



Hydrogenation in ionic liquids: An alternative methodology toward highly selective catalysis of halonitrobenzenes to corresponding haloanilines

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Abstract

Ionic liquids (ILs) were for the first time found to be alternatively excellent media for the heterogeneously catalyzed hydrogenation of halonitrobenzenes to corresponding haloanilines over three type catalysts of Raney nickel, carbon-supported platinum and palladium. The ionic liquids give rise to higher selectivity and lower dehalogenation in the hydrogenating process compared with that observed in conventional organic solvents.

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Keywords: Ionic liquids; Hydrogenation; Halonitrobenzenes; Haloanilines; Dehalogenation

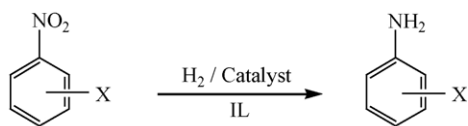
1. Introduction

Catalytic hydrogenation without dehalogenation of halonitrobenzenes to the corresponding haloanilines is an exciting challenge. It is well known that the hydrogenation is always accompanied by some hydrogenolysis of the aromatically bound halogen [1,2]. The art has attempted to solve the dehalogenation problem for many years. In most of the cases, the concepts behind these attempted solutions involve: (1) using metal sulfide catalysts [3,4], which are highly selective but considerably less active in this hydrogenation than the commonly used transition metal catalysts, (2) using various process modifiers, present in the solution phase, containing sulfur [5], nitrogen [6,7] and phosphorus [8,9] atoms such as thiophene, thioethers, morpholine, dicyanodiamide, polyamines, phosphites, phosphates and as well as inorganic base [10], such method as modifying a catalyst by additives to the reaction mixture has the advantage of combining high selectivity without losing too much activity and (3) using metal-modified catalysts [11,12], which were usually the supported platinum catalysts and Raney nickel modified with other kind of metals, such as Cu, Pb, Sn, Fe, etc. In general, platinum

catalyst is one of the best catalysts for minimizing dehalogenation while rapidly hydrogenating nitro groups, especially in the presence of the dehalogenation inhibitors; Raney nickel is also the most widely used catalyst with the combinational using of dehalogenation inhibitors; palladium catalyst even modified is of low selective hydrogenation and generally promotes extensive dehalogenation [13,14]. It is believed that the ease of dehalogenation depends on, besides the active metal, the halogen ($I > Br > Cl > F$), the overall structure and the reaction conditions [13,15]. A fair amount of work has gone into establishing conditions for retaining the halogen in the ring while hydrogenating the nitro group. Nevertheless, the dehalogenation-inhibition problem continues to be the focus of intense research [13,16], and the search of an alternative art for the selective hydrogenation of halonitrobenzenes should also be highly desired.

Ionic liquids (ILs) are attracting much interest in various areas of chemical synthesis, electrochemistry, separations and biotransformations, owing to their unique physicochemical characters [17,18]. Among these areas, catalysis in ILs is an exciting and burgeoning area of intense research and has been extensively reviewed recently [19–23]. It is reported that the use of ILs as reaction media for the catalytic transformations can have a profound effect on activity and selectivity. However, in the large majority of cases studied to date, ILs

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Scheme 1. Heterogeneously catalytic hydrogenation of halonitrobenzenes to corresponding haloanilines in ILs.

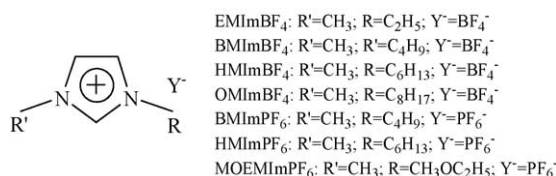


Fig. 1. Chemical structures of applied RMImY type ILs.

have been focused on the application in homogeneous catalysis or catalytic reactions in which catalysts were performed in situ, only a minority relates to catalysis using heterogeneous catalysts. Catalytic hydrogenation reactions are of exactly the same circumstances as other catalysis, as far as we know, only Hardacre and co-workers investigated the heterogeneous hydrogenation of α,β -unsaturated aldehydes in ILs using supported palladium catalyst and found better selectivity for the reduction of conjugated C=C bond by using ILs as solvents compared with conventional molecular organic solvents of toluene, cyclohexane and dioxane [24]. Thus, the remarkable performance of ILs in catalysis has drawn our attention and herein we report our preliminary results on the use of ILs for the heterogeneously catalyzed hydrogenation of halonitrobenzenes to haloanilines by choosing the important and typical substrates of *o*-chloronitrobenzene (*o*-CNB), *m*-chloronitrobenzene (*m*-CNB), *p*-chloronitrobenzene (*p*-CNB), *m*-bromonitrobenzene (*m*-BNB) and 3,4-dichloronitrobenzene (3,4-DCNB) over three standard catalysts of Raney nickel, Pt/C and Pd/C (Scheme 1) and the applied ILs were 1-alkyl-3-methylimidazolium based tetrafluoroborates (RMImBF₄) and hexafluorophosphates (RMImPF₆) (Fig. 1).

2. Experimental

2.1. Materials

5 wt.% Pt/C and 5 wt.% Pd/C were commercially available from Johnson Matthey. Raney nickel was prepared by alkali leaching from a commercially available crystalline Ni–Al alloy powders with 1:1 weight ratio [25]. ILs were prepared according to the procedures described in the literature [26] and fully characterized by IR (Bruker Equinox 55) and ¹H NMR (Bruker Avance 400) as follows, which were consistent with the literature data. Other materials were used as commercially available and without further purification.

2.1.1. EMImBF₄

IR (film, cm⁻¹): 3167 [γ (C–H) aromatic], 2962 and 2875 [γ (C–H) aliphatic], 1574 and 1456 [γ (C=C)], 1059 [γ (PF)]; ¹H NMR (CDCl₃, δ ppm): 8.42 (s, 1H), 7.34 and 7.29 (2s, 2H), 4.10 (m, *J* = 7.3 Hz, 2H), 3.78 (s, 3H), 1.36 (t, *J* = 7.3 Hz, 3H).

2.1.2. BMImBF₄

IR (film, cm⁻¹): 3160 [γ (C–H) aromatic], 2965 and 2877 [γ (C–H) aliphatic], 1570 and 1467 [γ (C=C)], 1059 [γ (BF)]; ¹H NMR (CDCl₃, δ ppm): 8.83 (s, 1H), 7.33 and 7.29 (2s, 2H), 4.19 (t, *J* = 7.5 Hz, 2H), 3.96 (s, 3H), 1.85 (m, 2H), 1.37 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

2.1.3. HMImBF₄

IR (film, cm⁻¹): 3161 [γ (C–H) aromatic], 2933 and 2862 [γ (C–H) aliphatic], 1574 and 1468 [γ (C=C)], 1061 [γ (BF)]; ¹H NMR (CDCl₃, δ ppm): 8.93 (s, 1H), 7.39 and 7.45 (2t, 2H), 4.19 (t, *J* = 7.4 Hz, 2H), 3.97 (s, 3H), 1.87 (m, 2H), 1.31 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 3H).

2.1.4. OMImBF₄

IR (film, cm⁻¹): 3160 [γ (C–H) aromatic], 2928 and 2858 [γ (C–H) aliphatic], 1574 and 1467 [γ (C=C)], 1060 [γ (BF)]; ¹H NMR (CDCl₃, δ ppm): 8.87 (s, 1H), 7.41 and 7.34 (2s, 2H), 4.14 (t, *J* = 7.4 Hz, 2H), 3.91 (s, 3H), 1.81 (m, 2H), 1.23 (m, 10H), 0.81 (t, *J* = 6.3 Hz, 3H).

2.1.5. BMImPF₆

IR (film, cm⁻¹): 3172 [γ (C–H) aromatic], 2966 and 2879 [γ (C–H) aliphatic], 1574 and 1467 [γ (C=C)], 836 [γ (PF)]; ¹H NMR (DMSO, δ ppm): 9.09 (s, 1H), 7.75 and 7.69 (2s, 2H), 4.16 (t, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 1.76 (m, 2H), 1.26 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

2.1.6. HMImPF₆

IR (film, cm⁻¹): 3171 [γ (C–H) aromatic], 2934 and 2863 [γ (C–H) aliphatic], 1574 and 1468 [γ (C=C)], 836 [γ (PF)]; ¹H NMR (DMSO, δ ppm): 9.09 (s, 1H), 7.75 and 7.68 (2t, 2H), 4.15 (t, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 1.78 (m, 2H), 1.28 (m, 6H), 0.86 (t, *J* = 7.2 Hz, 3H).

2.1.7. MOEMImPF₆

IR (film, cm⁻¹): 3172 [γ (C–H) aromatic], 2944 and 2840 [γ (C–H) aliphatic], 1576 and 1454 [γ (C=C)], 1124 [γ (C–O)], 836 [γ (PF)]; ¹H NMR (DMSO, δ ppm): 9.12 (s, 1H), 7.76 and 7.73 (2s, 2H), 4.41 (t, *J* = 6.1 Hz, 2H), 3.94 (s, 3H), 3.75 (t, *J* = 6.1 Hz, 2H), 3.34 (s, 3H).

2.2. Hydrogenation procedure

Hydrogenations were carried out in a Parr 25 mL stainless steel autoclave (Model 4591) provided with a process controller. In a typical procedure for the hydrogenation of *p*-CNB over 5% Pd/C in BMImBF₄: the reactor was charged with 0.02 g catalyst, 1.97 g (12.5 mmol) *p*-CNB and 7.5 mL

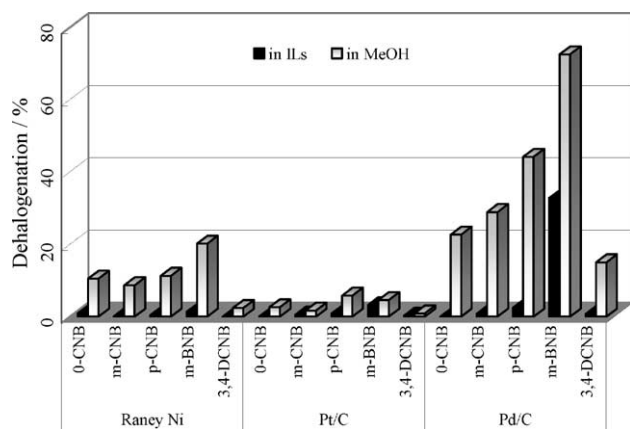


Fig. 2. Variation of dehalogenation extent on the selective hydrogenation of halonitrobenzenes over Raney Ni, Pt/C and Pd/C in RMImBF₄ (black) and MeOH (grey).

BMImBF₄. Air was flushed out of the reactor with nitrogen at room temperature; hydrogen was then fed into the reactor. Next, heating commenced with stirring at the speed of 600–650 rpm. When the designated temperature 100 °C was reached, the hydrogen was fed to the constant pressure 200 psig. The hydrogenating process was monitored intermittently by GLC (Agilent 6890) analysis of samples drawn from the reaction mixture and was stopped at the point of total conversion of *p*-CNB.

2.3. Analysis

All samples were characterized qualitatively by Agilent 6890N/5973N GC/MS equipped with a HP-5MS column, 30 m × 0.25 mm × 0.25 μm. Quantitative analyses were carried out with HP6890 GC equipped with a flame ionization detector and a HP-5 column, 30 m × 0.32 mm × 0.25 μm. The concentrations of reactants, dehalogenated products and desired products were directly given by the system of GC chemstation according to the area of each chromatograph peak. The dehalogenation was used as evaluated standard for the hydrogenation selectivity, which was calculated by: $100 \times (\sum \text{dehalogenated products} / \sum \text{all products})$. The spectra data of MS (*m/z*, %) for desired haloanilines are as follows. *o*-CAN: 127(100), 100, 92, 73, 65 and 52; *m*-CAN: 127(100), 100, 92, 73, 65 and 52; *p*-CAN: 127(100), 100, 92, 73, 65 and 52; *m*-BAN: 171(100), 92, 65 and 52; and 3,4-DCAN: 161(100), 134, 126, 99, 90, 73, 65 and 52.

3. Results and discussion

The hydrogenation results of the above five substrates over Raney Ni, 5% Pt/C and 5% Pd/C catalysts under different conditions with RMImBF₄ as solvent are summarized in Table 1 and depicted graphically in Fig. 2. Methanol (MeOH) was selected as a reference molecular organic solvent as it is most widely applied in heterogeneously catalytic hydrogena-

tion and moreover, it has a similar polarity to RMImBF₄ and therefore dissolves a similar range of compounds [27].

As shown, although both an elevated temperature and a higher pressure were required when compared with MeOH, the heterogeneously hydrogenation reductions could proceed in BMImBF₄ smoothly (except *o*-CNB over Raney Ni, which could proceed smoothly only in EMImBF₄ among the ILs investigated herein, and so far we have not discovered the reason). The conversions of halonitrobenzenes could reach to ca. 100% and almost none of hydrogenation intermediates, e.g. azo and azoxy compounds, etc., were discovered in the obtained products. The mass transfer effects are likely to be the main reason for the reduced rates in BMImBF₄ in two ways: (1) the viscosity of BMImBF₄ is higher than that of MeOH and this subsequently reduces the diffusion rate of the substrates to the surface of the catalyst and (2) the hydrogen solubility in BMImBF₄ is low and less than that in MeOH and this limits the availability of hydrogen at the catalyst site [28].

However, to our surprise, markedly low dehalogenation was observed with RMImBF₄ as media in comparison with MeOH. Over Raney nickel catalyst, ca. 98.7–100% purity of haloaniline with less than 1.3% dehalogenation were obtained in BMImBF₄ or EMImBF₄ (Entries 1–5) in contrast to 79.8–97.6% purity with 2.4–20.2% dehalogenation in MeOH (Entries 6–10). When using Pt/C catalyst (Entries 11–20), the extent of selectivity improvement in BMImBF₄ was not as clear as that obtained by using Raney nickel, but the dehalogenation was also decreased and the largest amplitude variation was found for hydrogenation of *p*-CNB from 5.8% dehalogenation in MeOH to 0.9% in BMImBF₄ (Entries 13 and 18). The most apparent improvement was discovered when hydrogenations were performed over Pd/C catalyst (Entries 21–30) with the minimum dehalogenation variation being 14.3%, i.e. from 15.0% in MeOH to 0.7% in BMImBF₄ for 3,4-DCNB (Entries 25 and 30), while the maximum could be reached to 41.7%, i.e. from 44.2% in MeOH to 2.5% in BMImBF₄ for *p*-CNB (Entries 23 and 28). It was observed that the dehalogenated products were all the corresponding dehalogenated anilines except for Entries 24 and 29, in which dehalogenated nitrobenzene (i.e. nitrobenzene) was also detected. This means that a simultaneous hydrogenation of the nitro group and hydrogenolysis of bromine in *m*-BNB occurred during the hydrogenating process over Pd/C catalyst both in BMImBF₄ and in MeOH (Entries 24 and 29), while hydrogenolysis of halogen is usually a subsequent reaction from the haloanilines.

Anyway, in all cases investigated, the promoting effect of ILs induces a lower dehalogenation of halonitrobenzenes to corresponding benzenamines, while a higher dehalogenation usually occurs with conventional molecular organics as solvents at an elevated temperature and a higher pressure. This behavior may have one of two explanations: (1) either the chemisorbed strength of haloanilines on the catalyst surface decreases when using ILs as reaction media due to the relative strong IL–haloaniline interaction, with the former

Table 1
Catalytic hydrogenation results of halonitrobenzenes in RMImBF₄ and MeOH^a

Entry	Catalyst	Solvent	Halonitrobenzene	<i>T</i> (°C)	<i>P</i> (psig)	Time (min)	Dehalogenation ^b (%)	Haloaniline purity ^b (%)
1	Raney Ni	EMImBF ₄	<i>o</i> -CNB	100	450	130	0.9	99.1
2		BMImBF ₄	<i>m</i> -CNB	100	450	120	0.1	99.9
3			<i>p</i> -CNB	100	450	100	0.4	99.6
4			<i>m</i> -BNB	100	450	150	1.3	98.7
5			3,4-DCNB	100	450	165	0	~100
6		MeOH	<i>o</i> -CNB	80	200	180	10.5	89.5
7			<i>m</i> -CNB	80	200	150	8.7	91.3
8			<i>p</i> -CNB	80	200	150	11.3	88.7
9			<i>m</i> -BNB	80	200	30	20.2	79.8
10			3,4-DCNB	80	200	30	2.4	97.6
11	5% Pt/C	BMImBF ₄	<i>o</i> -CNB	100	200	180	0	~100
12			<i>m</i> -CNB	100	200	120	0.5	99.5
13			<i>p</i> -CNB	100	200	140	0.9	99.1
14			<i>m</i> -BNB	100	200	120	3.2	96.8
15			3,4-DCNB	100	200	130	0.3	99.7
16		MeOH	<i>o</i> -CNB	30	40	110	2.6	97.4
17			<i>m</i> -CNB	30	40	130	1.7	98.3
18			<i>p</i> -CNB	30	40	125	5.8	94.2
19			<i>m</i> -BNB	30	40	50	4.6	95.4
20			3,4-DCNB	30	40	60	0.9	99.1
21	5% Pd/C	BMImBF ₄	<i>o</i> -CNB	100	200	240	0	~100
22			<i>m</i> -CNB	100	200	150	0.8	99.2
23			<i>p</i> -CNB	100	200	110	2.5	97.5
24			<i>m</i> -BNB	100	200	140	8.7 + 24.1 ^c	67.2
25			3,4-DCNB	100	200	120	0.7	99.3
26		MeOH	<i>o</i> -CNB	30	40	120	22.7	77.3
27			<i>m</i> -CNB	30	40	60	29.0	71.0
28			<i>p</i> -CNB	30	40	90	44.2	55.8
29			<i>m</i> -BNB	30	40	160	46.3 + 26.3 ^c	27.4
30			3,4-DCNB	30	40	140	15.0	85.0

^a Amount: IL or MeOH (7.5 mL), halonitrobenzene (12.5 mmol), Raney Ni (5 wt.%), 5% Pt/C (0.4 wt.%) and 5% Pd/C (1 wt.%).

^b Determined by GLC.

^c The dehalogenated products were aniline (the former) and nitrobenzene (the latter).

acting as Lewis acid and the latter as Lewis base, and hence haloanilines are easily desorbed from the catalyst surface and dehalogenation is restrained; (2) or hydrogenation catalysts exhibit a lower activity for C–halo bond hydrogenolysis in ILs. In order to check these hypotheses, experiments of the hydrodehalogenation of haloanilines over Pd/C, which caused the most considerable dehalogenation among the three type catalysts explored herein, were performed in MeOH and BMImBF₄, respectively, and quite different behaviors of hydrodehalogenation were observed. With *p*-chloroaniline (*p*-CAN) as example (Fig. 3), during the subsequent reduction after total conversion of *p*-CNB, the hydrodechlorination of *p*-CAN continued to proceed in MeOH and finally yield considerable amount of aniline (AN), while the similar performance disappeared in BMImBF₄ with no apparent hydrodechlorination occurred.

Moreover, it is worth noting that increasing the carbon number of the side chain on the imidazolium cation or changing the anion type could further inhibit the dehalogenation while the hydrogenation activity maintained. This behavior of ILs is especially effective for hydrogenations of susceptible to hydrogenolysis. Table 2 lists the hydrogenation results of *m*-BNB over Pd/C in different ILs. It was apparent that the

dehalogenation could be inhibited from 32.8% in BMImBF₄ to 16.2% in HMImBF₄, and be further inhibited to 2.1% in OMImBF₄ (Entries 1–3). The hydrodehalogenation was found to be fairly low in hexafluorophosphate anion based ILs

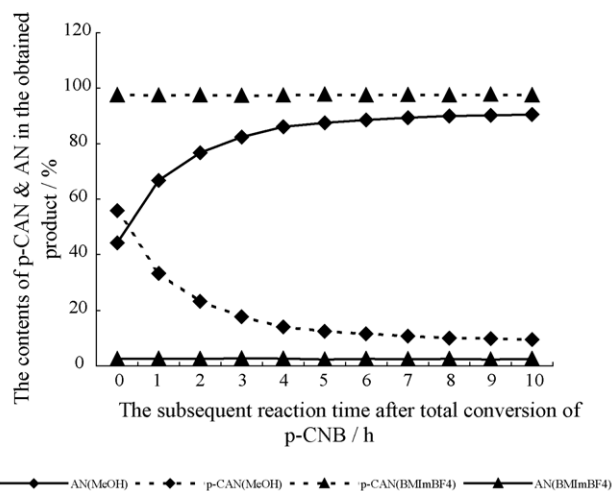


Fig. 3. The product distribution in the subsequent reduction process after total conversion of *p*-CNB over Pd/C in MeOH and BMImBF₄.

Table 2
Hydrogenation results of *m*-BNB over Pd/C in different ILs^a

Entry	Solvent	<i>T</i> (°C)	<i>P</i> (psig)	Time (min)	Conversion ^b (%)	Dehalogenation ^b (%)	Haloaniline purity ^b (%)
1	BMImBF ₄	100	200	140	~100	32.8	67.2
2	HMImBF ₄	100	200	170	~100	16.2	83.8
3	OMImBF ₄	100	200	180	~100	2.1	97.9
4	BMImPF ₆	100	200	360	~100	0	~100
5	HMImPF ₆	100	200	180	~100	0	~100
6	MOEImPF ₆	100	200	210	~100	2.2	97.8

^a Amount: IL (7.5 mL), *m*-BNB (12.5 mmol) and 5% Pd/C (1 wt.%).

^b Determined by GLC.

Table 3
Hydrogenation results of *p*-CNB over Pd/C in recovered BMImBF₄

Entry	Cycle	<i>T</i> (°C)	<i>P</i> (psig)	Time (min)	Conversion (%)	Dehalogenation (%)	Haloaniline purity (%)
1	Fresh BMImBF ₄	100	200	150	~100	2.5	97.5
2	Recycle 1	100	200	150	~100	3.2	96.8
3	Recycle 2	100	200	160	~100	2.8	97.2
4	Recycle 3	100	200	145	~100	1.4	98.6
5	Recycle 4	100	200	180	~100	2.9	97.1
6	Recycle 5	100	200	200	~100	2.6	97.4

(Entries 4–6). This showed that both the anions and cations of the ILs had a strong impact on the catalytic selectivity and the hydrogenation properties could be tuned by the proper choice of ILs.

The catalyst system in ILs was further investigated for its recyclability and the result using Pd/C-BMImBF₄ catalyst system is summarized in Table 3. The Pd/C-BMImBF₄ system was easily separable from the hydrogenation mixture by distillation of the desired product under vacuum or by extraction of the obtained products with diethyl ether and the remained catalyst system could be reused at least five times without apparent decrease of activity and selectivity. The similar circumstance was also observed in Pt/C-BMImBF₄ and Raney Ni-BMImBF₄ catalyst systems, respectively.

4. Conclusion

From the studies presented herein, it would appear that significant improvements could be achieved in the hydrogenation of halonitrobenzenes to the corresponding haloanilines over easily available catalysts in ILs with excellent selectivity of lower dehalogenation, and the selective hydrogenation of halonitroaromatics could be applicable to monohalo- and polychloro-substituted nitrobenzenes as well. To the best of our knowledge, it is the first report about the heterogeneously catalyzed selective hydrogenation of halonitrobenzenes in ILs and the obtained facts may open new opportunities and alternatives of great interest for this kind of hydrogenation reductions. Moreover, the novel approach was advantageous from the environmental benign point of view since it did not employ the conventional volatile solvents and the catalyst system could be easily recycled and efficiently reused. Fur-

ther studies are still on going and the results will be reported in due course.

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