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On the mechanism of the reactivity of 1,3-dialkylimidazolium salts under basic to acidic conditions: a combined kinetic and computational study.

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Abstract: Comprehensive spectroscopic kinetic studies illustrate an alternative mechanism for the traditional free-carbene intermediated H/D exchange reaction of 1,3-dialkylimidazolium salts under neutral (D₂O) and acidic conditions (DCI/D₂O 35 wt % solution). The deuteration of high purity [bmim]Cl in D₂O is studied at different temperatures, in absence of catalyst or impurities, to yield an activation energy. DFT transition-state modelling, of a small water cluster and [bmim] cation, also yields an activation energy which strongly supports the proposed mechanism. The presence of basic impurities are shown to significantly enhance the exchange reaction, which brings into question the need for further analysis of technical purities of ionic liquids and the implications for a wide range of chemical reactions in such media.

In the last decades, there are indications that some of the more basic 1,3-dialkylimidazolium ionic liquids, **1**, are ‘non-innocent’, as reaction media.^[1] This has been attributed to the basicity of the anion counterpart,^[2] but is also dependent on the acidity of the cation at the C2 position of the imidazolium ring.^[3] The acidic nature of 1,3-dialkylimidazolium ionic liquids **1**, has also been a versatile source for the facile generation of N-heterocyclic carbenes (NHCs), with an extensive range of synthetic and catalytic applications.^[4]

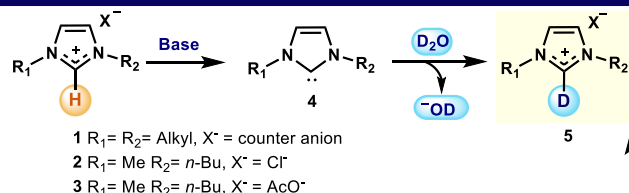
Mechanistically, the traditional ‘free-carbene’ pathway involves the formation of a covalent bond between the intermediate NHC and a suitable substrate, after deprotonation of the NHC precursor (**1**), using strong or mild basic conditions.^[5]

A particular well-known application of NHCs are H/D exchange processes, which constitute an essential diagnostic tool to gain mechanistic insight into a myriad of chemical and biological processes.^[6] This also allows access to isotopically labelled compounds with interesting pharmaceutical profiles^[7] or perdeuterated solvents for analytics,^[8] among many other applications. 1,3-Dialkylimidazolium salts also exhibit considerable advantages to participate in neutral H/D-exchange processes that enable the use of the sustainable and cost-effective deuterium oxide, as deuterium source. Indeed, the structural versatility of these salts allows tailoring at will their acid-base properties to facilitate such isotopic exchange processes.^[9]

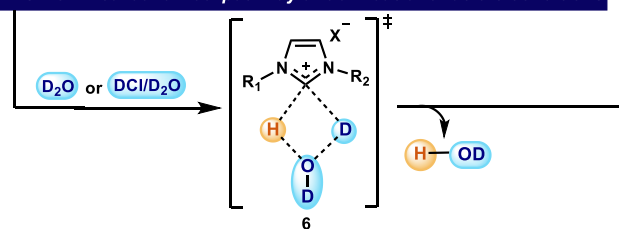
It is well-known that the proton at the C2 position of the imidazolium ring is labile enough^[10] to undergo deprotonation, upon strong or mild basic conditions to generate imidazole-2-ylidene species,^[4, 5] that can further react with D₂O^[11] (Scheme 1, up). Surprisingly, only a few isolated examples have been reported of such isotopic exchange processes proceeding upon neutral conditions, none of which provide solid mechanistic insight into the reactivity.^[12] Only recently, Gehrke and Hollóczki illustrated computationally that the ‘free-carbene’ species are not necessarily involved in organocatalytic processes, with simple aldehyde substrates.^[13]

Herein, we present an experimental and computational study that renders a concise mechanistic rationale for the H/D exchange at

Traditional pathway: ‘free-carbene’ mechanism under basic conditions



This work: ‘carbene-free’ pathway under neutral or acidic conditions



Scheme 1. Reported mechanism under basic conditions and mechanism proposed in this work under neutral and acidic conditions. Dotted lines in **6**, denote bonds which are broken and formed simultaneously.

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the C2 position of imidazolium ionic liquids under neutral conditions. A concerted 'carbene-free' mechanism is proposed (**Scheme 1**, bottom). These studies are not only consistent with but also complement the mechanistic scenario, initially proposed by Gehrke and Holl oczki,^[13] for the conjugation with aldehydes.

To begin our studies, we selected chloride as the counter anion, since it is reported that its reduced basicity prevents it from reacting with reducing ends in cellulose, as opposed to the acetate which does allow for this reaction to occur.^[14] 1-butyl-3-methylimidazolium chloride ([bmim]Cl), **2**, was prepared according to a modified literature procedure^[15] to very high purity (supporting information).

The H/D exchange under neutral conditions was investigated, by ¹H NMR (change in normalized relative intensities for C2-H), in the temperature range of 300.25 K to 339.45 K (**Figure 2**). The natural logarithmic plots yielded the rate constants (supporting information Figures S6-S10). The Arrhenius plots (natural logarithmic plot versus the inverse of temperature) gives a linear trend, as shown in **Figure 2** (inset), from which the activation energy (E_a) for the H/D conversion is obtained. Using the Arrhenius equation [Eq. (1)] (where A is a pre-exponential factor and R is the ideal gas constant) an experimental value of 31.1 kcal/mol was obtained for E_a .

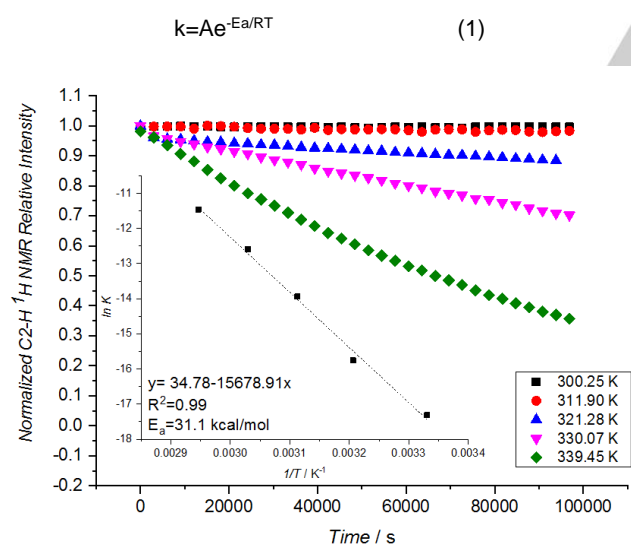


Figure 2. Initial 1st order kinetics, as a function of temperature for C2-H deuteration, in excess of D₂O, leading to an Arrhenius plot (inset).

The reaction was also investigated computationally using DFT transition-state modelling. This was achieved by carrying out relaxed potential-energy surface scans (TPSS density functional,^[16] Grimme's D3 dispersion correction,^[17] RI approximation^[18] and the def2-SVP^[19] basis sets), with varying C2-H bond lengths, for [bmim]Cl and a cluster of 21 water molecules. The maximum energy structure was stripped of the chloride anion and all but 3 water molecules. A transition-state search was performed using hybrid Hessian matrices. Full QM Hessian matrices using the def2-TZVP basis sets^[19] were then calculated to confirm the nature of the equilibrium and transition-

state structures. The Hessian matrices were employed to calculate thermal corrections for the energies under the harmonic approximation. The COSMO solvation model^[20] ($\epsilon=80$ for water) was applied, effectively charge-shielding the cationic charge but not offering any species with significant dynamically restricted Lewis basicity, in the absence of the explicit chloride anion. Thus, the obtained activation free energy should represent a value as close to 'neutral' conditions as possible. The calculated ΔG_a for the H/D exchange was 31.3 kcal/mol at 310 K, compared to the experimental value of 31.1 kcal/mol.^[21-22] The transition-state geometry is shown in **Figure 3**, where a concerted proton exchange occurs, mediated by H-bound water molecules.

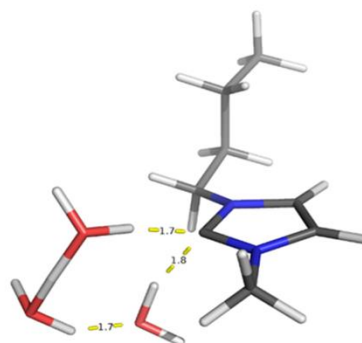


Figure 3. The geometry of the optimized transition state for the reaction in study, modelled as a proton exchange. The leaving proton is at the bottom. Distances shown in Å, correspond to H-bond distances.

The kinetic data for H/D conversion of **2** under different environments, such as neutral (D₂O), acidic (DCI/D₂O 35 wt. % solution) and basic conditions (sodium deuterioxide solution (NaOD 40 wt. %), triethylamine (Et₃N) or 1-methylimidazole (1-Melm)), are reported in **Table 1**. For comparison of deuteration kinetics for imidazolium ionic liquids containing chloride vs the more basic acetate anion, high purity 3-butyl-1-methylimidazolium acetate ([bmim][OAc]), **3**, was prepared and the deuteration kinetics reported in **Table 1** for one temperature under neutral conditions.

In the case of **2**, a long reaction time and heating are needed to reach a good yield in C2 H/D exchange under neutral conditions (Experiment 2, **Table 1**), whereas, deuterium incorporation at C2 in **3** is complete at room temperature after 4.8 hours (Experiment 1, **Table 1**). The differences in reactivity are assumed to be related to the basicity of the counter anions.^[2] Acetate anion is more basic than chloride, therefore it has an enhanced catalytic effect.

The catalytic effect of basic impurities is also observed in the H/D conversion at C2 for **2**. Screening with different added amounts of 1-Melm at 311.90 K clearly illustrates the effect of the base on the kinetics (Experiments 3-7, **Table 1**). The more base that is added, the faster are the deuteration kinetics. The presence of 3 % of stronger bases such as Et₃N and NaOD (40 wt.% solution) also increase the deuterium labelling at C4 and C5 (Experiments 8-9, **Table 1**).

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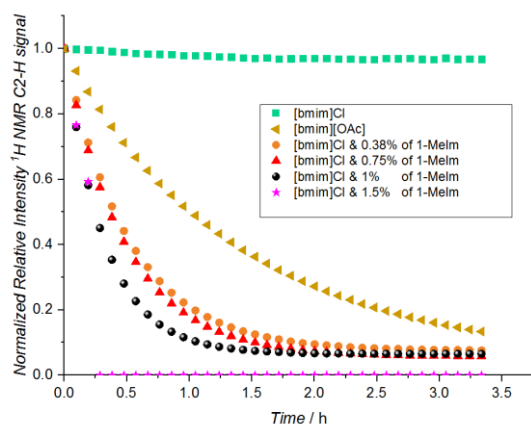
Table 1. Kinetic data for the deuteration in experiments 1-2 (neutral conditions, excess of D₂O), 3-9 (basic conditions), and 10-14 (acidic conditions), together with the D incorporation.

Experiment	Conditions ^[a]	Ionic Liquid (IL)	mol% with respect to the IL	Temperature / K	Time / h	D incorporation / %		
						C2	C4	C5
1	Pure D ₂ O	3	82	311.90	4.8	97	20	26
2	Pure D ₂ O	2	82	339.45	27	53	7	7
3	1-Melm	2	0.38	311.90	3.3 ^[b]	99	15	20
4	1-Melm	2	0.75	311.90	0.85 ^[b]	99	15	20
5	1-Melm	2	1	311.90	0.57 ^[b]	99	15	20
6	1-Melm	2	1.5	311.90	0.29 ^[b]	99	15	20
7	1-Melm	2	3	311.90	0.16 ^[b]	99	16	21
8	Et ₃ N	2	3	300.25	0.16 ^[b]	99	19	24
9	NaOD (40 wt. %)	2	3	300.25	0.16 ^[b]	99	31	37
10	DCI (35 wt. %)	2	1	300.25	192	10	13	16
11	DCI (35 wt. %)	2	10	300.25	192	7	10	12
12	DCI (35 wt. %)	2	50	300.25	192	11	14	19
13	DCI (35 wt. %)	2	100	300.25	192	6	9	13
14	DCI (35 wt. %)	2	200	300.25	192	0	2	4

[a] ionic liquid (0.370 – 0.424 mmol) in D₂O (34.4 mmol), [b] these time increments, corresponding to 99% conversion, were selected from the arrayed kinetic data.

The H/D exchange under neutral conditions mainly occurs at C2 while the deuterium incorporation at C4 and C5 is less significant, while under basic conditions the deuteration is more effective for all positions of the ring. However, in acidic environment (Experiments 10-14, **Table 1**) the D incorporation slows down considerably and H/D exchange is even slightly preferential at C4 and C5, over C2. At elevated acid concentrations (Experiments 13-14) the H/D exchange is rather much slower. Again, this confirms the effect that basicity has on the exchange kinetics.

Figure 4 illustrates the effect on H/D conversion of the counter anion (chloride or acetate under neutral conditions) vs the inclusion of 1-Melm (explicit neutral base). These comparative experiments were all recorded at 311.90 K. Kinetics for C2-H/D exchange on **2**, under neutral conditions, is clearly slowest by a large margin. Conversion of the high purity chloride, **2**, to high purity acetate, **3**, allows for a considerable rate increase, under neutral conditions. However, the incorporation of 1-Melm allows for the most rapid kinetics, with 1.5 mol% affording almost complete conversion near the start of the experiment time-frame. The more rapid kinetics were also observed when a commercial sample of **2** was used, without the addition of any base (supporting Information Figure S3). This indicates that the presence of basic impurities in commercial ionic liquids may have a huge impact on the validity of any chemistry performed within.

**Figure 4.** Effect of different counter ions and basic impurities on the H/D conversion at 311.90 K.

To put the results in context, the H/D exchange of imidazolium ionic liquids is observed under neutral aqueous conditions via a concerted 'carbene-free' transition-state involving proton-deuteron exchange. The presence of additional explicit base is shown to catalyse the reaction, which has implications for a wide range of applied chemistries using technical purity ionic liquids. Under neutral conditions, water is clearly also acting as both a weak base and acid.

Computational vs experimental activation energies are the same magnitude, which gives very strong support for this alternative mechanism, considering the presence of basic impurities has a major catalytic effect on the exchange kinetics. This mechanism is also confirmed by Gehrke and Hollóczki^[13] who showed computationally that the Gibbs free energy barriers for a series of conjugation reactions, between aldehydes and NHC precursors, all show lower energy barriers for the 'carbene-free' (associative) vs 'free-carbene' (dissociative) mechanism. In addition, no experimental evidence has yet been produced which has clearly identified free carbene in ionic liquid solution.

Daud et al.^[4b] have given tentative evidence for the spontaneous formation of carbene (as a non-rate limiting step), in mixtures of 1-ethyl-3-methylimidazolium acetate ([emim][OAc]) and 1-ethyl-2,3-dimethylimidazolium bistriflimide. This conclusion is based on the lack of observation of a kinetic isotope effect when comparing the kinetics of reaction of the C2 protonated vs the C2 deuterated version of [emim][OAc], with anisaldehyde. However, it is not clear how the kinetic isotope effect should affect the kinetics of the concerted mechanisms proposed herein and in the Gehrke report. Nevertheless, Arduengo^[4f] and others^[4] have clearly demonstrated that the presence of strong enough bases does allow for even isolation of imidazolium carbenes. Therefore, it should be assumed that 'free-carbene' will form at some point and is more a matter of equilibration, depending on the presence of more or less unconjugated basic species (anions or impurities) and temperature conditions.

Based on these combined results, it is emphasised that the effect of impurities on different chemistries should be tested, in particular when technical purity ionic liquids are used. In regard to biomass processing, which utilises the more basic ionic liquids,

such as 1-ethyl-3-methylimidazolium acetate initial reports are already appearing to show the influence of such impurities.^[23] However, in the past **2** has been widely used as an ionic liquid or as one of the customary precursor to generate NHCs species. It has been demonstrated that impurities may be more responsible for chemistry than the anion choice, neglecting the effect of physical properties.

Acknowledgements

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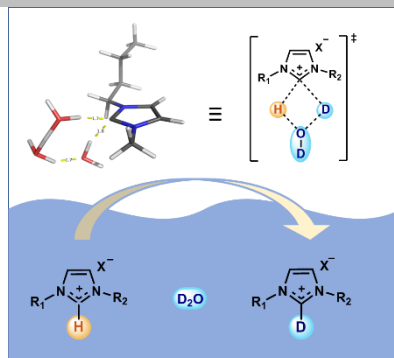
Keywords: ionic liquids • transition states • kinetics • carbenes • hydrogen bonds

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- [21]. The possibility of a sequential deuteration mechanism was also investigated. The calculations suggested that a stepwise mechanism is not feasible, in agreement with our experimental data (see supporting information section 6d, pages 5-6 and section 11, pages 22-27).
- [22]. Our methodology was further validated by calculations of the solvation contribution to the free energy barrier. The calculations show that the uncertainty in the solvation entropy contribution to the energy barrier is 0.8 kcal/mol, which is a small fraction of the full barrier value (see supporting information section 6e, page 6).
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Entry for the Table of Contents

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DFT transition-state modelling yields a 'carbene-free' mechanism for the archetypical deuterium exchange at C2 in imidazolium ionic liquids. This was also confirmed through determination of an experimental activation energy, almost identical to the DFT result. Impurities in technical ionic liquids are plainly implicated in enhanced reactivity.



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