n-butylpyridinium tetrafluoroborate, an ionic liquid, and its use as a medium for catalytic hydrogenation

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Abstract:
The use of “green chemistry” to obtain ionic liquids by microwave techniques proves to be useful and efficient. The solvent-free route that is obtained by using this technique allows the experiment to reduce the amount of exposure to water as well as shorten the reaction times. The reaction was done in two separate parts to obtain an intermediate compound, which was n-butylpyridinium bromide ([BuPy][Br]), and use that compound to isolate and obtain the ionic liquid when reacted in acetonitrile with sodium tetrafluoroborate. The major findings included good yields of the intermediate and final products on a small and large scale. Overall the use of the microwave technique proved to be relatively simple and efficient when obtaining the ionic liquid that could be used to conduct further reactions. More studies have included attempting to use this solvent in homogeneous catalytic hydrogenation reactions and to delineate factors which challenge this potential application. Further, if successful this would represent the first ionic liquid used in earth abundant metal hydrogenation catalysis.

Experimental Procedure:
Microwave reactions:
The set up for this part of the experiment was a 10 mL round bottom flask with the pyridine and 1-bromobutane in the bottom. This flask was attached to a drying tube and placed in a 150 mL beaker. The 150 mL beaker was filled with 80 mL of water. The starting temperature of this water was recorded and it was heated at 50 percent power (calibrated 350W) for 40 seconds. The temperature was recorded and the reaction was heated for another 40 seconds. After the first two rounds of heating, the water was changed out to keep the temperature below 100 deg C and the new starting temperature was recorded. After two rounds, a white precipitate had formed. This process was repeated 12 more times with the water change after every two rounds of heating. After the fourth round, the white precipitate turned clear. The goal of the reaction was to create one visible layer from the two that it began with (solvent-free).

The pyridine and 1-bromobutane product was then washed with diethyl ether three times and then separated. The top layer was the ether and excess 1-bromobutane, so the bottom layer was the product of the microwave portion of creating the ionic liquid, which was n-butylpyridinium bromide, [BuPy][Br]. Proton and carbon NMR were taken of this compound to ensure that the product was in fact n-butylpyridinium bromide. This reaction was repeated on the 10 mmol scale as well as a 1 mol scale. The temperature was recorded and the reaction was heated for another 40 seconds. After the first two rounds of heating, the water was changed out and the new starting temperature was recorded. After two rounds, a white precipitate had formed. This process was repeated 12 more times with the water change after every two rounds of heating. After the fourth round, the white precipitate turned clear. The goal of the reaction was to create one visible layer from the two that it began with (solvent-free).

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Ion-exchange reactions:
The next step was to distill acetonitrile for the ion exchange in creating the ionic liquid. Once this was completed, 2.157 g of n-butylpyridinium bromide, 3 mL of acetonitrile, and 1.210 g of tetrafluoroborate were added in a round bottom flask and stirred for three days. After the three day period that the product was vacuum filtered to isolate the product. The filtrate was then evaporated and the crude product was vacuum-dried overnight. Another reaction was done using 2.165 g of n-butylpyridinium bromide, 5 mL of acetonitrile and 1.842 g of KPF6. This was also stirred and isolated.

Experimental Results:

Figure 1. Proton NMR of intermediate
Figure 2. Carbon NMR of intermediate
Figure 3. Set-up for microwave intermediate
Figure 4. Microwave to produce [BuPy][Br] intermediate which shows layers
Figure 5. Result of Ion-Exchange gives room temperature ionic liquid: [BuPy][BF4]

Results and Discussion
We know that the microwave portion of the experiment was successful based on the results in Table 1. Both the proton NMR and the carbon NMR showed the right peaks to determine that the compound was indeed the [BuPy][Br].

The ionic liquid yields are shown in Table 2.

Attempts to use this media in water-sensitive catalytic hydrogenation reactions is ongoing.

Table 2. Ion Exchange Reactions

<table>
<thead>
<tr>
<th>Trial #</th>
<th>Amount butylpyridinium bromide</th>
<th>Amount acetonitrile</th>
<th>Salt</th>
<th>Amount salt</th>
<th>Percent yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.157 g</td>
<td>3 mL</td>
<td>NaBF4</td>
<td>1.210 g</td>
<td>78.00%</td>
</tr>
<tr>
<td>2</td>
<td>2.165 g</td>
<td>5 mL</td>
<td>KPF6</td>
<td>1.842 g</td>
<td>89.78%</td>
</tr>
</tbody>
</table>

Table 1. Summary of microwave reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product Weights</th>
<th>% Yield of Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>10mmol</td>
<td>2.48 g</td>
<td>78.00%</td>
</tr>
<tr>
<td>1mol</td>
<td>87.3 g</td>
<td>89.78%</td>
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</table>

References and Notes: