# Imidazolium Cations with Exceptional Alkaline Stability: A Systematic Study of Structure–Stability Relationships

Kristina M. Hugar, Henry A. Kostalik, IV, and Geoffrey W. Coates*

Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301, United States

S Supporting Information

ABSTRACT: Highly base-stable cationic moieties are a critical component of anion exchange membranes (AEMs) in alkaline fuel cells (AFCs); however, the commonly employed organic cations have limited alkaline stability. To address this problem, we synthesized and characterized the stability of a series of imidazolium cations in 1, 2, or 5 M KOH/CD_3OH at 80 °C, systematically evaluating the impact of substitution on chemical stability. The substituent identity at each position of the imidazolium ring has a dramatic effect on the overall cation stability. We report imidazolium cations that have the highest alkaline stabilities reported to date, >99% cation remaining after 30 days in 5 M KOH/CD_3OH at 80 °C.
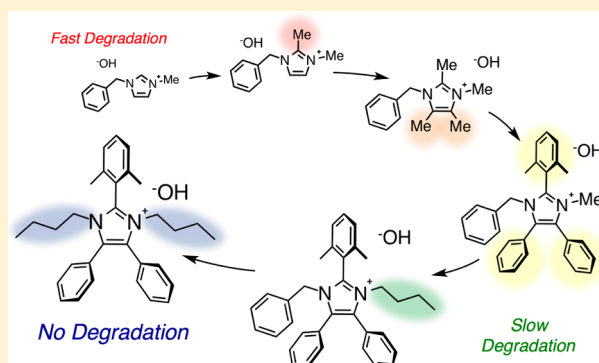
INTRODUCTION

The environmental and financial implications of our near exclusive dependence on fossil fuels have expedited research efforts to develop more effective methods of extracting the energy stored in chemical bonds.[1] Fuel cells have emerged as attractive electrochemical conversion devices due to their high energy density and their ability to produce energy more cleanly and efficiently as compared to conventional systems, such as internal combustion engines.[2] In particular, proton exchange membrane fuel cells (PEMFCs) have been useful in many commercial applications.[3] However, widespread production is limited by the cost and durability of the materials, specifically the platinum electrodes and electrolyte membrane.[4] To address these challenges, alkaline fuel cells (AFCs) have been investigated, which operate by transporting hydroxide ions through the electrolyte under basic conditions.[5] At elevated pH, oxygen reduction is more facile and lower overpotentials are required, enabling the use of non-noble metal catalysts in AFCs.[6] Indeed, the earliest examples of commercial fuel cells used aqueous potassium hydroxide solutions as the electrolyte medium to facilitate anion conduction. Unfortunately, the performance of these early fuel cells was compromised by exposure to carbon dioxide, a common component of feedstock gases, which reacts with hydroxide to produce carbonate salts.[7] To overcome this issue, alkaline anion exchange membranes (AAEMs), which are generally comprised of organic cations covalently linked to a polymer backbone, are employed to prevent the formation of mobile salts and retain the conductive organic cation/hydroxide species.[8]

Tetraalkylammonium cations have been appended to various polymer architectures to prepare AAEMs, including perfluorinated membranes,[9] aromatic polysulfones,[10] poly(arylene ethers),[11] poly(arylene ether ketones),[12] polyphenylenes,[13] polystyrenes,[14] and various aliphatic backbones.[15] Despite exhibiting high initial conductivity, numerous studies, such as those by Boncella and co-workers,[16e] have demonstrated that ammonium cations degrade rapidly under fuel cell operating conditions, limiting their utility and making the improvement of AAEM stability a critical priority.[16] Of note, the alkaline stability of membranes composed of a variety of polymer backbones was followed using ^{1}H NMR spectroscopy by Nuñez and Hickner.[16a] The disadvantages of using ammonium cations, particularly the ubiquitous benzyl trimethylammonium (BTMA) cation, have spurred investigations into the stability of other positively charged moieties in the presence of hydroxide, such as guanadinium,[17] phosphonium,[18] diazabicyclooctane-based (DABCO),[19] benzimidazolium,[20] morpholinium,[21] pyridinium,[22] pyrrolidinium,[23] metal organic frameworks (MOFs),[24] and ruthenium[25] cations (Chart 1). Marino and Kreuer recently described a class of quaternary spiroammonium compounds that exhibited improved alkaline stability as compared to the acyclic counterparts.[19a] Polymers containing base-stable cationic groups are also useful in other applications, including electrolysis,[26] gas separation,[27] desalination[28] and as stimuli-responsive materials.[29] Our group reported a polyethylene membrane containing a tetrakis-(dialkylamino)phosphonium cation that exhibited excellent stability;[30] however, the synthesis of this cation requires several difficult multistep reactions. Ideally, the best candidates for practical fuel cell devices are cations that are easy to make and incorporate into polymers, while maintaining optimal conductivity and stability.

Chart 1. Selected Cations Investigated for Use in Alkaline Anion Exchange Membranes (AAEMs)
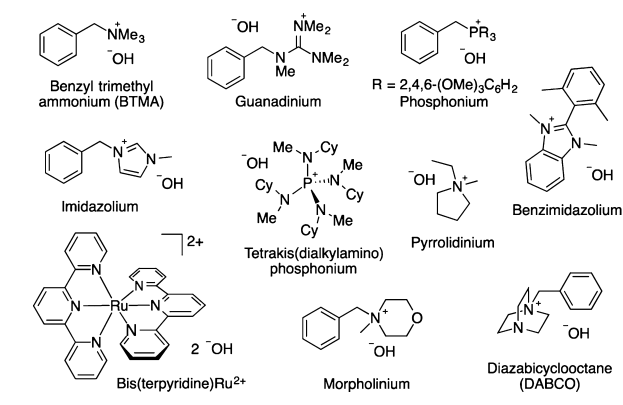
Imidazoles are a class of organic compounds that are amenable to synthesis because they are prepared by a modular route, with easily modified substituents, and are readily converted to the cationic form via alkylation. Additionally, they are stabilized by charge delocalization like the virtually inert tetrakis(dialkylamino)phosphonium cations. Researchers have attached *N*-methyl[31] or *N*-alkyl[32] benzyl imidazoliums to polymers and investigated them as alternatives to ammonium cations, and while these cations transport hydroxide sufficiently, the chemical stabilities of unsubstituted imidazoliums are generally much too low for fuel cell applications.[33] In fact, imidazolium cations with higher stability would be beneficial in many applications, such as organocatalysis,[34] solar cell electrolytes,[35] phase transfer catalysis,[36] and as carbon material precursors,[37] in addition to AAEMs. Imidazoliums degrade under alkaline conditions via four distinct mechanisms, and the identities of the substituents direct the degradation pathways (Scheme 1).[38] By selecting the appropriate substituents, several degradation routes are inhibited, thus deterring reactions
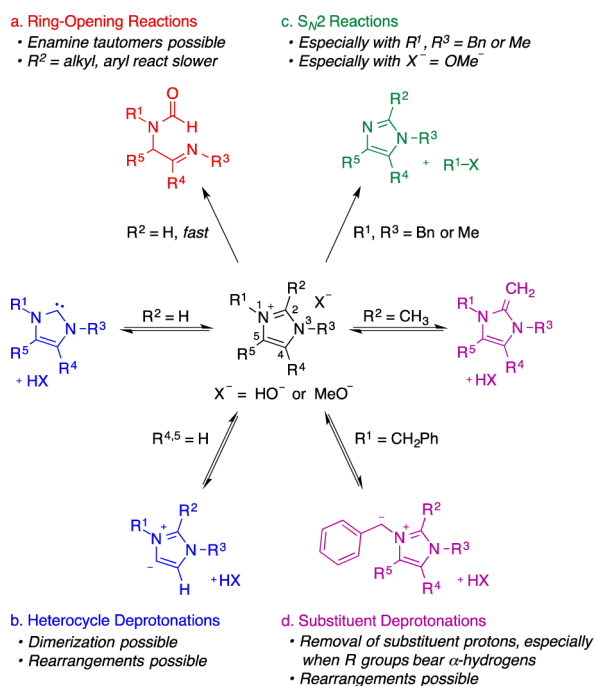
between the organic cation and reactive counteranions. Accordingly, recent studies on polymers containing imidazoliums with methyl groups in the C2 position suggested that this substitution improved alkaline stability compared to unsubstituted imidazoliums.[39] The numbering system of the imidazolium cation is described in Scheme 1. The attenuation in reactivity is attributed to steric factors, where nucleophilic addition and subsequent ring-opening of the heterocycle are hindered by the C2-methyl group (Scheme 1a).

Several researchers have explored the effect of C2 substitution on alkaline stability.[40] Specifically, studies on a related class of class of compounds, benzimidazolium cations, by Beyer,[20c] Holdcroft,[20e] and co-workers highlight the importance of bulky substituents at the C2 position. Density functional theory (DFT) calculations by Pivovar,[41a] Ramani,[41b] and others[41c,d] predict that substitution at the C4 and C5 positions will improve stability. These claims are supported experimentally in original work conducted by Wang et al.,[40e] which investigated imidazoliums with C4,5 methyl groups. Presumably, C4,5 substitution improves imidazolium stability by preventing deprotonation reactions (Scheme 1b). The degradation pathways discussed thus far only involve reactions directly at the ring positions (Scheme 1a and b); however, reactions with the peripheral substituents are also predicted (Scheme 1c and d). In fact, deprotonation of the peripheral substituents containing α-hydrogens is readily observed in basic solutions that contain protic deuterated solvents, as evidenced by hydrogen/deuterium exchange. Imidazolium reactivity is easily regulated by substituent variation, and eliminating the sites of vulnerability prevents degradation. The synthetic convenience, simplistic modification, and resonance stabilization of imidazoliums make them attractive targets, and we hypothesized that these features would enable the creation of cations with exceptional base stability.

Model compound studies, wherein the degradation rates of small molecules are assessed under alkaline conditions, are effective at determining the relative stabilities of a series of compounds. Once promising cations are identified, they must be incorporated into polymers where the collective stability of the AAEM can be determined under real-world operating conditions. In a recent report from Mohanty et al.,[42] a variety of quaternary ammonium hydroxide complexes were prepared and studied under relevant fuel cell operating temperatures. Several other protocols have been reported for determining model compound stabilities; however, the conditions vary widely, making productive comparisons between individual accounts difficult.[40] To rigorously assess the performance of new cations, we have developed an NMR spectroscopy method that unambiguously ranks the stability of cations.[43] Solutions of the cation are prepared in basified methanol-d_3 (KOH/CD$_3$OH) and stored in flame-sealed NMR tubes at 80 °C. At uniform time intervals, the solutions are analyzed by ^{1}H NMR spectroscopy for the amount of cation remaining relative to an internal standard.[44] The use of CD$_3$OH precludes a hydrogen/deuterium exchange process that causes a reduction in the cation signals (not related to degradation) and obscures new product signals. Methanol is a more universal solvent and conveniently dissolves organic cations and potential degradation products, a consideration of paramount importance for NMR spectroscopy studies. Key aspects of the degradation routes were revealed with this new protocol, which facilitates the design of new imidazoliums with strategically placed substituents to prevent decomposition.

Scheme 1. Degradation Pathways of Imidazolium Cations under Alkaline Conditions

Scheme 2. Summary of Model Compounds Investigated, Including the Synthesis of Imidazoliums with Varied Substitution Patterns
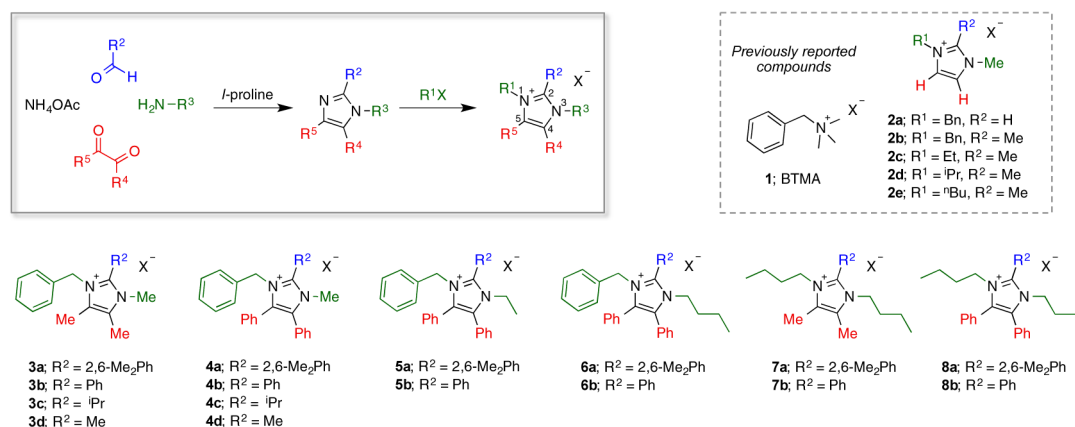
To date, investigations of imidazolium substitution patterns have been typically restricted to commercially available imidazoles. Fortunately, tetrasubstituted imidazoles, the neutral precursors to imidazoliums, can be prepared using simple multicomponent reactions.[45] Herein, we report the synthesis of a variety of imidazoliums (Scheme 2), systematically altering the structures to examine the precise influence of substitution patterns on the alkaline stability. Ultimately, these experiments led to the synthesis of imidazolium cations with higher resistance to reaction with bases and nucleophiles than any previously reported model compound studies. Furthermore, the synthetic accessibility of imidazoliums simplifies their incorporation into polymer architectures to achieve AAEMs with high conductivities and stabilities.

■ RESULTS AND DISCUSSION

Initially, we explored the impact of C4,5 substitution on cation stability by evaluating imidazoliums with hydrogen, methyl, or phenyl groups in the C4,5 positions (Figure 1). Methyl groups were installed at the C2 position because these substituents produce cations that are more stable than their C2-unsubstituted counterparts. To start, we investigated imidazo-
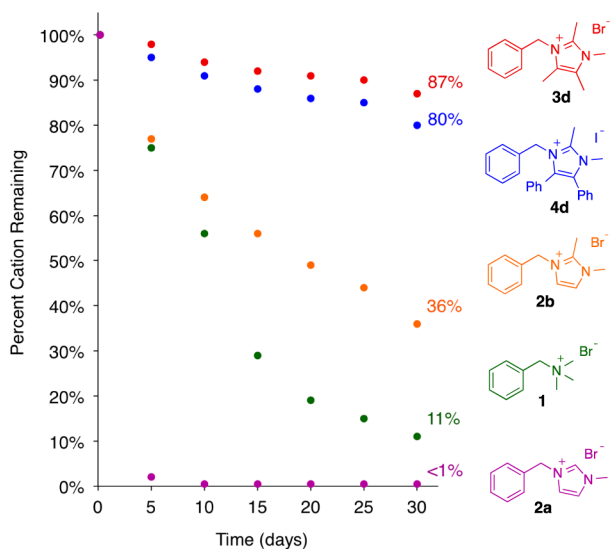
liums with N1-benzyl and N3-methyl groups, as the majority of imidazolium-based AAEMs reported in the literature have these functionalities. This series of cations was compared to benzyl trimethylammonium (1) (BTMA) and the C2 unsubstituted imidazolium, 1-benzyl-3-methylimidazolium bromide (2a) (Scheme 2).

As previously reported, 2a degrades rapidly under mildly basic conditions, with less than 2% cation remaining after 5 days.[43] In contrast, the imidazolium with a C2-methyl substituent (2b) reacts more slowly, leaving 36% remaining after 30 days. This simple imidazolium 2b is already an improvement over BTMA (1), which degraded to 11% remaining in the same time. BTMA degrades by nucleophilic attack at the benzylic and methyl positions, producing N,N-dimethylbenzylamine and benzyl methyl ether, as evident by ^{1}H NMR spectroscopy.[30] The resonances for similar nucleophilic displacement products (benzyl methyl ether, dimethyl ether, and the corresponding N1-benzyl or N3-methyl imidazoles) are not observed for 2a or 2b indicating that S_N2 reactions did not occur (Scheme 1c). Nucleophilic addition of hydroxide to the C2 position and concomitant ring-opening is reported for imidazolium degradation (Scheme 1a); however, the amide and imine signals corresponding to this degradation pathway are not observed for either compound. In fact, analysis by ^{1}H NMR spectroscopy indicates that imidazolium decomposition is more complicated than suggested in Scheme 1. We propose that the initial product(s) formed are not stable under the protocol conditions and undergo further degradation or rearrangement reactions. Additional work is needed to confirm the identity of the products and elucidate the secondary degradation mechanism(s). Introducing substituents to the C4,5 positions results in a substantial increase in stability. The imidazolium with C4,5-phenyl substituents (4d) degrades moderately faster than the C4,5-methyl version (3d), yielding 80% and 87% cation after 30 days, respectively. The degradation products for 3d are not yet identified, although 3d does not appear to degrade by an S_N2 mechanism. A small amount of nucleophilic displacement is observed for 4d; however, other degradation pathways are more prominent. Deprotonation of substituent hydrogens (i.e., C2-methyl or benzylic protons) followed by rearrangement is a plausible mode of degradation for both 3d and 4d (Scheme 1d). These examples strongly indicate that imidazolium stability is enhanced by C4,5 substitution, which agrees with the results obtained by Yan,[40e] Zhang,[38a] and co-workers. Therefore, this work focuses on compounds with

Figure 1. Stability of C4,5-substituted imidazolium cations (0.05 M) in 1 M KOH/CD$_3$OH at 80 °C.

C4,5-methyl or phenyl substituents, but other alkyl and aryl substituents should behave similarly.

Next, we investigated the effects of C2 substitution on imidazolium stability (Scheme 3). Imidazoliums generated from

Scheme 3. Influence of C2 Substituents on Imidazolium Stability: Percent Cation Remaining after 30 days at 80 °C[a]
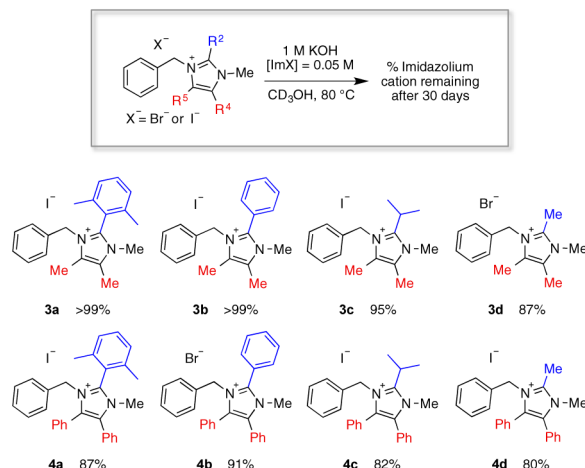
[a]Determined by ^{1}H NMR spectroscopy.

commercially available imidazoles (C2-methyl, isopropyl or phenyl groups, and C4,5-hydrogens) were previously studied by Lin et al.[40d] Holdcroft and co-workers investigated bulky C2-aryl groups and found that 2,6-dimethylphenyl substituents improved the stability of benzimidazoliums, as compared to phenyl groups alone.[20e] For comparison, we combined these four C2 substituents with our substitution patterns and evaluated their impact on imidazolium stability by reporting the percent cation remaining after 30 days (approximately 720 h).

Imidazoliums with C4,5-methyl substituents (Scheme 3, 3a–3d) are more stable than the analogous compounds with phenyl groups (Scheme 3, 4a–4d). In fact, little decomposition is observed over 30 days for the C4,5-methyl-substituted compounds, with the exception of 3d, as discussed previously. For this reason, the C4,5-phenyl-substituted series, which experienced moderate degradation, is used to analyze trends in the impact of C2 substitution (vide infra).

Imidazoliums with aryl groups at the C2 position (Scheme 3, 4a and 4b) are more base-stable than those with alkyl groups (Scheme 3, 4c and 4d). This observation contrasts with C2 trends observed by Yan and co-workers where alkyl substituents improved stability as compared to phenyl groups.[40d] The degradation rates for C2-aryl-substituted compounds (Scheme 3, 4a and 4b) are very similar (87% and 91% cation remaining, respectively). Likewise, varying the steric bulk of the C2-alkyl substituent does not strongly influence the base stability (Scheme 3, 4c and 4d). These results indicate that nucleophilic addition to the C2 position is not a major degradation pathway for 4a–4d. Amide and enamine resonances are not observed by ^{1}H NMR spectroscopy, suggesting that ring-opening decomposition is not occurring (Scheme 1a). The lack of ether and imidazole degradation products suggests that imidazoliums with C2-alkyls (4c and 4d) do not degrade by S_N2 attack, leaving substituent deprotonation and subsequent rearrangement reactions as potential decomposition routes (Scheme 1d). In contrast, the

imidazoliums with C2-aryls (4a and 4b) clearly degrade by S_N2 attack at the nitrogen substituents, and the resonances for benzyl methyl ether, dimethyl ether, and both imidazole products are observed (Figure 2, diagnostic signals are
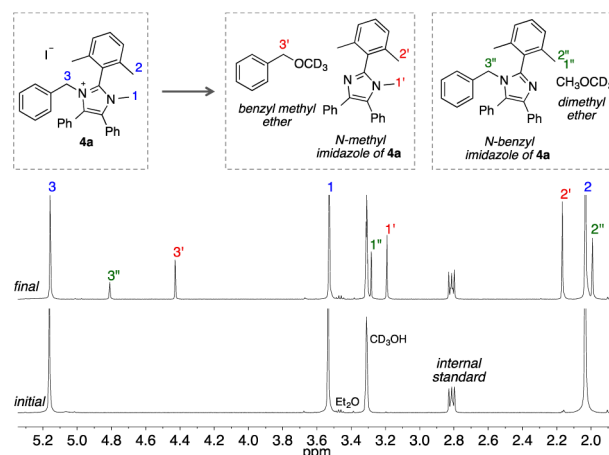

Figure 2. Degradation of 4a after 3 months in 1 M KOH/CD₃OH at 80 °C.

highlighted for 4a). Imidazoliums 4a and 4b react via S_N2 pathways primarily at the benzylic position followed by the N3-methyl position as evidenced by the distribution of products in the ^{1}H NMR spectra. Overall, C2-aryl groups improve the resistance of the imidazolium cation to base and were selected for continued examination.

We evaluated the impact of changing the nitrogen substituents by increasing the steric bulk of the N3-alkyl group from an N3-methyl to an N3-ethyl or N3-butyl. Synthesizing imidazoliums with both N1- and N3-butyl groups eliminated the reactive benzylic position altogether. We assessed imidazoliums with C4,5-phenyl groups because stability trends were more apparent with faster degradation rates (Scheme 4); although, after determining the best N1 and N3 substituents, we reinvestigated imidazoliums with C4,5-

Scheme 4. Influence of N1 and N3 Substituents on Imidazolium Stability: Percent Cation Remaining after 30 days at 80 °C[a]
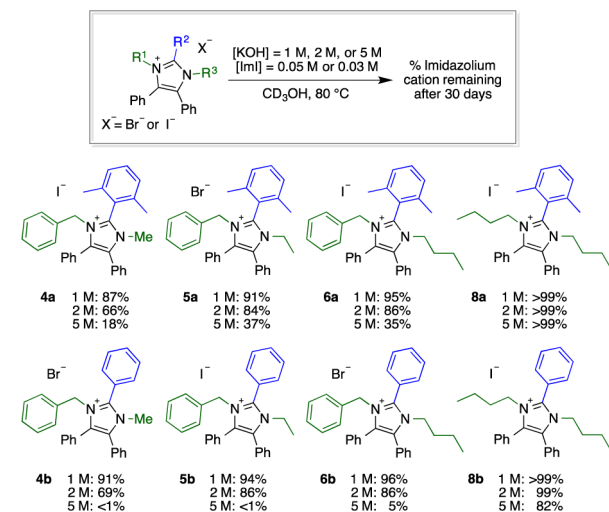
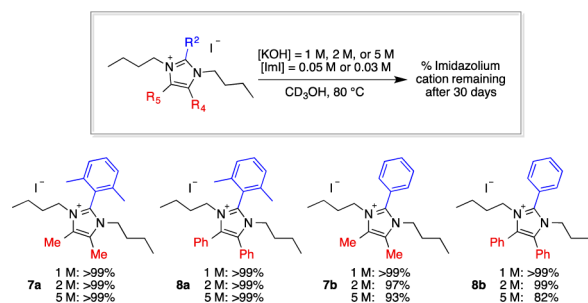[a]Determined by ^{1}H NMR spectroscopy.

methyl groups. To delineate trends in stability in a more convenient time frame, we raised the base concentration from 1 to 2 or 5 M KOH, increasing the rate of the degradation reactions.

In a series of benzyl imidazoliums with either C2-phenyls (Scheme 4, **4b**, **5b**, and **6b**) or C2-aryls (Scheme 4, **4a**, **5a**, and **6a**), the stability improved by switching from N3-methyl to N3-ethyl or N3-butyl substituents. A similar result was reported by Gu et al.,[40b] which showed that *n*-butyl groups improved imidazolium stability as compared to methyl groups. For example, in 1 M KOH, 87% of **4a** remains after 30 days, whereas 91% and 95% of **5a** and **6a** remain, respectively. The differences became larger as the concentration of base increases to 2 M KOH; 66% of **4a** remains, while 84% and 86% of **5a** and **6a** remain, respectively. When comparing 1 to 2 M KOH conditions (Scheme 4, **4a–6a** and **4b–6b**), the reaction rates increase consistently with the increase in base concentration and degradation continues to occur by an S_N2 mechanism. A decrease in nucleophilic attack at the α-carbon of the N3-substituent is observed as the length of the N3-alkyl group increases, which explains the prior observation that longer alkyl chains improve cation stability. ^{1}H NMR signals corresponding to ethylene or 1-butene are not readily detected, suggesting that Hofmann elimination (deprotonation and elimination of alkyl groups that contain β-hydrogens) is not a major degradation pathway for alkyl imidazoliums. An increase in degradation rate larger than predicted is observed for **4b**, **5b**, and **6b** in 5 M KOH, and ^{1}H NMR signals related to new degradation products are observed. At very high concentrations of base, these imidazoliums degrade by a mechanism other than S_N2 attack at the substituents bound to the nitrogens. The trend is only observed for the C2-phenyl imidazoliums (Scheme 4, **4b**, **5b**, and **6b**), which suggests that the new degradation pathway involves addition of base to the C2 position. One possible explanation involves the participation of multiple species of base ($^-$OH or $^-$OMe) in the rate-determining step of the reaction, resulting in a higher order dependence of base under very high concentrations of base. It is important to emphasize that the goal of increasing the base concentration is to accelerate reactions that occur at 1 M KOH, not to introduce new degradation pathways. Stability studies that are conducted in excess base are not necessarily representative of fuel cell operation, and extrapolating degradation rates must be judiciously considered. Nevertheless, a cation that is stable under such caustic conditions will likely demonstrate excellent stability at lower base concentrations. Importantly, this facilitates membrane electrode assembly (MEA) fabrication due to the improved cation stability at elevated temperatures in the absence of water.

Replacing the N1-benzyl with an N1-butyl group and retaining the N3-butyl group led to the most stable imidazoliums in the series (**8a** and **8b**) for which signal integrations are essentially unchanged at 2 M KOH after 30 days and very little degradation is observed even at 5 M KOH (Scheme 4, **8a** and **8b**). Interestingly, the stability of **8b** with a C2-phenyl group is only slightly altered at 5 M KOH, unlike **4b**, **5b**, and **6b**, which appear to react with methoxide at the C2 position at high base concentrations. This may indicate that an N1-butyl group is more effective than an N1-benzyl group at blocking nucleophilic addition to the C2 position of the imidazolium ring. Alternatively, a more soluble organic cation with aliphatic groups may remain better solvated, which can reduce the effective strength of the base, shielding the cation

from interaction with the neighboring nucleophile. The results in Scheme 4 establish that imidazoliums with N1-butyl groups are less prone to nucleophilic attack as compared to the N1-benzyl counterparts and addition reactions at the C2 position are least likely with 2,6-dimethylphenyl substituents. We prepared optimized imidazoliums, which incorporated the best substituents at each of the ring positions, and assessed their alkaline stability (Scheme 5).

Scheme 5. Optimization of Base Stable Imidazoliums: Percent Cation Remaining after 30 days at 80 °C[a]

1 M: >99%
2 M: >99%
5 M: >99%
7a

1 M: >99%
2 M: >99%
5 M: >99%
8a

1 M: >99%
2 M: 97%
5 M: 93%
7b

1 M: >99%
2 M: 99%
5 M: 82%
8b

[a]Determined by ^{1}H NMR spectroscopy.

As predicted, imidazoliums with methyl groups at the C4,5 positions (Scheme 5, **7a** and **7b**) are quite stable at 2 M KOH concentrations. At 5 M KOH concentrations, the stability of **7b** drops off; however, the stability remains higher than the analogous cation **8b** with C4,5 phenyl groups. Significant changes in the signal integrations for **7a** are not observed over 30 days, even at 5 M KOH and 80 °C (Figure 3). By systematically screening substituent effects on the overall imidazolium stability, we developed cations with exceptionally high resistance to reaction with base.

We compared the stability of **7a** and **8a** to imidazoliums that have been previously reported, and some important trends are highlighted (Figure 4). Imidazoliums with substitution at the C2 position demonstrate greatly improved stability over the unsubstituted version and better resistance to degradation than BTMA. Introducing alkyl substituents to the nitrogens consistently enhances the stability as compared to the benzylic counterparts. The best stability is observed when both N1- and N3-alkyls are larger than methyls and substituents are present at the C4,5 positions. The use of 2 and 5 M test conditions permits quantitative comparison between highly stable systems.

■ CONCLUSIONS

The effect of imidazolium substituents on base stability was systematically studied. The model compounds were assessed for stability under alkaline conditions by ^{1}H NMR spectroscopy, and the degradation modes were analyzed. On the basis of these structural trends, we rationally modified the imidazolium ring to install substituents that would impede reaction with anions. Ultimately, we arrived at cations that were stable under the harsh alkaline conditions we assessed, in excess of operating fuel cell hydroxide concentrations. We found that C4 and C5 substitution was very important to the alkaline stability of the imidazolium cations, with methyls groups slightly improving the stability relative to phenyl groups. Moreover, methyl groups offer an advantage over phenyl groups when used in AAEMs because they increase the ion exchange capacity (IEC) of the membrane. Substitution at the C2 position inhibited degrada-
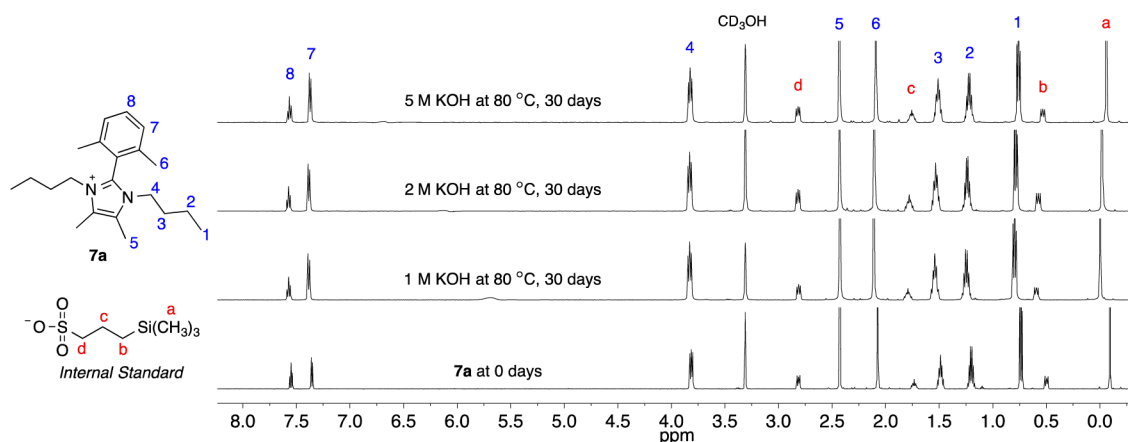
Figure 3. Analysis of **7a** under alkaline conditions using ^{1}H NMR spectroscopy in CD$_3$OH. Residual signals between 5.5−7.0 ppm are due to solvent; see the Supporting Information for discussion on solvent suppression.[44]
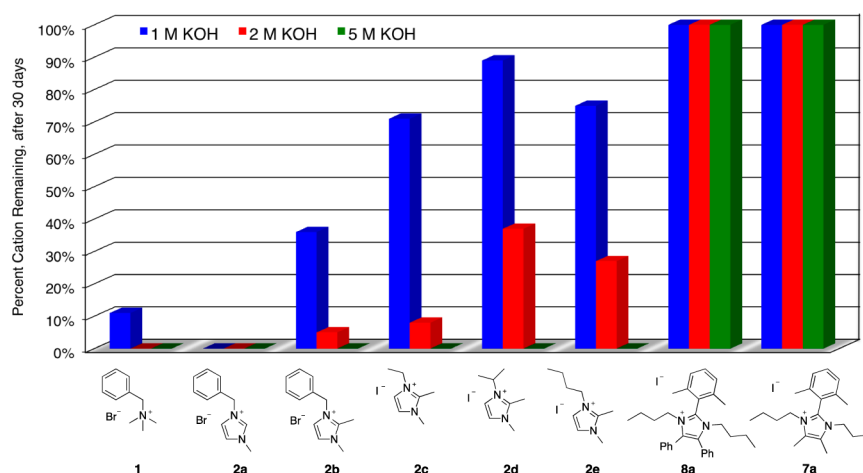

Figure 4. Comparison of model compound stabilities, percent remaining after 30 days at 80 °C (determined by ^{1}H NMR spectroscopy relative to an internal standard).[44]

tion, and 2,6-dimethylphenyl substituents were the most effective. The use of alkyl substituents on the nitrogens, particularly *n*-butyl groups, prevented degradation better than benzyl or methyl groups. Because the majority of polymerization techniques applied to synthesize AAEMs append cations to benzylic positions, it will be necessary to develop new synthetic routes to attach the base-stable imidazoliums to polymers. Furthermore, several of the commonly employed polymer architectures have been discovered to be unstable under fuel cell operating conditions.[46] Developing AAEMs based on inert polymer backbones, such as the recent work by Coughlin and co-workers,[47] which describes the synthesis of a copolymer of isoprene and ammonium-functionalized styrene, may bypass these issues. Future work will focus on appending these cations to highly stable polymer architectures and characterizing the membranes for hydroxide conductivity and alkaline stability.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures, full characterization data, and copies of spectra. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b02879.

AUTHOR INFORMATION

Corresponding Author

*coates@cornell.edu

Notes

The authors declare no competing financial interest.

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