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Base Stability of Aminocyclopropeniums

by MyVan Baranoski, Frederick L Beyer, Robert Lambeth, and Nicole Zander

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14. ABSTRACT
Cyclopropenium cations with differing amino-functional groups were synthesized and tested for their utility in anion exchange membranes for alkaline fuel cells. A series of aminocyclopropeniums were synthesized and their base stability probed in situ using time-resolved proton nuclear magnetic resonance (^{1}H NMR) under conditions designed to mimic those encountered in alkaline fuel cells to test their utility in anion exchange membranes. While the aminocyclopropeniums showed poor base stability, the cyclopropenium cation may have beneficial properties in neutral pH applications such as antimicrobial fabrics and coatings.

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cyclopropenium, anion exchange membrane, alkaline stability, aminocyclopropenium, cation

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1. Introduction

Polymers containing cationic functional groups have the potential to be used in a wide range of applications, including antimicrobial coatings and fabrics, electrolyzers, anion exchange membranes in alkaline fuel cells, and redox flow batteries.[1,2] These applications present challenging materials science problems because of the orthogonal properties that are typically required. For example, in alkaline fuel cells, high affinity for hydroxide (OH^-) is required, although hydroxide causes degradation of the cation needed for that affinity.

Most of the work in cation-containing polymers focused on a small number of functional groups including ammonium, phosphonium, imidazolium, and pyridinium ions, which are generally application specific with limited ability to tune physical properties.[3] Their successful use in alkaline fuel cells has been hindered due to the highly nucleophilic nature of the hydroxide anion, which is able to attack the covalently attached cation through multiple reaction pathways, rendering the material neutral.[2,4] In addition, compared to ionic liquids, ion mobility in solid polyelectrolytes is significantly reduced, with the movement of free anions limited to the interstitial space between the polymer chains.

A key issue with anion exchange membranes is the cation lifetime in a high pH environment (>pH 13). The cyclopropenium ion is an aromatic and unusually electron-rich cation that has improved dispersion of charge relative to many other cations.[5,6] A new class of polyelectrolytes was developed from cyclopropenium ions by Killops et al.[5] These materials are predicted to have high thermodynamic stability,[7] and Killops' data suggest this to be the case.

In this work, cyclopropenium cations with differing amino-functional groups were synthesized and tested for their utility in anion exchange membranes for alkaline fuel cells. To determine cyclopropenium ion alkaline stability, a series of aminocyclopropeniums were synthesized and their base stability probed in situ using time-resolved proton nuclear magnetic resonance (^{1}H NMR) under conditions designed to mimic those encountered in alkaline fuel cells to test their utility in anion exchange membranes.

2. Methods and Procedures

All operations were performed using standard Schlenk techniques under a nitrogen atmosphere to reduce exposure to water. The ^{1}H NMR spectra were collected using a Bruker 600 MHz Avance instrument in deuterated chloroform ($CDCl_3$), referenced to residual solvent peaks.

Pentachlorocyclopropane was prepared from sodium trichloroacetate and trichloroethylene.[8] The amines were used as obtained commercially. All reagents were obtained from commercial sources and used as received unless otherwise noted.

2.1 General Syntheses of Tris(dialkylamino)cyclopropenium Chloride[9]

Pentachlorocyclopropane (1 equivalent) was added to dry dichloromethane (CH_2Cl_2) (approximately 0.01 M). This was stirred at 0 °C under a nitrogen atmosphere. Eight equivalents of amine were slowly added. Following the complete addition of the amine, the solution was stirred at 0 °C for a further 4 h, and allowed to come to ambient temperature and stirred overnight (16 h) before heating to reflux (65 °C) for 5 h. The solution, usually yellow/orange in color, was then placed under vacuum to remove the solvent.

2.2 Synthesis of Tris(diethylamino)cyclopropenium Chloride #1

Pentachlorocyclopropane (C_3Cl_5H, 0.51g, 2.33 mmol) and diethylamine ($HNEt_2$, 1.34 g, 18.7 mmol) were combined using the method listed under General Syntheses. Dichloromethane was removed in vacuo and 20 mL of acetone was added to precipitate diethylammonium chloride, which was then filtered from the solution comprising the triaminocyclopropenium salt. Acetone was removed in vacuo and the resulting solid was dissolved in 20 mL of CH_2Cl_2. The organic solution was washed with dilute sodium hydroxide (NaOH) (15 mL) followed by hydrochloric acid (HCl) (15 mL) and then water (H_2O) (3 × 15 mL). The organic solution was dried over sodium sulfate (Na_2SO_4). The organic solvent was removed under vacuum to give an orange liquid (0.59 g, 86% yield) that slowly solidified under high vacuum overnight. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.42 (q, 12H, NC*H*$_2$), 1.27 (t, 18H, NCH_2CH_3).

2.3 Synthesis of Tris(dipropylamino)cyclopropenium Chloride #2

C_3Cl_5H (0.51g, 2.33 mmol) and dipropylamine ($HNPr_2$, 1.92 g, 18.7 mmol) were combined using the method listed under General Syntheses. Dichloromethane was removed in vacuo and 20 mL of acetone was added to precipitate dipropylammonium chloride, which was then filtered from the solution comprising the triaminocyclopropenium salt. Acetone was removed in vacuo and the resulting solid was dissolved in 20 mL of CH_2Cl_2. The organic solution was washed with H_2O (3 × 15 mL). The organic solution was dried over Na_2SO_4. The organic solvent

was removed under vacuum to give an orange liquid (0.64 g, 75% yield) that slowly solidified under high vacuum overnight. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.26 (t, 12H, NC*H*$_2$), 1.64 (m, 12H, NCH_2CH_2), 0.92 (t, 18H, $NCH_2CH_2CH_3$).

2.4 Synthesis of Tris(dibutylamino)cyclopropenium Chloride #3

C_3Cl_5H (0.51g, 2.33 mmol) and dibutylamine ($HNBu_2$, 2.4 g, 18.7 mmol) were combined using the method listed under General Syntheses. Dichloromethane was removed in vacuo and 20 mL of acetone was added to precipitate dipropylammonium chloride, which was then filtered from the solution comprising the triaminocyclopropenium salt. Acetone was removed in vacuo and the resulting solid was dissolved in 20 mL of CH_2Cl_2. The organic solution was washed with H_2O (3 × 15 mL). The organic solution was dried over Na_2SO_4 and the solvent was removed under vacuum. The remaining liquid was washed with diethyl ether (4 × 15 mL) to remove residual amine (0.93 g, 86% yield). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.29 (t, 12H, NC*H*$_2$), 1.59 (m, 12H, NCH_2CH_2), 1.31 (m, 12H, $NCH_2CH_2CH_3$), 0.94 (t, 18H, C*H*$_3$).

2.5 Synthesis of Diethylaminobis(diisopropylamino) cyclopropenium Chloride #4

C_3Cl_5H (0.5g, 2.33 mmol) was added to dry CH_2Cl_2. This was stirred at 0 °C under a nitrogen atmosphere. Diisopropylamine ($HN(iPr)_2$, 1.4 g, 14.0 mmol) was added dropwise using a syringe pump and the solution was allowed to return to room temperature and stirred for approximately 36 h. $HNEt_2$ (0.34 g, 4.65 mmol) was added dropwise and the reaction was stirred for an additional 5 days. Approximately 3 mL of concentrated HCl was added to precipitate excess amine, which was then filtered from the solution comprising the aminocyclopropenium salt. The solution was washed with 1M HCl (4 mL × 5) to remove any residual amine. The solution was dried over Na_2SO_4 and the solvent was removed under vacuum (0.59 g, 74% yield). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.86 (m, 4H, N(iPr)*H*), 3.56 (q, 4H, N*CH*CH_3), 1.36 (d, 24H, N(iPr)*H*), 1.27 (t, 6H, NCH_2CH_3).

2.6 Synthesis of Diethylaminobis(dicyclohexylamino) cyclopropenium Chloride #5

C_3Cl_5H (0.5g, 2.33 mmol) was added to dry CH_2Cl_2. This was stirred at 0 °C under a nitrogen atmosphere. $HNCy_2$ (2.54 g, 14.0 mmol) was added dropwise using a syringe pump and the solution was allowed to return to room temperature and stirred for approximately 36 h. $HNEt_2$ (0.34 g, 4.65 mmol) was added dropwise and the reaction was stirred for an additional 12 h. Approximately 3 mL of concentrated

HCl was added to precipitate excess amine, which was then filtered from the solution comprising the aminocyclopropenium salt. The solution was dried over Na_2SO_4 and the solvent was removed under vacuum. The crude product was recrystallized in hexanes (0.81 g, 69% yield). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.57 (q, 4H, N*CH*$_2$CH$_3$), 3.33 (m, 4H, NCy*H*), 1.05-1.95 (m, 46H, Cy*H*, NCH$_2$C*H*$_3$).

The base stability of the aminocyclopropeniums was probed in situ using time resolved ^{1}H NMR under conditions designed to mimic those encountered in alkaline fuel cells. A 1M potassium hydroxide (KOH) stock solution was prepared by dissolving KOH (323.6 mg, 5.77 mmol) and 1,4-dioxane (12.7 mg, 0.144 mmol) in 5.77 mL of deuterated methanol (CD_3OH). Dioxane is used as an internal standard; 0.0375 mmol of aminocyclopropenium was dissolved in the stock solution (0.75 mL) and transferred into a nuclear magnetic resonance (NMR) tube. The tube was then placed in the spectrometer, and heated to 80 °C. The resonances associated with the alkyl substituents were then recorded over time. Integration of a selected signal in the model compound relative to the signal related to dioxane provided the quantity of model compound.

3. Results and Discussion

Figure 1 illustrates the 5 cyclopropenium cations with different amino substituents that were explored in this study. Substituents were selected to determine if structural factors affect the base stability of aminocyclopropeniums.

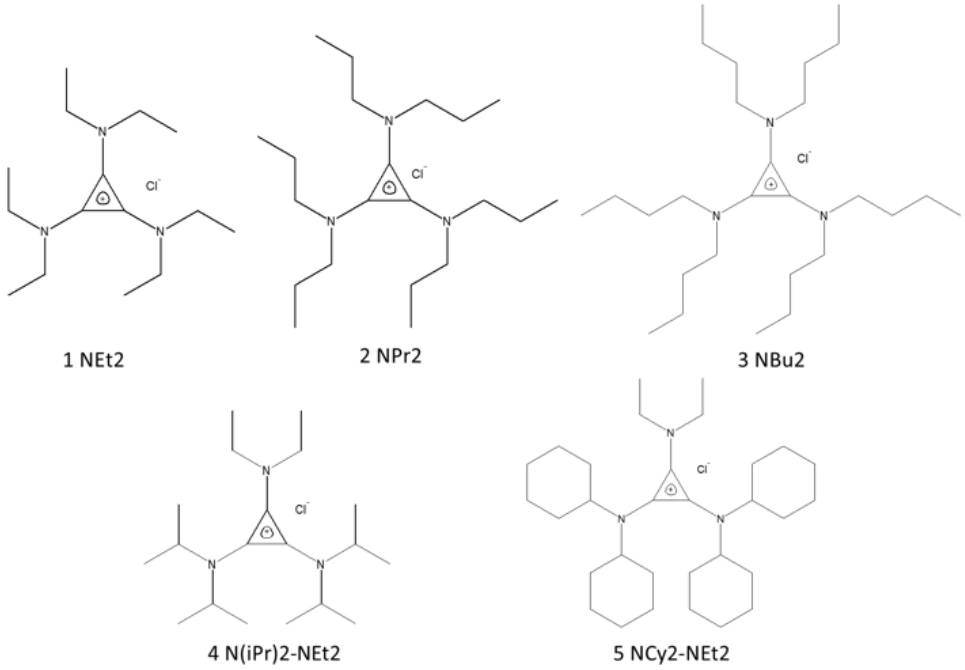


Fig. 1 Selected aminocyclopropenium cations for alkaline stability

The base stability was determined by dissolving the aminocyclopropenium in a 1M KOH stock solution and probing in situ using time resolved ^{1}H NMR for 14 h at 80 °C. A typical example of the NMR data is shown in Fig 2. The selected signal of the model compound at 3.45 ppm integrated relative to the signal related to dioxane at 3.66 ppm provided the quantity of the compound.

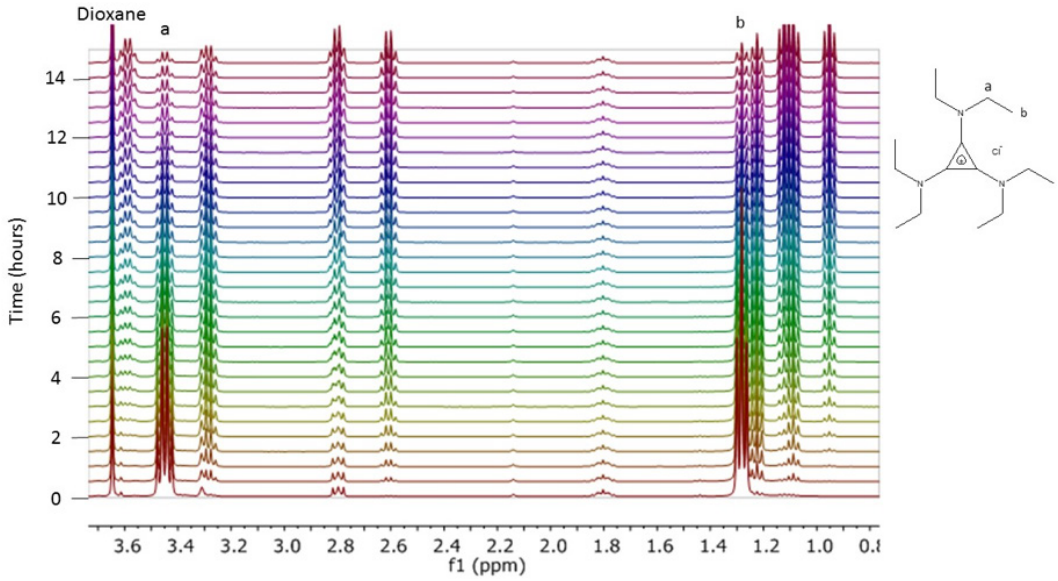
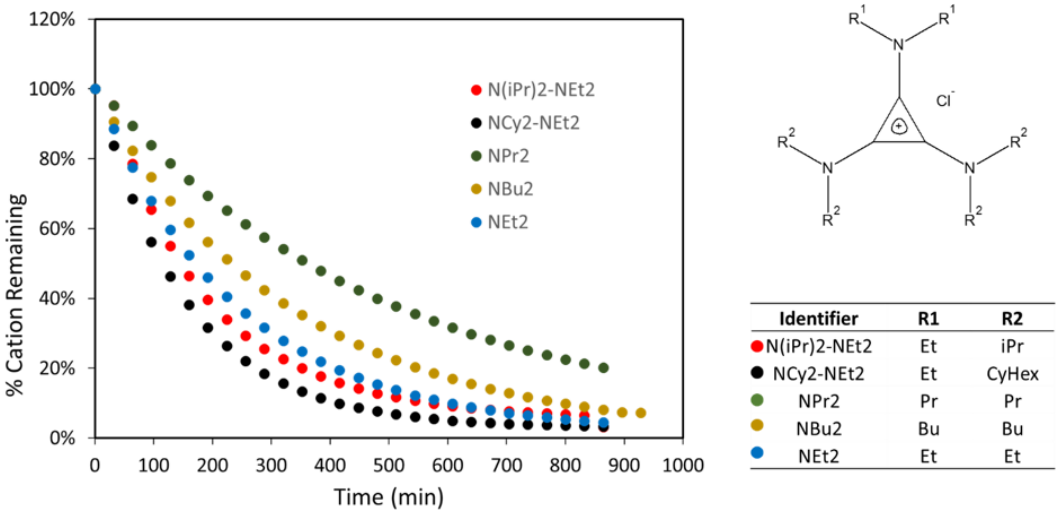


Fig. 2 Time resolved ^{1}H NMR of tris(diethylamino)cyclopropenium cation in 1M KOH/CD_3OH at 80 °C

The results of the study are illustrated in Fig. 3. The aminocyclopropeniums show 5%–15% degradation within 30 min. After 6.5 h, there is less than 50% cation remaining.



Identifier	R1	R2
N(iPr)2-NEt2	Et	iPr
NCy2-NEt2	Et	CyHex
NPr2	Pr	Pr
NBu2	Bu	Bu
NEt2	Et	Et

Fig. 3 Fraction of aminocyclopropenium cations remaining (left) in 1M KOH/CD_3OH at 80 °C, as determined from ^{1}H NMR data

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The aminocyclopropeniums with simple alkyl and bulky substituents showed poor base stability, with only 5%–20% of cation remaining after 14 h. In comparison, a study of a tetrakis(dialkylamino)phosphonium cation showed no degradation over 20 days at 80 °C.[10] To determine if poor cation base stability translates to polymers with poor stability, a cyclopropenium polymer with isopropylamine substituents was also evaluated using the same time-resolved NMR method and found to also quickly degrade under the same conditions, suggesting that cyclopropenium is not stable under these conditions.

These results could be explained by the findings reported by Yoshida et al.[11] where aminocyclopropeniums undergo hydrolysis in alkaline conditions at room temperature to give a diaminocyclopropenone and an acrylamide derivative (Fig. 4).

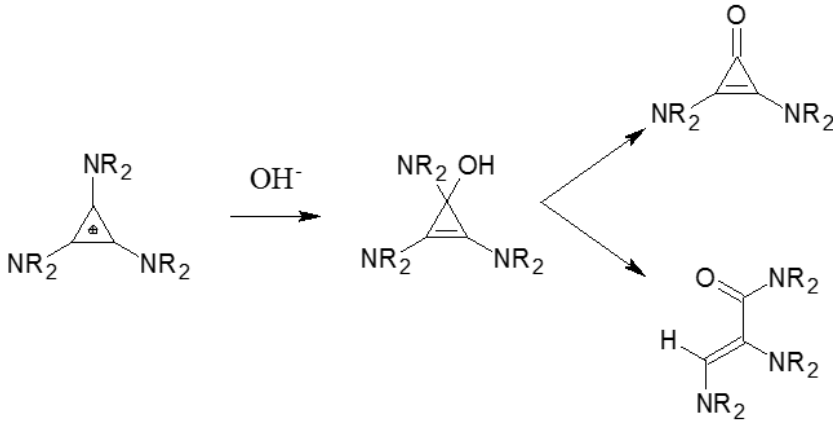

Fig. 4 Alkaline hydrolysis of aminocyclopropeniums

Yoshida et al. further explained that the distribution of the products appeared to be dependent on the basicity of the amino groups attached to the cyclopropenium ring, the alkali used, and its concentration. As an example, 1,2,3-tris-(N-methylanilino)cyclopropenium perchlorate in methanol was stirred at room temperature with 0.3% aq KOH for 40 h. This yielded the cyclopropenone at 22% and the acrylamide at 65%. Alkaline hydrolysis is the most likely degradation route for the aminocyclopropeniums examined in this study.

4. Conclusions

This report details the synthesis of various aminocyclopropenium salts with differing alkyl substituents and their base stability. The aminocyclopropeniums showed poor base stability, showing 5%–15% degradation within 30 min, less than 50% cation remaining after 6.5 h, and only 5%–20% of cation remaining after 14 h. Other cations had little to no degradation under similar conditions over longer

time periods. These results are consistent with literature findings where aminocyclopropeniums undergo alkaline hydrolysis at room temperature. While base stability hinders their utility as anion exchange membranes in alkaline fuel cells, the cyclopropenium cation may have beneficial properties in neutral pH applications such as antimicrobial fabrics and coatings.

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List of Symbols, Abbreviations, and Acronyms

^{1}H NMR	proton nuclear magnetic resonance
ARL	US Army Research Laboratory
C_3Cl_5H	pentachlorocyclopropane
CD_3OH	deuterated methanol
$CDCl_3$	deuterated chloroform
CH_2Cl_2	dichloromethane
H_2O	water
HCl	hydrochloric acid
HN(iPr)	diisopropylamine
$HNPr_2$	dipropylamine
$HNBu_2$	dibutylamine
$HNEt_2$	diethylamine
KOH	potassium hydroxide
mmol	millimole
Na_2SO_4	sodium sulfate
NaOH	sodium hydroxide
NCH_2CH_3	triethylamine
NMR	nuclear magnetic resonance
OH^-	hydroxide
pH	potential of hydrogen

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