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Hydroxide based decomposition pathways of alkyltrimethylammonium cations

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ABSTRACT

A systematic study that altered the number of β-hydrogen atoms susceptible to Hofmann elimination and introduced increased steric hindrance of substituted (ethyl, *n*-propyl, isobutyl, and neopentyl) alkyltrimethylammonium cations was performed. The mechanism of the thermal decomposition of these four ammonium cations in deuteroxide form was studied using evolved gas analysis (EGA) because of their potential importance in alkaline membrane fuel cells or electrolyzers. The products of the decomposition reactions are in many cases the expected Hofmann elimination products (trimethylamine and olefins), however, as the number of β-hydrogen atoms decrease or they become more sterically encumbered (from the addition of adjacent methyl groups), nucleophilic attack of hydroxide on the methyl groups increases in relative importance. The use of deuterated water and deuteroxide in our study shows that deprotonation of the tetraalkylammonium ions establishes a rapid equilibrium between the nitrogen ylide species that is formed by methyl group deprotonation and water that scrambles deuterium into the methyl groups of the amine. The results of this work show that at high temperature and low water content tetraalkylammonium hydroxide salts are relatively unstable in membranes.

1. Introduction

While an enormous effort has been directed towards the development of proton exchange membrane fuel cells (PEMFCs) in recent years, the development of alkaline fuel cell versions of PEMFCs is relatively much less explored [1]. Alkaline membrane fuel cell (AMFC) systems have traditionally been ignored by the fuel cell community due to the concerns over carbonate formation from the reaction of OH^- ions with CO_2 contaminants in the oxidant gas stream leading to the formation of carbonate/bicarbonate ($CO_3{}^{2-}/HCO_3{}^-$) [2–4]. However, alkaline membrane fuel cells (AMFCs) can offer some advantages over their PEMFC counterparts. The basic medium allows for the use of non-precious electrode catalysts made from inexpensive metals such as Fe/Co/Ni/Ag versus the use of the precious and expensive Pt used in PEMFCs [5–9]. Another concern with AMFCs is the stability of the membrane at high pH necessary for good hydroxide ion conductivity, especially at elevated temperatures [10,11].

Early studies on membrane development have focused on the use of ammonium cations $[NR_4]^+$ tethered to a polymer backbone for hydroxide ion transport. In this regard, a number of recent publications have focused on the development and testing of these ammonium cation tethered polymers for membrane use [12–23]. While many of these efforts have been directed towards the polymer membrane stability at high pH and temperature, very little has been done to study the effect of these variables on the stability of the ammonium cations themselves. Previous work has shown that the hydroxide ion in the membrane can react with ammonium cations *via* nucleophilic attack or as a Bronsted base. Furthermore, the formation of nitrogen ylide species through reversible deprotonation/protonation of methyl groups attached to the nitrogen cations was observed offering another reaction pathway for decomposition [24–26].

We have previously reported the detailed mechanism of thermal decomposition of tetramethylammonium hydroxide, $[NMe_4][OH]$, using thermogravimetric analysis (TGA) as well as evolved gas analysis (EGA) with the identity and quantities of the evolved gases analyzed by Fourier-transform infrared (FTIR) spectroscopy and mass spectrometry (MS) [24]. While $[NMe_4][OH]$ showed good stability under the conditions studied due to its compactness and the lack of β-hydrogen atoms susceptible to Hofmann elimination, it is impractical for fuel cell usage as a free ion not tethered to the polymer membrane. Ammonium cations are typically tethered to a polymer backbone *via* post polymerization modification of the polymers containing pendant alkyl chloride functional groups through reaction with trimethylamine to give substituted alkyltrimethylammonium functional groups, $[RNMe_3]^+$. The cations presented in this study are analogues of tethers that could be used in anion exchange polymers. Most polymer systems studied to date have used a benzyl group as the point of attachment (R = Bn), however there have been recent reports of systems utilizing aliphatic points of cation attachment such as the neopentyl

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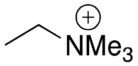
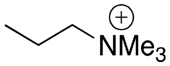
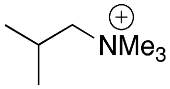
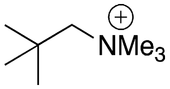
Table 1
Alkyltrimethylammonium cations studied.

Cation	Name	# of β-hydrogens
	Ethyltrimethylammonium (ETMA)	3
	*n*-Propyltrimethylammonium (PTMA)	2
	Isobutyltrimethylammonium (ITMA)	1
	Neopentyltrimethylammonium (NTMA)	0

(Np)-like groups used recently by Coates and coworkers [17,20]. Both the benzyl and neopentyl linkages result in no β-hydrogen atoms present to undergo Hofmann elimination due to the assumed severe instability of these cations. However, this limits the number of potential polymer backbones. Here, we present a fundamental and systematic study of the stability of $[RNMe_3]^+$cations where the number of β-hydrogens susceptible to Hofmann elimination and the steric hindrance to this reaction are probed.

We have chosen to use the substituted trimethyl version of ammonium cations in this study for various reasons. The first of which is it allows us to focus on a single substitution point of attack for the decomposition reactions (for which the methyl amine groups are not directly associated). Additionally, the synthesis of the singly substituted trimethylammoniums is straightforward and does not have significant steric issues associated with quanternizing the nitrogen. Finally, the use of three methyl groups allows for the more compact and hydrophilic ammonium cations to be studied. In practical materials, increasing the size and hydrophobicity would be expected to play a detrimental role on water uptake and conduction of membrane materials employing these cations. In Table 1 we show the four cations employed in this study with nomenclature used in this paper as well as the number of β-hydrogen atoms susceptible to Hofmann elimination. The mechanism of thermal decomposition of ethyltrimethylammonium deuteroxide, $[EtNMe_3][OD]{\cdot}xD_2O$, *n*-propyltrimethylammonium deuteroxide, $[n\text{-}PrNMe_3][OD]{\cdot}xD_2O$, *iso*-butyltrimethylammonium deuteroxide, $[i\text{-}BuNMe_3][OD]{\cdot}xD_2O$, and neopentyltrimethylammonium deuteroxide, $[NpNMe_3][OD]{\cdot}xD_2O$, was studied using TGA and EGA. The deuteroxides were chosen for this study as it has been previously reported that nitrogen ylide formation on the methyl group of the ammonium cations has a low barrier and the use of the deuteroxide counter ions enables the detailed observation of these species *via* isotopic scrambling in the decomposition products [24]. The formation of ylides can be important in degradation for these or similar cations, particularly when similar cations are placed into polymeric systems where the likelihood of ylide species further reacting with the polymer backbone or other cations/tethers is greatly enhanced.

2. Experimental

2.1. Materials

Ethyltrimethylammonium iodide, 1-bromopropane, 1-bromo-2-methylpropane, neopentylamine, trimethylamine (45% in H_2O), silver (I) oxide, methyl iodide, potassium carbonate, acetonitrile, diethyl ether, dimethylsulfoxide-d_6 (DMSO), methanol-d_4 (MeOD) and deuterium oxide (D_2O, 99.95% atom D) were purchased from commercial sources and used as received. All alkyltrimethylammonium deuteroxides were stored under an argon atmosphere in tightly sealed vessels at −30 °C prior to experiments.

Ethyltrimethylammonium deuteroxide (**1**) – To a 100 mL round bottom flask under an active argon flow was added ethyltrimethylammonium iodide (1.06 g, 4.92 mmol) and 15 mL H_2O with a Teflon coated magnetic stir bar. The solution was cooled to 0 °C and Ag_2O (2.24 g, 9.65 mmol) was added. The reaction was allowed to come to room temperature over a period of 2 h and then was filtered through a plug of celite. The water was then removed *via* lyophilization to yield 0.54 g of the white solid $[EtNMe_3][OH]{\cdot}xH_2O$. Preparation of $[EtNMe_3][OD]{\cdot}xD_2O$ was achieved by dissolution of $[EtNMe_3][OH]{\cdot}xH_2O$ in deuterium oxide followed by solvent evaporation *via* dynamic vacuum at room temperature. This process was repeated three times to afford 0.50 g of $[EtNMe_3][OD]{\cdot}xD_2O$ as a white solid. ^1H NMR (D_2O, 300 MHz): 3.28 (q, 2H, $J = 7.2$ Hz, CH_2), 2.97 (s, 9H, $N(CH_3)_3$), 1.24 (t, 3H, $J = 7.2$ Hz, CH_3). ^{13}C NMR (DMSO, 75 MHz): 63.6 (CH_2), 53.7 ($N(CH_3)_3$), 9.4 (CH_3).

n-Propyltrimethylammonium bromide (**2**) – A 100 mL round bottom flask was charged with 1-bromopropane (5.8 mL, 63.8 mmol), trimethylamine (45% in H_2O, 20 mL, 126 mmol), and 20 mL acetonitrile. The reaction was heated at 40 °C for 5 h and then cooled to room temperature. The solvent was removed *via* rotary evaporation to leave an oily residue. Diethyl ether was added to precipitate the product, which was filtered and washed with additional ether. The product was dried *in vacuo* overnight to yield 10.1 g (87%) of a white solid. ^1H NMR (MeOD, 300 MHz): 3.61 (m, 2H, $CH_2{-}N(CH_3)_3$), 3.42 (s, 9H, $N(CH_3)_3$), 2.03 (m, 2H, H_3CCH_2), 1.22 (t, 3H, $J = 7.2$ Hz, CH_3). ^{13}C NMR (MeOD, 75 MHz): 69.1 ($CH_2{-}N(CH_3)_3$), 53.7 ($N(CH_3)_3$), 17.5 (H_3CCH_2), 10.9 (CH_3).

n-Propyltrimethylammonium deuteroxide (**3**) – To a 100 mL round bottom flask under an active argon flow was added *n*-propyltrimethylammonium bromide (1.88 g, 10.3 mmol) and 15 mL H_2O with a Teflon coated magnetic stir bar. The solution was cooled to 0 °C and Ag_2O (4.75 g, 20.5 mmol) was added. The reaction was allowed to come to room temperature over a period of 2 h and then was filtered through a plug of celite. The water was then removed *via* lyophilization and the product, $[n\text{-}PrNMe_3][OH]{\cdot}xH_2O$, was dissolved in deuterium oxide followed by solvent evaporation *via* dynamic vacuum at room temperature. This process was repeated three times to afford 0.87 g of $[n\text{-}PrNMe_3][OD]{\cdot}xD_2O$ as a colorless oily solid. ^1H NMR (D_2O, 300 MHz): 3.16 (m, 2H, $CH_2{-}N(CH_3)_3$), 2.98 (s, 9H, $N(CH_3)_3$), 1.70 (tq, 2H, $J = 7.8$, 4.2 Hz, H_3CCH_2), 0.87 (t, 3H, $J = 7.2$ Hz, CH_3). ^{13}C NMR (DMSO, 75 MHz): 66.2 ($CH_2{-}N(CH_3)_3$), 51.7 ($N(CH_3)_3$), 15.7 (H_3CCH_2), 10.5 (CH_3).

Isobutyltrimethylammonium bromide (**4**) – A 100 mL round bottom flask was charged with 1-bromo-2-methylpropane (6.0 mL, 55.2 mmol), trimethylamine (45% in H_2O, 18 mL, 114 mmol), and 20 mL acetonitrile. The reaction was heated at 40 °C for 5 h and then cooled to room temperature. The solvent was removed *via* rotary evaporation to leave an oily residue. Diethyl ether was added to precipitate the product, which was filtered and washed with additional ether. The product was dried *in vacuo* overnight to yield 8.76 g (81%) of a white solid. ^1H NMR (MeOD, 300 MHz): 3.33 (d, 2H, $J = 5.1$ Hz, $CH_2{-}N(CH_3)_3$), 3.21 (s, 9H, $N(CH_3)_3$), 2.20 (dt, 1H, $J_1 = 6.9$ Hz, $J_2 = 5.1$ Hz, $HCCH_2$), 1.14 (d, 3H, $J = 6.9$ Hz, CH_3). ^{13}C NMR (MeOD, 75 MHz): 75.1 ($CH_2\text{-}N(CH_3)_3$), 54.2 ($N(CH_3)_3$), 25.0 (H_3CCH), 23.2 (CH_3).

Isobutyltrimethylammonium deuteroxide (**5**) – To a 100 mL round bottom flask under an active argon flow was added **4** (1.29 g, 6.58 mmol) and 15 mL H_2O with a Teflon coated magnetic stir bar. The solution was cooled to 0 °C and Ag_2O (3.05 g, 13.2 mmol) was added. The reaction was allowed to come to room temperature over a period of 2 h and then was filtered through a plug