Increasing the Alkaline Stability of N,N-Diaryl Carbazolium Salts Using Substituent Electronic Effects

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ABSTRACT: Anion-exchange membrane fuel cells (AEMFCs) have attracted the attention of the scientific community during the past years, mostly because of the potential for eliminating the need for using costly platinum catalysts in the cells. However, the broad commercialization of AEMFCs is hampered by the low chemical stability of the cationic functional groups in the anion-conducting membranes required for the transportation of hydroxide ions in the cell. Improving the stability of these groups is directly connected with the ability to recognize the different mechanisms of the OH⁻ attack. In this work, we have synthesized eight different carbazolium cationic model molecules and investigated their alkaline stability as a function of their electronic substituent properties. Given that N,N-diaryl carbazolium salts decompose through a single-electron-transfer mechanism, the change in carbazolium electron density leads to a very significant impact on their chemical stability. Substituents with very negative Hammett parameters demonstrate unparalleled stability toward dry hydroxide. This study provides guidelines for a different approach to develop stable quaternary ammonium salts for AEMFCs, making use of the unique parameters of this decomposition mechanism.

KEYWORDS: fuel cell, quaternary ammonium, Hammett parameters, alkaline stability, anion-exchange membrane

INTRODUCTION

Anion-exchange membrane fuel cells (AEMFCs) have emerged as attractive candidates for energy conversion and storage, especially for automotive and portable applications.¹–³ The ability to eliminate the need for platinum catalysts due to their alkaline media, and the subsequent cost reduction, is one of the driving forces for the research and development of AEMFCs.¹–⁸ However, there are significant scientific and technological obstacles that inhibit the broad utilization of AEMFCs. The anion-exchange membrane (AEM), which acts as a solid electrolyte, suffers from a limited lifetime under dry alkaline conditions in which these cells operate.⁹,¹⁰ This chemical instability stems from chemical reactions between the hydroxide and the positively charged groups, typically leading to uncharged products, causing performance decay during the fuel cell operation.¹¹,¹²

Hydroxide anions have been shown to present varied reactivities, acting as strong bases, nucleophiles, and even reducing agents;¹³ the reactivity that, in turn, may be significantly affected by the hydration level of the medium.¹⁴ In AEMs, quaternary ammonium (QA) functional groups degrade mainly through two prevalent pathways: E₂ (or Hofmann) elimination, which is typically the fastest mechanism and takes place in the presence of β hydrogens to the QA or nucleophilic attack (S₈₂) on the α carbon, which occurs when no β hydrogens are available (Scheme 1).¹⁶,¹⁷ Countless QA functional groups have been probed and tested under harsh alkaline conditions in an attempt to address this technological challenge.¹⁸–²¹ Some trends in their alkaline stability have been established;²²,²³ however, despite the efforts, no QAs with sufficient lifetime have been found to date, especially under low hydration conditions where OH⁻ is even more reactive.

One of the leading QAs in the literature is benzyl trimethylammonium (BTMA), which currently exhibits the highest half-life under dry alkaline conditions,²⁵,²⁶ 109 h at room temperature under 0.5 M KOH. Some additional QAs showed even better chemical stability when tested under aqueous hydroxide conditions, such as the piperidinium-based 6-azonia-spiro[5.5]undecane (ASU),²⁷ albeit under dry conditions, BTMA is still superior.²⁸ Imidazolium functional groups have also attracted attention lately because of their increased stability after structural modifications.²⁹–³⁰ In a
Scheme 1. Typical Decomposition Mechanisms of QA Salts in the Presence of Hydroxide: E2 (a) and S_N2 (b)

Scheme 2. Birch-like SET Reaction between Hydroxide and 9,9-Di-p-tolycarbazolium

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**EXPERIMENTAL SECTION**

**Materials.** 2,2′-Dinitrobi phenyln and 2,2′-diodo-1,1′-biphen ylen were purchased from TCI Chemicals. Iodobenzene, 4-iodothioani sole, and boron tribromide were purchased from Acros Organics. 4- Iodotoluene was purchased from Alfa Aesar. 4-Iodo anisole and trifluoromethane sulfonate were purchased from Sigma-Aldrich. Dry dimethyl sulfoxide-$d_{6}$ (99.96% D) was purchased from Cambridge Isotope Laboratories. 4-5a, 4-5b, and 4-5g were prepared as previously described. NMR tubes (Wilmad-LabGlass) with a septum were used for the kinetic studies. All materials, unless otherwise stated, were used without additional purification. Schlenk glassware was dried in an oven at 120 °C prior to use. Xylenes were passed through alumina and deoxygenated by argon bubbling for 10 min, followed by three freeze–thaw–pump cycles. Flash column chromatography was performed with silica gel 60 (230–400 mesh) from Merck. TLC was performed on silica gel 60 F254 plates from Merck.

**Methods.** NMR spectra were recorded on a Bruker AVANCE III 400 MHz or Avance 300 MHz spectrometer. The chemical shifts are referenced to the signal at $\delta$ 0.00 (tetramethylsilane) or partially undeuterated solvent peaks. The coupling constants ($J$) are reported in Hz. Peak multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (double doublet), dt (double triplet), br (broad), and m (multiplet). High-resolution mass spectrometry was performed on a Waters LCT Premier Mass Spectrometer (ESI) or a Bruker maXis Impact with an APCI solid probe. The crystal structures were measured on a Kappa CCD diffractometer or a Bruker diffractometer.

**General Synthetic Procedure for the Preparation of Para-Substituted N,N-Diphenyl-2-(2-aminophenyl)anilines (4c–e).** The synthetic approach is based on the procedure previously developed by us. In an oven-dried Schlenk flask, amine 2 (1 equiv) and 4-iodophenol (2.1 equiv) were dissolved in xylene (2.8 mL), and the flask was deoxygenated using three freeze–pump–thaw cycles, before backfilling with argon. KOBu (2.2 equiv) was added, and the mixture was left stirring for 10 min at room temperature. Then, Cu (0.2 equiv) and 1,10-phenanthroline (0.2 equiv) were added, and the mixture was stirred for 3.5 h at 125 °C. The mixture was allowed to cool to room temperature and the solids were filtered and washed with CHCl₃. The remaining solid was then dissolved in 25% NH₄OH and the solution was extracted with CHCl₃. The organic phases were combined and evaporated. The concentrated paste was redissolved in CHCl₃ and extracted with NH₄OH until no blue color was observed. To separate the unreacted amine 2, the organic phase was then washed with saturated NaHCO₃, dried over Na₂SO₄, filtered, and evaporated. The amines 4c–4e and 4g were further purified by column chromatography using CHCl₃ as an eluent.
Scheme 3. General Synthetic Procedure for the Preparation of Different N-N-Diaryl Carbazolium QAs

NMR (101 MHz, CDCl₃): δ 154.71, 147.30, 143.45, 141.86, 136.10, 132.73, 130.66, 128.77, 128.07, 127.78, 126.31, 124.56, 123.90, 118.60, 115.71, 114.26, 55.65. HRMS (APCI Solid Probe MS⁺): [M⁺] calcd, 496.19; [M⁺] found, 496.18.

**Synthesis of N,N'-Bis(4-methylthiophenyl)-1,1'-biphenyl-2,2'-diamine (4d).** Prepared using 1-bromo-4-iodo benzene (3d, 3.02 mmol). Compound 3d was obtained as a hygroscopic purple solid (0.5 g, 1.011 mmol, 18.6% yield). 1H NMR (400 MHz, DMSO): δ 8.37−8.31 (m, 2H), 8.26 (dt, J = 5.0, 3.9 Hz, 2H), 7.84−7.72 (m, 4H), 7.38−7.25 (m, 6H), 3.62 (td, J = 7.6, 4.8 Hz, 6H). HRMS (APCI Solid Probe MS⁺): [M⁺] calcd, 352.1332; [M⁺] found, 352.1342.

General Synthetic Procedure for the Preparation of N-N-Disubstituted Carbazolium Salts (5a-h). The amine (4a-e, 1 equiv) was dissolved in glacial acetic acid (4.1 mL) in an Erlenmeyer flask and cooled to 0 °C. The concentrated acetic acid was then washed with a metallic spatula before NaNO₂ (4.65 equiv) in water was added, and the mixture stirred for 1 h at 40 °C. The solvents were evaporated, and the residue dissolved in CHCl₃. The insoluble part was filtered and washed with CHCl₃. The filtrate was concentrated in vacuo and the product purified by dissolution in water and washing with ether. Water and acetic acid were removed from the product using a lyophilizer.

**9,9-Bis(4-hydroxyphenyl)-carbazolium Hexafluorophosphate (5f).** A solution of BBr₃ (3.56 g, 14.19 mmol) in dry methylene chloride (12.8 mL) was slowly added to a Schlenk flask containing an ice-bath-cooled solution of 5e (0.52 g, 1.18 mmol) in dry methylene chloride (10 mL). The mixture was allowed to reach room temperature and was stirred for 48 h. Then, the reaction mixture was cooled in an ice bath and quenched with 1.25 M HCl in MeOH (25 mL). The solvents were evaporated in a rotovap until a thick paste was left. A small amount of ethyl acetate (EtOAc) was then added, and the insoluble part (carbazolium 5f) was filtered and washed with more EtOAc. After drying under vacuum, 5f-Br was obtained as a yellowish solid (0.407 g, 0.94 mmol, 80% yield). For further purification, carbazolium 5f-Br was converted to hexafluorophosphate by salt metathesis with NH₄PF₆. Extraction with methylene chloride provided the pure 5f in the PF₆⁻ form. 1H NMR (400 MHz, DMSO): δ 10.41 (s, 2H), 8.36 (d, J = 7.6 Hz, 2H), 7.96 (d, J = 8.3 Hz, 2H), 7.81 (d, J = 7.5 Hz, 2H), 7.69 (t, J = 7.4 Hz, 2H), 7.73 (d, J = 9.3 Hz, 4H), 6.87 (d, J = 9.3 Hz, 3H). 13C NMR (101 MHz, DMSO): δ 159.74, 151.32, 138.23, 132.48, 131.61, 130.10, 124.33, 123.97, 121.96, 117.17. HRMS (APCI Solid Probe MS⁺): [M⁺] calcd, 352.1332; [M⁺] found, 352.1342.

9,9-Dimethyl Carbazolium Hexafluorophosphate (5h). Methyl triflate (0.654 g, 4 mmol) was added dropwise to a suspension of carbazole (0.167 g, 1 mmol) and K₂CO₃ (0.330 g, 2.4 mmol) in dichloroethane (5 mL), and the mixture was refluxed overnight. The mixture was allowed to cool to room temperature and the solvent removed in vacuo. The product was purified via flash column chromatography using EtOAc, followed by methanol, to provide the almost pure 5h as a white solid (0.103 g, 0.33 mmol, 30% yield). For further purification, the material was dissolved in water and precipitated as PF₆⁻ salt by addition to an NH₄PF₆ saturated aqueous solution. 1H NMR (400 MHz, DMSO): δ 8.37−8.31 (m, 2H), 8.26 (dt, J = 7.0, 3.9 Hz, 2H), 7.84−7.72 (m, 4H), 3.68 (s, 6H). 13C NMR (101 MHz, DMSO): δ 149.21, 131.64, 130.39, 129.52, 122.76, 118.22, 55.36. HRMS (APCI Solid Probe MS⁺): [M⁺] calcd, 196.1126; [M⁺] found, 196.1084.

**General Procedure for Kinetic Studies.** Kinetic studies were performed following the protocol developed by our group, in which the extent of hydroxide microsalvation by water is controlled. For every experiment, two solutions were prepared inside a glovebox. Solution 1 consisted of a dry 18-crown-6-KOH complex (226 mg), dissolved in dry DMSO-d₆ (0.5 mL). Solution 2 consisted of the carbazolium salt (0.035 mmol) dissolved in dry DMSO-d₆ (0.1 mL). Solution 1 was added to the NMR tube and sealed with a rubber septum, Teflon, and paraffin. Solution 2 was transferred into a 1 mL disposable syringe and sealed with paraffin. The NMR tube and the syringe were taken out of the glovebox. Mesitylene (1.6 μL) was added as an internal standard. For the experiments requiring the addition of water (72 μL, 8 water molecules per hydroxide) was injected into the NMR tube. The volume of the added water was subtracted from the volume of DMSO-d₆ used to dissolve the CE/KOH complex (solution 1). The carbazolium salt solution was injected into the NMR tube just before starting the kinetic measurements in the NMR, forming a 0.5 M KOH solution (confirmed by titration). After the injection, the tube was manually mixed and inserted into the NMR instrument.
RESULTS AND DISCUSSION

In our recent study, we showed that hydroxide reacts with DACs via SET to one of the freely rotating phenyl rings, without scission of the carbazole C−N bonds, similar to the first step of Birch reduction.34 This unusual decomposition mechanism should be very sensitive to electronic effects in the aromatic substituents, and therefore, we decided to synthesize additional DACs and quantify this effect, to develop DACs with enhanced chemical stability toward dry hydroxide.

Our synthetic approach was based on a modified literature procedure in which C−N arylation of a triarylamine was made possible by an intramolecular coupling using a diazonium salt (Scheme 3).32 Amine 2 was prepared in large scale by the reduction of 2,2-dinitro biphenyl (1) under acidic conditions in ethanol using zinc powder. Then, Ullman coupling of 2 with 2.1 equiv of para-substituted iodosobenzenes (3a−e) was carried out using Cu(I) catalysis. In every case, amines 4a−e were isolated from the reaction mixture using column chromatography. The final coupling step was done by diazotization of 4a−e in acetic acid by addition of a saturated aqueous solution of NaNO2 at 0 °C for 20 min, followed by the addition of urea to the reaction mixture and heating to 40 °C for 1 h. DACs 5a−e were isolated by filtration and extraction into the aqueous layer.

Hammett parameters offer a numerical value for substituent effects in terms of electron donation or withdrawing.35 DACs 5a−e Hammett parameters span from 0.230 to −0.268. Additional DACs with even more negative Hammett parameters could, in theory, be prepared by the demethylation of 5c−d, producing −OH and −SH groups, which, under alkaline conditions, deprotonate to −O− and −S− (Hammett parameters −0.81 and −1.21, respectively). As the direct
Ullman coupling of amine 2 with 4-iodophenol and 4-iodothiophenol failed to provide a pure product, the hydroxyl derivative was obtained by demethylation of 5c using BBr₃ (Scheme 4). Demethylation of 5d was tried by different methods, including sodium 2-methyl-2-propanethiolate,[36] but 5d remained unsclathed, and therefore, the compound with a —SH substituent could not be prepared at this stage.

As the decomposition of 5a—b was shown to occur only by SET to the freely rotating phenyl rings, we decided to address this decomposition mechanism by testing DACs that lack such rings. To this end, two additional carbazolium salts were prepared: spirobiscarbazolium 5f[34] was prepared using the same synthetic strategy but using 1 equiv of 2,2′-di-iodo-1,1′-biphenyl (3f) instead of monoaryl iodosides to form the first carbazole after two sequential Ullman coupling reactions; and N,N-dimethyl carbazolium (5h) was prepared by direct methylation of carbazole using trifluoromethane sulfonate (Scheme 5).[37]

Single crystals of 5a, 5b, 5c, 5e, 5f, and 5g were grown by slow evaporation of the solvent, and their solid-state structures are presented in Figure 1. To increase the solubility in organic solvents, counteranions were exchanged with PF₆⁻ and crystallized as hexafluoroporphates (with the exception of 5f, which crystallized as bromide).

The carbon—nitrogen distances of DACs 5a—5c and 5e—5g are presented in Table S11, in the Supporting Information. C—N bonds are slightly longer for hydroxy-substituted carbazolium 5f (1.532 and 1.524 Å for the C—N bonds of the freely rotating aryls) compared to the parent unsubstituted 5a (1.517 and 1.508 Å). Surprisingly, the C—N bond distances are mostly unaffected by the electronic properties of the para substituent, for example, C—N bond distances of the free aryls of electron-withdrawing bromide substituents 5e are almost unchanged (1.519 and 1.509 Å). As previously noted,[32] DACs present unusually long C—N bonds compared to nonquaternary, acidic ammonium salts, where these bond distances are usually around 1.465 Å,[38] however, such long C—N bonds were also seen in the quaternary Ph₃NMe⁺ cation.[39]

With all these new carbazolium QAs at hand, we decided to compare their alkaline stability using the protocol previously developed in our group,[26] in which completely dry KOH was prepared by titrating potassium metal with water in molten 18-crown-6 (CE). This starting solution had only ca. 0.1 water molecules per hydroxide, and through controlled water addition, average hydration of the hydroxide ions was then controlled, tuning their reactivity by changing their first solvation sphere. Importantly, we have previously shown that this protocol provides results compatible with alkaline tests done in aqueous solutions when hydroxide with a hydration ratio (λ) beyond 4 is prepared.[26,27] As most of the carbazolium salts readily degrade under dry CE/KOH conditions, we carried out most of the kinetic experiments using a 8:1 water/hydroxide molar ratio (equivalent to ca. 6 M KOH_w). The decay in the concentration of the carbazolium salt in time was followed via ¹H NMR spectroscopy, and the results are summarized in Figure 2.

As the hydroxide is in large excess (ca. 15 times) compared to the QAs, pseudo-first-order kinetics is assumed, and a good fit is obtained for ln[QA] against reaction time. In this case, the rate constant (k) for each QA can be calculated using the equation for the first-order reaction kinetics ln[QA] = −kt + ln[QA]₀ from the slope of the linear trend lines in Figure 2b, with [QA] referring to the remaining carbazolium fraction at time t, while [QA]₀ refers to the starting QA fraction (100%). The half-lives were subsequently calculated by the equation t₁/₂ = ln(2) × k⁻¹. The rate constants and the calculated half-lives are summarized in Table 1.

As seen in Figure 2 and Table 1, DACs 5a, 5d, 5g, and 5h decompose very rapidly. The unsubstituted 9,9-diphenylcarbazolium (5a) has a half-life of around 1 h, close to that of 9,9-thioanisolecarbazolium acetate (5d) and the spirocarbazolium acetate (5g), which present a half-life of 0.5 h. 9,9-Dimethylcarbazolium hexafluorophosphate (5h) also shows quite rapid kinetics, with a calculated half-life of only a few minutes (Table 1). As expected, 9,9-dibromocarbazolium acetate (5e) displays the fastest degradation, given that it has electron-withdrawing groups. 5a decomposes quite rapidly, showing a half-life of ca. 1 h. By inserting an electron-donating methyl group in the para position of the free aryl rings, the DAC stability increases and a half-life of 3.5 h is measured (5b). Bearing in mind the inner sphere SET decomposition, we expected electronic factors to play a major role in the stability of these QAs, and indeed, by
Further increasing the electron-donating capacity of the substituent, significantly higher half-lives are obtained. Thus, 5c, which bears para-methoxy substituents, shows a half-life of 8.7 h. For para–OH substituents, the increase of the stability is dramatic, as the phenoxide generated in situ impedes the inner sphere SET. With eight water molecules ($\lambda = 8$), the calculated half-life of 9,9-dihydroxy carbazolium (5f) is more than 1700 h, which is a few orders of magnitude more stable than the other QAs tested.

In order to quantify this substituent effect and to further substantiate the SET mechanism, we plotted $\log(k/k_{o})$ versus Hammett parameters of the substituent $\sigma_p$ (Figure 3), where $k$ is the rate constant of the degradation reaction of a substituted DAC and $k_{o}$ is the rate constant of the unsubstituted DAC (5a). In Figure 3a, it can be seen that the normalized reaction kinetic constant correlates linearly with the Hammett parameter. The slope of the graph (reactivity parameter $\rho$) is very steep, indicating a very strong electronic effect of the substituent on the degradation reaction. This plot vividly demonstrates the power of using these QAs with only aromatic substituents in order to obtain kinetically stable AEMs—because by relatively simple means of tuning the electronic properties of the aromatic rings, more than 3 orders of magnitude increase in stability can be achieved. The high and positive reactivity parameter ($\rho = 4.8$) indicates a strong development of negative charge in the transition state of the degradation reaction, and hence, the more electron donating the substituent is, the slower the degradation reaction. Large $\rho$’s have been reported in the literature, and they are typical in reactions involving SETs, including the Birch reduction. Further analysis of the data reveals that there is a more satisfactory correlation between the modified Hammett $\sigma_p^*$ parameters and the first-order rate constants (Figure 3). This indicates that the resonance contribution has a significant impact on the reaction kinetics as well.

Encouraged by the significantly enhanced stability with electron-donating groups, we decided to test DAC 5f further, using harsher conditions, where only an average of ca. 0.1 and 1 water molecules per hydroxide is present in the medium ($\lambda = 0$ and $\lambda = 1$). The alkaline stability of QAs under low hydration conditions is of foremost importance for future AEMFC applications, as models indicate that at high operating current densities, the hydroxide hydration number is significantly reduced. Therefore, 5f is directly compared under these harsh dry alkaline conditions against three of the most stable molecules in the literature: ASU, a substituted imidazolium, and BTMA. Under very dry conditions ($\lambda = 0$), ASU and imidazolium decompose immediately, and the first NMR show only decomposition products, but 5f can be compared to BTMA. Astoundingly, DAC 5f showed improved stability even when compared to BTMA (Figure 4a), which had, up to now, shown the highest longevity when tested under these dry conditions ($\lambda = 0$). The calculated half-life of carbazolium 5f reaches 138.6 h, beyond that of BTMA (109 h, Table 2).

When some water is present ($\lambda = 1$, Figure 4b), 5f is still more stable than BTMA, ASU, and imidazolium, showing higher stability and a high half-life of 1155 h compared to 792 h for BTMA, 60 h for ASU, and 40 h for imidazolium (Table 2). However, when hydroxide is fully hydrated in its first solvation sphere (Figure 4c, $\lambda = 8$), a small decay is observed during the first 100 h, but 5f is still more stable compared to BTMA and ASU. However, the superior alkaline stability of carbazolium 5f under dry conditions ($\lambda = 0, 1$) makes it a great candidate for future fuel cell applications, and it also suggests that by creating more electron-rich DACs, even better stabilities could be obtained.

**CONCLUSIONS**

To conclude, the synthesis and the alkaline stability of eight differently substituted carbazolium molecules were presented. Linear free energy relationship (LFER) studies of the electronic effect of the para substituent at the free rotating aryls on alkaline stability have shown to fit a Hammett-type trend, with a very strong reactivity parameter ($\rho = 4.3$). These results provide additional support for a SET decomposition mechanism and demonstrate that substituent electronic effects are efficient tools in tuning the stability of these QAs toward hydroxide. Particularly, the introduction of para-hydroxide groups (compound 5f) enhanced the half-life by more than 3 orders of magnitude. This stable cationic molecule was further studied under harsher conditions where it was compared to leading QAs in the literature, including BTMA, ASU, and a substituted imidazolium salt. While carbazolium 5f is perhaps one of the most complicated QAs prepared to date for AEMFC applications, it demonstrates superior stability compared to all other QAs tested under low hydration conditions ($\lambda = 0$ or 1). In fact, 5f presents the leading QA stability under dry alkaline conditions. Stability under low hydration conditions is of foremost importance for developing a stable AEM for commercial AEMFCs. 5f can be easily incorporated into a polymer by reacting one of its hydroxyl groups or the ring itself with electrophilic functional groups in polymers or by direct polymerization of a vinyl-substituted version to make a polystyrene-like membrane. Such polymer...
would have a maximum theoretical IEC of 2.06 mmol g\(^{-1}\), which is in the appropriate range for conducting AEMs. This study also emphasizes the importance of understanding and controlling the mechanisms of the QA decomposition reactions for the rational design of highly stable QAs.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c14132.

Isolation of byproducts, NMR spectra, data from kinetic measurements, mass spectra, and crystallographic data (PDF)

Crystallographic data of 5e (CIF)

Crystallographic data of 5c (CIF)

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**Notes**

The authors declare no competing financial interest.

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