

Full Research Paper

Organo-niobate Ionic Liquids: Synthesis, Characterization and Application as Acid Catalyst in Pechmann Reactions

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Abstract: The combinations of 1-butyl-3-methylimidazolium chloride with NbCl₅ yielded ionic mixtures with different melting point temperatures and acidity depending on the niobium molar fraction. The mixtures were characterized by thermal (DSC) and spectroscopic (FT-IR and ¹H NMR) analysis. The Pechmann reactions of different phenols with ethylacetoacetate, producing coumarins, was used as model to evaluate the catalytic behavior of these mixtures as acid Lewis catalyst. These reactions were carried out using acidic mixtures of 60 mol%.

Keywords: ionic liquids; niobium pentachloride; Pechmann reaction

1. Introduction

Ionic liquids (or “molten salts”), especially those derived from the dialkylimidazolium cation, have emerged as an alternative class of solvents in a wide range of processes due to their distinct physical-chemical properties, which can be finely tuned by varying the alkyl substituents and the ions [1]. Indeed, they have been largely used in two-phase organometallic and enzymatic catalysis, organic synthesis, electrochemistry, analytical chemistry, separation processes, etc [2-9]. It is interesting to

highlight that they have been described as green substitutes for organic solvents mostly because of their low vapor pressure, no flammability, recyclability and low toxicity characteristics [10].

Among all classes of ionic liquids, those obtained by mixing 1,3-dialkylimidazolium or alkyipyridinium halides with aluminium chloride are the most traditional and studied ones, affording ionic mixtures with physical-chemical properties mainly depending upon the molar fraction of the aluminium compound. Due to the acceptor/donor patterns, these ionic liquids present Lewis properties also dependent on the amount of the aluminium halide. It is worth mentioning that the Lewis acidity can be expressed in terms of the molar fraction of the aluminium compound (x), being called acidic the mixtures with $x > 0.5$ (or 50 mol%), basic when $x < 0.5$ and neutral when $x = 0.5$.

Despite the inconvenience of the great reactivity of these compounds towards air and water, their Lewis acidity makes them especially useful in Ziegler-Natta type catalytic systems and acid catalyzed organic reactions. In this sense, several papers relating the use of these compounds as alternative media for olefin dimerization, alkylation, Friedel-Crafts, Diels-Alder and Pechmann reactions have been published [11-16].

More recently, other halometalate anions were prepared and some were used as acid catalysts in organic reactions. For example, it was described that the combination of equimolar amounts of solid 1-butyl-3-methylimidazolium chloride (BMICl) and solid indium trichloride affords the new ionic liquid $\text{BMI} \cdot \text{InCl}_4$ [17]. Acidic mixtures containing excess of 5 mol% in InCl_3 were used in the tetrahydropyranylation of alcohols [17]. The preparation of the ionic liquid 1-ethyl-3-methylimidazolium hexafluoronioate has also been described, but its Lewis acidity was not explored in acid catalysis [18].

We wish to report here that the combination of BMICl with niobium pentachloride affords ionic mixtures with different melting point temperatures depending upon the niobium molar fraction. Like the aluminum or indium analogues, these mixtures also possess Lewis acidity and were suitably used as alternative acid catalysts in the synthesis of coumarins by the Pechmann reaction.

2. Results and Discussion

2.1 Preparation of ionic mixtures

The association of 1-butyl-3-methylimidazolium chloride and niobium pentachloride, as shown in Figure 1 for 50% composition, yields pale brown solids at room temperature, which become browned-red viscous ionic liquids when melted, probably affording anionic species such as NbCl_6^- . Some spectroscopic and physical-chemical properties of these ionic mixtures depend upon their compositions, as can be seen in Table 1.

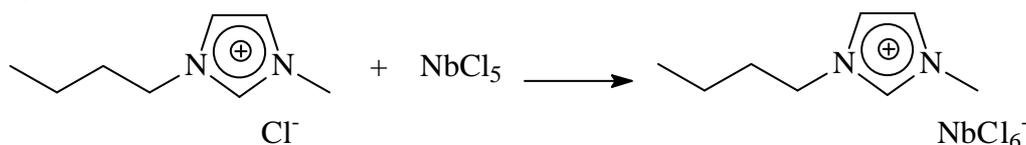
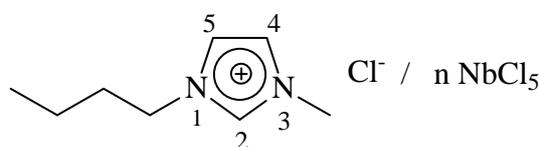


Figure 1. Association of 1-butyl-3-methylimidazolium chloride and niobium pentachloride.

Spectroscopic studies using $^1\text{H-NMR}$ and FT-IR strongly suggest that the niobium anionic species interacts through hydrogen bonds with the aromatic imidazolium hydrogens. Indeed, the $^1\text{H-NMR}$ spectrum of the 50 mol% mixture showed that the hydrogen in the position 2 of the imidazolium ring undergoes a downfield shift (from 9.4 ppm to 10.0 ppm). Moreover, as has already been pointed out in the literature for hydrogen-bond interactions between the halometallates anions and the imidazolium ring hydrogens [19], the appearance of bands in the $3050\text{-}3150\text{ cm}^{-1}$ region in the IR spectra of these ionic liquids was observed. Furthermore, the C-H stretching band at 3065 cm^{-1} due to the interaction of free-chlorine and the imidazolium ring hydrogens completely disappeared in the ionic mixtures.

Table 1. Some spectroscopic and physical-chemical properties of 1-butyl-3-methyl-imidazolium chloride/ niobium pentachloride ionic mixtures.



Composition (NbCl_5 mol%)	Melting point ($^\circ\text{C}$)	^1H chemical shift (ppm relative to DMSO-d_6)	Wavenumber (cm^{-1}) relative to aromatic C-H \cdots Cl stretching				
70	42	9.4	3098	3115	3122	3144	3159
60	51	9.4	3098	3115	3120	3145	3160
50	57	10.0	3098	3114	—	3146	3161
40	36	9.4	3098	3111	—	3145	—

2.2 Pechmann reaction

Classically, the Pechmann reaction refers to the condensation of β -ketoesters with phenols in the presence of excess of acid catalysts to produce 4-substituted heterocyclic compounds denominated coumarins, involving tandem hydroxyalkylation, transesterification and dehydration [20]. In the presence of an acid ionic liquid mixture with 60 mol% in Nb (0.5 mmol of total niobium content), the Pechmann's reaction of α -naphthol (25 mmol) and acetoacetate (25 mmol) at $60\text{ }^\circ\text{C}$ produce 32 % of coumarin with 100 % of selectivity in 2 h (see Figure 2). Utilizing superior quantity of this ionic mixture, i.e. 3 mmol of Nb, it was achieved 52 % reaction yield with 100 % selectivity in 1 h.

This method has been extended to a series of phenols using comparable reaction conditions (ionic mixture prepared with 60 mol% in Nb, with 0.5 mmol of total niobium content, 25 mmol of different phenols and 25 mmol acetoacetate at $60\text{ }^\circ\text{C}$ for 2 h). Reaction yields up to 40 % were achieved and Table 2 summarizes the reaction yields and the main characterization of the obtained 4-substituted coumarins obtained from α -naphthol, pyrogallol and resorcinol.

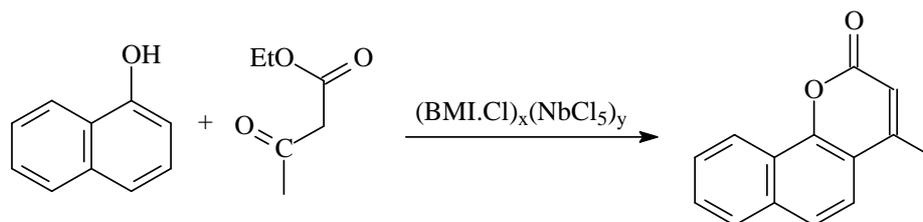


Figure 2. Pechmann's reaction of α -naphthol with ethylacetoacetate in organo-niobate ionic mixture.

Table 2. Synthesis of coumarins via Pechmann reaction using the niobium based ionic liquid as catalyst.^A

Entry	Phenol	Product	Yield (%) ^B	Chemical Shifts (¹ H NMR, 300 MHz)	Main Frequencies (mid IR)	Melting Points (°C)	
						Found	Lit.[5]
1			32	8.35 [m, 1H, H ₁₀]; 8.03 [m, 1H, H ₇]; 7.86 [d, 1H, J _{HH} = 8.6 Hz, H ₆], 7.78 [d, 1H, J _{HH} = 8.6 Hz, H ₅] 7.69 [m, 2H, H ₉ , H ₈]; 6.50 [s, 1H, H ₃]; 2.52 [s, 3H, CH ₃].	3067, 3023 [v(C-H) aromatic]; 2958, 2850 [v(C-H methyl group)]; 1714 [v(C=O)]; 1083 [v(C-O)].	158	152
2			40	10.05 [s, 1H, H ₈]; 9.29 [s, 1H, H ₇]; 7.09 [d, 1H, J _{HH} = 8.6 Hz, H ₆], 6.81 [d, 1H, J _{HH} = 8.6 Hz, H ₅]; 6.12 [s, 1H, H ₃]; 2.35 [s, 3H, CH ₃].	3415 [v(O-H) phenolic]; 3237 [v(O-H) phenolic]; 2964, 2856 [v(C-H methyl group)]; 1652 [v(C=O)]; 1064 [v(C-O)].	242	244
3			34	10.56 [s, 1H, H ₇]; 7.59 [d, 1H, J _{HH} = 8.6 Hz, H ₅]; 6.80 [d, 1H, J _{HH} = 8.6 Hz, H ₆]; 6.70 [d, 1H, J _{HH} = 8.6 Hz, H ₈]; 6.12 [s, 1H, H ₃]; 2.36 [s, 3H, CH ₃].	3076, 3013 [v(C-H) aromatic]; 2958, 2858 [v(C-H methyl group)]; 1679 [v(C=O)]; 1068 [v(C-O)].	180	185

^A Reactions conditions: 60 °C, 2 h; ^B Isolated products.

Some *o*- and *p*-substituted phenols, such as *o*-cresol and 4-phenyl-phenol, were also tested but no reaction was observed. This behavior was expected as already pointed out for the Pechmann reaction that electron-donor substitutes can enhance the activity when in meta position and diminish the reactivity of the phenol when in ortho or para positions [20].

Therefore, the combinations of 1-butyl-3-methyl-imidazolium chloride and niobium pentachloride produce ionic mixtures with their physical-chemical properties depending upon the niobium concentration. The ionic mixture of 60 mol% in Nb was found to be useful as catalyst to produce 4-substituted coumarins by the Pechmann reaction of α -naphthol, pyrogallol and resorcinol with ethylacetoacetate. Despite the moderate yields obtained in these transformations, we believe the organo-niobates described herein can be of potential utility as acid catalysis in other organic reactions as well.

3. Experimental Section

3.1 General

All manipulations were performed under dry, oxygen-free nitrogen atmosphere using standard Schlenk tube techniques. All solvents were used as commercially obtained. Infrared (film in NaCl for organoniobate mixtures and KBr pastille for coumarins) spectra were recorded in the 4000-400 cm^{-1} region using a BOMEM Hartman & Braun MB-Series FTIR spectrophotometer. $^1\text{H-NMR}$ spectra were recorded at 300 MHz using a Varian Mercury Plus 300 instrument. Hydrogen shifts are positive downfield relative to external SiMe_4 . Calorimetric experiments were carried out on a Shimadzu DSC 500, under helium, with heating rate of 10 $^\circ\text{C min}^{-1}$. The coumarins were also characterized by gas chromatography on a GCMS-QP5050A Shimadzu equipped with a pona column (length: 50m, thickness: 0.42 μm , diameter: 0.15mm). Helium was the carrier gas (column flow: 0.5 mLmin^{-1}); the temperature range was from 50 $^\circ\text{C}$ to 250 $^\circ\text{C}$ at a heating rate of 10 $^\circ\text{C min}^{-1}$, using toluene as reference. Melting points for coumarins were obtained in a Thomas Hoover Uni-melt capillary apparatus.

3.2 Materials

1-Butyl-3-methylimidazolium chloride was prepared according to literature procedures [21]. Commercial niobium pentachloride obtained from CBMM (Companhia Brasileira de Metalurgia e Mineraço) was distilled under vacuum and stored under nitrogen atmosphere. Ethylacetoacetate was distilled and stored under nitrogen atmosphere. The phenols were dried under low pressure by azeotropic distillation using toluene.

3.3 Organo-niobate ionic liquids preparation

The preparation of the organo-niobate ionic liquids was carried out by mixing 1-butyl-3-methyl-imidazolium chloride (BMICl) with niobium pentachloride using different amounts of the metal

chloride (40, 50, 60 and 70 mol% in Nb) using standard Schlenk technique. The desired amounts of BMICl and NbCl₅ were placed in a Schlenk tube and kept under magnetic stirring at 60 °C until complete homogenization was obtained.

3.4 Pechmann reaction procedure

The Pechmann reaction procedure used in this paper was adapted from the literature [22]. A mixture of phenol, ethylacetoacetate and ionic liquid (60 mol% in Nb), in a molar ratio of 50:50:1, respectively, was kept at 60 °C under efficient magnetic stirring for 2h. Then, the reaction was quenched by the addition of cold distilled water. The solid organic products were filtered, dissolved in hot acetonitrile and recrystallized at low temperature.

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