][g]	Pd–C (5%)	[$N(CH_3)_4$][OOCH]	10

[a] Reaction conditions: 1 ml of ionic liquid; C_6H_5X 4.9 mmol; Z[OOCH] 5.0 mmol. 90 °C, substrate/catalyst = 418. Conversion determined by GC after 2 h. The only product found was benzene in all cases. [b] Substrate/catalyst = 358. [c] Substrate/catalyst = 276. [d] Substrate/catalyst = 393. [e] Atmospheric pressure (1.1 bar). [f] The ionic liquid phase in entry 10 was washed with diethyl ether, than water and then re-used by adding more substrate. [g] $scCO_2$ (117 bar).

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sources using Pd–C as catalyst and [emim]BF_4 as ionic liquid. Tetramethylammonium formate was found to give higher conversion (entries 4–9, Table 1).

Under the conditions used, the formate salts are soluble in the ionic liquid to some degree, but not completely. A kinetic study revealed a zero-order relationship with respect to the substrate, hence indicating that the rate-limiting step involves the formate salt, but not the arylhalide, either being the dissolution of the salt in the ionic liquid phase or the oxidation over palladium.

That the solubility of the formate salt plays an important role is mirrored by the results obtained when using different ionic liquids with different abilities to dissolve the salt (entries 10–13, Table 1). For example, when the poorly soluble sodium formate salt was used, the reaction proceeded more slowly (cf. entries 5 and 4, Table 1).

The conversion was higher using [emim][Tf_2N], [emim][$OOCCF_3$] or [$HNEt_3$][L-lactate]. In the case of the ionic liquid [emim][Tf_2N] after the separation of the ionic liquid 6% of conversion was obtained in a second run (entry 14, Table 1). Supercritical carbon dioxide has been successfully used in combination with ionic liquids as biphasic medium in homogeneous catalysed reactions.[24] In our case, the use of $scCO_2$ did not improve the results (entry 15, Table 1).

These results prompted us to further investigate the formate salts, Na[OOCH] (5 M, aq.) and [NEt_3H][OOCH], using Pd–C and $Pd(OAc)_2$ for the catalysed reduction of various chlorinated, brominated and iodinated aromatic compounds in the presence and absence of ionic liquid (Tables 2 and 3).

As can be seen from Table 2, the presence of the ionic liquid [emim][BF_4] has an effect on both the selectivity and the activity, regardless of which catalyst is used. When Pd–C or $Pd(OAc)_2$ was used with Na[OOCH] (aq) as the hydrogen source, it was found that the dehalogenation of chlorobenzene proceeded faster than that of iodobenzene when no ionic liquid was present (entries 1–3 and 7–9, Table 2). Iodobenzene was reported to react slowly also using Pd–C with formate salts[25] or hydrogen gas[26] as hydrogen source in water–ethanol solutions and this was attributed to an inhibition effect due to the strong adsorption of the substrate on the Pd. However, for the same hydrogen source, when ionic liquid is added the dehalogenation of chlorobenzene and iodobenzene occurs at higher rate than

Table 2. Conversion in the dehalogenation of different substrates[a]

Entry	Catalyst	Ionic liquid	Hydrogen source[b]	Substrate	Conversion (%)
1	Pd–C[a]	—	Na[OOCH](aq)	C_6H_5Cl	2
2	Pd–C[a]	—	Na[OOCH](aq)	C_6H_5Br	2
3	Pd–C[a]	—	Na[OOCH](aq)	C_6H_5I	0.2
4	Pd–C[a]	[emim][BF_4]	Na[OOCH](aq)	C_6H_5Cl	10
5	Pd–C[a]	[emim][BF_4]	Na[OOCH](aq)	C_6H_5Br	5
6	Pd–C[a]	[emim][BF_4]	Na[OOCH](aq)	C_6H_5I	18
7	$Pd(OAc)_2$][c]	—	Na[OOCH](aq)	C_6H_5Cl	60
8	$Pd(OAc)_2$][c]	—	Na[OOCH](aq)	C_6H_5Br	4
9	$Pd(OAc)_2$][c]	—	Na[OOCH](aq)	C_6H_5I	0.2
10	$Pd(OAc)_2$][c]	[emim][BF_4]	Na[OOCH](aq)	C_6H_5Cl	16
11	$Pd(OAc)_2$][c]	[emim][BF_4]	Na[OOCH](aq)	C_6H_5Br	8
12	$Pd(OAc)_2$][c]	[emim][BF_4]	Na[OOCH](aq)	C_6H_5I	17
13[d]	$Pd(OAc)_2$][c]	—	Na[OOCH](aq)	C_6H_5Cl	14
14[d]	$Pd(OAc)_2$][c]	—	Na[OOCH](aq)	C_6H_5I	16
15	Pd–C	—	[NEt_3H][OOCH]	C_6H_5Cl	43
16	Pd–C	—	[NEt_3H][OOCH]	C_6H_5Br	30
17	Pd–C	—	[NEt_3H][OOCH]	C_6H_5I	69
18	Pd–C	[emim][BF_4]	[NEt_3H][OOCH]	C_6H_5Cl	5
19	Pd–C	[emim][BF_4]	[NEt_3H][OOCH]	C_6H_5Br	7
20	Pd–C	[emim][BF_4]	[NEt_3H][OOCH]	C_6H_5I	21
21	[$Pd(OAc)_2$][c]	—	[NEt_3H][OOCH]	C_6H_5Cl	14
22	[$Pd(OAc)_2$][c]	—	[NEt_3H][OOCH]	C_6H_5Br	18
23	[$Pd(OAc)_2$][c]	—	[NEt_3H][OOCH]	C_6H_5I	64
24	[$Pd(OAc)_2$][c]	[emim][BF_4]	[NEt_3H][OOCH]	C_6H_5Cl	5
25	[$Pd(OAc)_2$][c]	[emim][BF_4]	[NEt_3H][OOCH]	C_6H_5Br	25
26	[$Pd(OAc)_2$][c]	[emim][BF_4]	[NEt_3H][OOCH]	C_6H_5I	41

[a] Reaction conditions: 1 ml of ionic liquid; C_6H_5X 4.9 mmol; Z[OOCH] 5.0 mmol, 90 °C, 2 h. Substrate/catalyst = 418. [b] Palladium on active carbon (5%); NaOOCH (5 M, aq.). [c] Substrate/catalyst = 276. [d] 70 mg of sodium dodecylsulfate was added per 0.5 ml of water.

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Table 3. Selectivity in transfer-hydrodehalogenation of dihalogenated benzenes 4-YC_6H_5X in [emim][BF_4][a]

					Products (%)			
Entry	Catalyst	H source	Substrate	Conversion (%)	Cl–Ph	Br–Ph	I–Ph	H–Ph
1	Pd–C (5%)	Na[OOCH] (aq.)	$BrIC_6H_4$	0.3	—	92	1	7
2	Pd–C (5%)	Na[OOCH] (aq.)	$ClBrC_6H_4$	1	83	3	—	14
3	$Pd(OAc)_2$[b]	Na[OOCH] (aq.)	$BrIC_6H_4$	15	—	74	0	12
4	Pd–C (5%)	[NEt_3H][OOCH]	$ClBrC_6H_4$	1	69	0	—	8
5	Pd–C (5%)	[NEt_3H][OOCH]	$BrIC_6H_4$	48	—	93	0	6

[a] Reaction conditions: 0.5 ml of ionic liquid; 4-YC_6H_5X 4.9 mmol; Z[OOCH] 5.0 mmol, 90 °C, 2 h. Substrate/catalyst = 418, 2 h, 90 °C.
[b] S/C = 276.

that of either bromobenzene (entries 4–6 and 10–12, Table 2). The presence of the ionic liquid may prevent the inhibition effect of the iodobenzene. Addition of sodium dodecylsulfate as a phase transfer agent in the absence of the ionic liquid for the substrates chloro- and iodobenzene provided similar results as when the ionic liquid was used (entries 13 and 14 vs 10 and 12, Table 2).

Using [NEt_3H][OOCH] as the hydrogen source with Pd–C or $PdOAc_2$ the dehalogenation of the haloaromatics follows the expected trend in that the conversion of the dehalogenation of iodobenzene is higher than for chloro- and bromobenzene (entries 13–24, Table 2). For the substrates chlorobenzene and iodobenzene, better results were generally obtained when the transfer-hydrodehalogenation was carried out in the absence of [emim][BF_4] than when it was present. While the conversions for chlorobenzene in [emim][BF_4] were low (up to 16%, entry 10, Table 2). The conversion observed for iodobenzene in the ionic liquid was up to 41% (entry 24, Table 2). In contrast, bromobenzene was dehydrogenated with higher conversions in the presence of the ionic liquid. The best conversion obtained for this substrate in the presence of ionic liquid was 25% (entry 23, Table 2).

Following these observations the dehalogenation of dihalogenated substrates was studied (Table 3), as were mixtures of mono-functionalised substrates (Table 4). In the dehalogenation of dihalogenated substrates in ionic liquid, the distribution of products shows that the tendency of dehalogenation follows the expected order I > Br > Cl. However, when mixtures of haloaromatics were studied, in the absence of ionic liquid the tendency for greater consumption of chlorobenzene respect to bromo- or iodo was maintained (entries 1 and 3, Table 4). When the reaction was performed with ionic liquid, the expected higher reactivity of iodobenzene was observed (entries 2 and 4, Table 4).

Table 4. Results of the haloaromatic consumption in mixtures PhCl : PhBr : PhI (1 : 1 : 1)[a]

		Consumption (%)		
Entry	Catalyst	Cl–Ph	Br–Ph	I–Ph
1	Pd–C (5%)	0.5	0.4	0
2[b]	Pd–C (5%)	0.5	0.5	2
3	$Pd(OAc)_2$[b]	0.9	0.7	0
4[b]	$Pd(OAc)_2$[b]	0.3	0.6	4

[a] Reaction conditions: 0.5 ml of ionic liquid; 4-YC_6H_5X 4.9 mmol; Z[OOCH] 5.0 mmol, 90 °C, 2 h. Substrate/catalyst = 418, 2 h, 90 °C.
[b] S/C = 276.

In conclusion, dehydrohalogenation of haloaromatics have been performed using Pd–C and $Pd(OAc)_2$ catalysts and several formate salts as hydrogen source, obtaining up to 69% for chlorobenzene using the substrate as a solvent and up to 40% using [emim] based ionic liquids. Bromobenzene was dehalogenated up to 25% conversion in [emim]BF_4 and iodobenzene up to 41% in the same ionic liquid (Table 2, entries 16–26). Since the removal of the aromatic hydrocarbon products is extremely facile due to their non-polar character, as quantified previously for benzene in several ionic liquids,[27] we believe that the system is worth studying further as it represents a potentially important 'green' process.

EXPERIMENTAL

Ionic liquids were synthesised according to published procedures.[28] In the typical experiment formate salt (5 mmol), halobenzene (4.9 mmol), catalyst and ionic liquid (1 ml) were mixed in a Schlenk flask and heated to 90 °C. After 2 h the mixture was allowed to cool and the benzene and unreacted starting material extracted by diethyl ether (1.5 ml). Yields were determined by GC (HP 5890 series II, column HP 5A, H_2 carrier gas; isothermal at 30 °C for 5 min followed by heating at the rate of 2 °C/min to 60 °C).

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