



1,3-Disubstituted imidazolium hydroxides: Dry salts or wet carbenes?

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ABSTRACT

The material known as 1-butyl-3-methylimidazolium hydroxide has been reported to be a 1:1 mixture of [BMIM]-cations and [OH]-anions and, as such, has been widely cited as a basic ionic liquid. 1,3-Disubstituted imidazolium-cations however, are prone to deprotonation at the C2-position of the imidazolium ring, a property readily exploited for the preparation of *N*-heterocyclic carbenes. Consequently, this reactivity may be unexpected and especially unwelcome when it leads to the decomposition of “[BMIM][OH]” itself, especially if the decomposition occurs during its use as a basic catalyst or reaction medium. Here, we highlight the putative “[BMIM][OH]”, as a case of particular inconsistency and inaccuracy in the literature and aim to dispel some of the persisting confusion surrounding its preparation, characterisation and use. The first part of this paper concerns the history, preparation and identity of so-called “[BMIM][OH]”, whilst the second part highlights some of the claimed activity, effects and problems associated with its use. Despite warnings in the literature, reports are still appearing in which mechanistic interpretations of reaction pathways and results are made without consideration of the unwanted reactivities of the 1,3-disubstituted imidazolium-cations employed. Future publications in which the use of “[BMIM][OH]” is reported should take into account the acidity of the [BMIM]-cation and the consequences this has for the chemistry being studied.

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1. Introduction

The chemical abstracts registry number 528818-81-7 is currently assigned to a material consisting of a 1:1 mixture of 1-butyl-3-methylimidazolium-cations and hydroxide-anions; more commonly known as the ionic liquid “[BMIM][OH]”. This material has attracted considerable interest over the last few years, following its first report in a 2003 patent application [1], and it is now commercially available from at least 3 different suppliers [2].

At the time of writing, a literature search using Scifinder Scholar™ revealed that “[BMIM][OH]” had garnered at least 161 references associated with some 388 index terms: the most frequent of which are shown in Fig. 1. Its HOMO and LUMO have been calculated and its basicity mentioned, but as an index term “carbene” is conspicuous by its absence. One hundred and seventeen of the 161 references associated with it are to journal articles, the remaining 44 to patents. “[BMIM][OH]” was first referred to as a decomposition product in a patent in 2001 [3] and since then has been reported with increasing frequency, as shown in Fig. 1. These publications have been cited 981 times (including self and cross citations).

1.1. Overview of reported use

The bulk of the interest in this material has centred on its remarkable properties as a synthetic reagent, particularly since it was reported in mid-2005 using the inconsistent terminology “catalyst and reaction medium” (albeit with turnover numbers of approximately 1.5) able to facilitate Michael additions [4]. This 2005 paper has received about 188 citations in the following years (SciFinder Scholar™ & Web of Science). Since then, “[BMIM][OH]” has been reported as a catalyst, reagent, and medium for a range of transformations. These include but are not limited to: aldol condensations and Michael additions [4–8]; combined Henry and Michael additions [9]; Mannich reactions [10]; Knoevenagel condensations [11–16]; combined Knoevenagel condensation and Michael addition [17]; multicomponent reactions [18–20]; Perkin reactions [12]; ketone thiolysis [21]; condensations of aldehydes and nitriles with thiophenol [22]; Markovnikovian additions of *N*-heterocycles to vinyl esters [23]; the debrominative decarboxylation of dibrominated α,β -unsaturated carboxylic acid to (*Z*)-vinyl bromides [24]; as a co-catalyst with chiral Co(salen) complexes and bimetallic salen complexes in the stereoselective coupling of CO₂ with racemic propylene oxide (or epoxy butane or epichlorohydrin) to form optically active cyclic carbonates [25,26]; the oxidative coupling of terminal alkynes to symmetrical 1,4-disubstituted 1,3-diynes at room temperature with added CuI [27]; alcohol [28,29] and aldehyde [30] oxidations; alkylation of substituted azoles [31]

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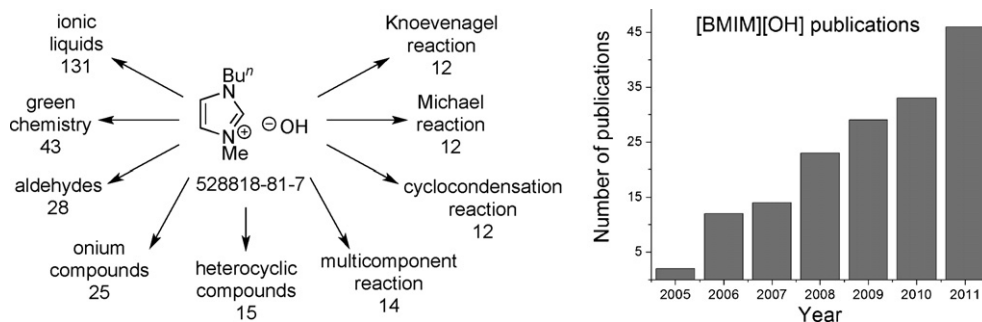


Fig. 1. “[BMIM][OH]” key index terms and the publication frequency associated with it obtained from Scifinder Scholar™.

and phenols [32] by alkyl halides; and the microwave-induced decarboxylation of indole-2-carboxylic acid [33]. It has been used in the wet etching of metal nitrides [34]; as a photoresist developer [35]; for metal oxide nanoparticle preparation [36–38]; and to prepare other ionic liquids by anion metathesis [39–44]. Remarkably, when used as a “catalyst and reaction medium” [5,33], “dual solvent and catalyst” [14] or as a basic solvent [45], it has frequently been reported to be easily reclaimed and recycled [5,14,15,17,33]. Additionally, “[BMIM][OH]” is frequently employed in solution at levels of, e.g., 20 mol%, [13] or 33 mol%, [7,32] or 60 mol% [17]; and therefore is not employed as an ionic liquid (as sometimes claimed) in these reports.

1.2. History and background of preparation

A 2003 US patent describes an electrochemical method for the preparation of aqueous solutions containing [BMIM]⁺_(aq) and [OH]⁻_(aq) ions at concentrations of 1–2 M [1]. A similar electrolytic procedure is also employed in a subsequent Chinese patent in 2005 [46]. The basic aqueous solutions are reacted “as is” with a variety of acids or electrophiles, such as carbon dioxide, to afford solutions containing [BMIM]-cations and conjugate-base anions. These salt products can be isolated, apparently, through the removal of water and are stable in pure form as ionic liquids, although tellingly (vide infra), no mention is made of trying to isolate the “[BMIM][OH]” intermediate as a dry salt. In this context, it seemed strange that a material formulated as pure “[BMIM][OH]” could be claimed.

Similarly Ohno and co-workers report the preparation of an aqueous solution of 1-ethyl-3-methylimidazolium hydroxide [EMIM][OH], by anion exchange of the bromide salt using an ion exchange resin such as Amberlite®-IRA400(OH), under ambient conditions [47]. The hydroxide solution was reacted immediately to change the anion. Regrettably, detailed experimental procedures are not disclosed in their initial publication [48]. A subsequent publication does not provide details of the concentrations of the solutions employed, and the [EMIM][OH] is neither isolated nor characterised [47].

2. Imidazolium-cation acidity and carbene formation

It is well known that the inherent acidity of the C2-hydrogen of an imidazolium-cation renders it reactive towards strong bases. In 1964 Olofson and co-workers reported deuterium for proton exchange at the C2-position of the 1,3-dimethylimidazolium-cation in aqueous borate buffer (pH 8.92) at 31 °C. The half-life of this reaction was determined to be 4.5 min [49]. In addition, both Dymek et al., and Giernoth and Bankmann have reported deuteration at the C2, C4 and C5 positions under basic conditions in D₂O at elevated temperatures [50,51] (Scheme 1).

Deprotonation at the C2-position of imidazolium-cations with bases, such as [R₂N]⁻, or alkoxides is a convenient and standard

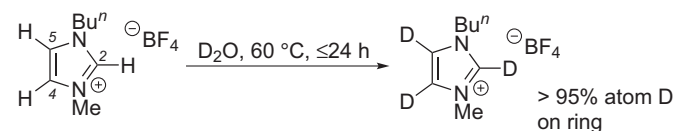
method for the preparation of *N*-heterocyclic (“Arduengo-type”) carbenes [52–54]: which, despite their stability compared with other classes of carbenes, are still extremely moisture sensitive, fuming in moist air [3].

A recent review by Chu et al. [55] clearly summarises the work of several other groups who previously reported the link between imidazolium salts and *N*-heterocyclic carbenes [49,56–58] and who have established which factors influence the acidity of the C2-position (and hence basicity of the conjugate carbene) of various imidazolium salts. These factors include solvent, effect of nitrogen substituents, and effect of the anion [59,60]. Amyes and co-workers, for example, have discussed the kinetics of formation and thermodynamic stability of such carbenes in water in detail. Based on their kinetics measurements, they additionally assert that imidazole-2-yl carbenes are 10⁸-fold more reactive towards water than a typical enolate-anion of the same thermodynamic basicity [60], thus accounting for the rapid H/D-exchange observed by Olofson more than 40 years ago.

Similarly, mixtures of [BMIM]-cations and basic anions such as hydroxide, alkoxide, amide (and to a lesser extent acetate and hydrogen carbonate), require the use of Schlenk-techniques or glovebox-conditions for preparation and manipulation. Furthermore, such mixtures decompose at room temperature or when heated, even in the absence of air [3,53,56].

These facts were known to Earle and Seddon, as early as 2001, who used kugelrohr-distillation to isolate the 1,3-dialkylimidazol-2-yl carbene products of the reaction of 1,3-dialkylimidazolium chlorides with potassium *tert*-butoxide. The resultant carbenes were then reacted with alcohols or acids to prepare unstable imidazolium salts containing basic anions. NMR data for the freshly prepared salts were reported (often as the sole means of characterisation; presumably due to difficulties in handling the materials for sample preparation), but the authors note that both the carbene precursors and the ionic products readily decompose in air, resulting in brown oils [3].

Chowdhury et al. devote the first section of their review on the reactivity of ionic liquids to “The incompatibility of imidazolium-based ionic liquids with bases” [53]. They comment “Noting [the basicity of the conjugate base singlet carbenes], it becomes immediately obvious that imidazolium-based ionic liquids are likely to be unstable under basic conditions and caution must be exercised in interpreting results obtained in reactions studied in such ionic



Scheme 1. Imidazolium ring deuteration at elevated temperature: we have also observed complete exchange in a sample of [BMIM][Br] in D₂O at pD 14 (excess NaOD), after several days at room temperature.

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