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DECOMPOSITION PATHWAYS OF AN ALKALINE FUEL CELL MEMBRANE MATERIAL COMPONENT VIA EVOLVED GAS ANALYSIS

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The mechanism of the thermal decomposition of $[NMe_4][OH]\cdot5H_2O$, tetramethyl ammonium hydroxide pentahydrate, was studied using DSC, TG and evolved gas analysis because of the importance of related ions in anion exchange membranes. The products of the reaction are trimethyl amine, methanol and dimethyl ether. The relative ratio of the products is determined by how much water remains in the sample as it is decomposing. Isotopic labeling experiments with D_2O show that deprotonation of the tetramethyl ammonium ion by hydroxide establishes a rapid equilibrium between tetramethyl ammonium ion and the nitrogen ylide species and water that scrambles the deuterium with the proton in the methyl groups. The results of this work also suggest that tetraalkyl ammonium cations may be more stable in hydroxide conducting membranes than previously believed.

Keywords: *alkaline membrane, tetraalkyl ammonium ion decomposition, ylide*

Introduction

In recent years, there has been an enormous effort directed toward the development of proton exchange membrane fuel cells (PEMFCs) as a means of supplying power for vehicles or portable electronic devices. In these devices, fuel is oxidized electrochemically to form only water or water and carbon dioxide while producing electricity. Fuel cells have the potential to provide a highly efficient means of generating electricity without the thermodynamic limitations of a Carnot engine while generating only benign by-products. The highly acidic environment created by these membranes limits the materials that can be used in these devices. This limits both potential fuel options (as some fuels are either unstable in the presence of acid: $NaBH_4$, N_2H_2 or are poorly catalyzed in acid (ethanol)) and the materials used as fuel cell components. Perhaps the most problematic of these limitations are the electrocatalysts that are limited to platinum and other related precious metals/alloys. An alternative to PEMFCs would be to perform the electro-oxidation reactions under alkaline conditions where non-precious metal electrocatalysts that use metals such as Co, Ag, Fe or Ni are highly active and reasonably stable.

While alkaline fuel cells using aqueous potassium hydroxide as an electrolyte have been well developed for space applications, the use of hydroxide conducting membrane materials to make an alkaline version of a PEMFC has received only very limited attention [1–4]. The primary limitation of AMFCs is the stability of the membrane at the high pH conditions necessary for good hydroxide conductivity.

The typical membrane materials that have been used as hydroxide ion conductors consist of ammonium cations $[NR_4]^+$ that are tethered to a polymer backbone. The hydroxide ion in the membrane can react with such organic cations via nucleophilic attack or as a Bronsted base. Such a reaction results in the removal of hydroxide ions leading to lower conductivity as well as destruction of the integrity of the polymer membrane itself. The motivation of the present work is to understand the nature of cation degradation reactions that are occurring in the alkaline membrane materials. We have embarked on a study of the mechanism of the thermal decomposition of $[NMe_4][OH]$ which serves as a small molecule model of the functional component of hydroxide conducting membrane materials. These studies involve thermal gravimetric analysis (TG) as well as evolved gas analysis (EGA) under conditions that are consistent with anticipated fuel cell applications to understand the mechanism of the decomposition reaction so that we may develop better membranes for AMFCs.

Previous work on the decomposition of tetramethyl ammonium hydroxide has been focused on the reactions that occur at much higher temperatures than what we observed in this study. A 'wet' decomposition mechanism occurs in water at 270°C. Under these conditions, the reaction products are methanol and trimethyl amine [5]. The 'dry' reaction involved drying $[NMe_4][OH]\cdot5H_2O$ at 65°C and then rapidly heating it

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to 135°C until complete decomposition occurred. These reaction conditions gave dimethyl ether (DME), trimethyl amine and water in a 1:2:1 ratio [6]. The data from these studies suggest that both nucleophilic attack of hydroxide on the $[NMe_4]^+$ cation as well as deprotonation of $[NMe_4]^+$ to generate the nitrogen ylide, Me_3NCH_2 occur during the decomposition of $[NMe_4][OH]$ [7]. The results reported in our work are consistent with these previous studies, but also demonstrate that the material decomposes at a lower temperature when it is dry and that the presence of water is critical in determining the product ratio as well as the likely mechanisms of decomposition.

Experimental

Materials

Tetramethylammonium hydroxide pentahydrate $[(CH_3)_4NOH\cdot 5H_2O$, 99%] was used as received from Acros Organics. Preparation of $(CH_3)_4NOD\cdot 5D_2O$ was achieved by dissolution of $(CH_3)_4NOH\cdot 5H_2O$ in deuterium oxide [D_2O, 99.95% atom D] purchased from Acros Organics, followed by solvent evaporation via dynamic vacuum at room temperature. This process was repeated three times at a D_2O:$(CH_3)_4NOH\cdot 5H_2O$ molar ratio of 16:1. The resulting material was stored in a desiccator with an open vial of D_2O to mitigate proton exchange with H_2O.

Instrumentation

Evolved gas analysis (EGA) was performed on the decomposition of materials to identify products in an effort to determine reaction pathways. Mass loss, gas speciation, quantification and isotopic measurements were carried out using a collection of instrumentation coupled together with heat traced stainless steel transfer lines. Decomposition reactions were performed in a horizontal large furnace Mettler-Toledo 851 TGA/SDTA thermogravimetric analyzer (TG). The reaction zone was constantly purged with nitrogen at 40 sccm as measured by an Agilent ADM1000 flowmeter. Evolved gases from the decompositions were carried by the purge gas from the outlet of the TG and flowed through a Thermo-Electron 380 Fourier transform infrared spectrometer (TG-FTIR) equipped with a Nicolet 2 meter heated gas cell (KBr windows). At the inlet to the gas cell a Pfeiffer Thermo-Star mass spectrometer (TG-MS) sampled the gas via a stainless steel capillary at a rate of 1 sccm (Fig. 1). FTIR difference spectra were taken at a resolution of 0.5 cm^{-1} after subtraction of the KBr and UHP N_2 background blank. The solid starting materials were contained in 900 μL alumina crucibles. In non-isothermal experiments crucibles were filled with ~25 mg of sample material, forming a thin layer to minimize mass transfer related problems. Non-isothermal temperature ramp rates consisted of 0.5 and 0.25°C min^{-1} starting from 30 and an endpoint of 175°C. Isothermal experiments differed slightly, they utilized a larger sample size of ~50 mg to provide more signal for MS detection without introducing errors related to diffusion during dehydration. Isothermal experiments initiated with a rapid ramp from 30 to 90°C and were followed by an isothermal segment at 90°C for 140 h. Quantitative gas calibration curves were developed for water, trimethylamine, methanol and dimethyl ether [8]. Gas phase water level calibration spectra were generated using a General Eastern (GE) DPG-300 dew point generator and measured with a GE 1121H two-stage chilled mirror sensor attached to a GE Optica hygrometer controller. Calibration spectra for the other gases were obtained by flowing gas standards purchased from Scott Specialty Gas at multiple concentration levels through the FTIR gas cell at an ambient pressure of ~770 mBar. Calibration curves with correlation values close to 1.0 were developed using TQ Analyst software employing the stepwise multiple linear regression (SMLR) technique expressing concentration as a function of absorbance at multiple frequencies. A Mettler-Toledo 822^e Differential Scanning Calorimeter (DSC) was used for thermal measurements of enthalpy change [ΔH]. Data presented uses the convention of exothermic heat flow as positive. Samples were contained in 40 μL aluminum crucibles with pin hole punched lids. To eliminate instrument artifacts during heating an empty crucible was used as the reference. The reference signal was automatically subtracted from the recorded signal during the experiment. Indium (*m.p.*=156.60°C) was used as the calibration standard for sample temperature and tau lag adjustments on both TG and DSC instrumentation.

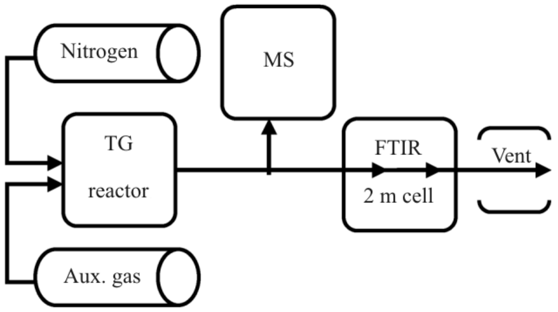


Fig. 1 Schematic diagram of EGA experiment

Results and discussion

A thermal curve (TG/DSC) of the decomposition of $[NMe_4][OH]\cdot 5H_2O$ when heated at 0.50°C min^{-1} is shown in Fig. 2 demonstrating that several endothermic transitions occur in the material as the sample is heated. The lowest temperature transitions (37 and 46°C) are associated with reorientation of the cations [9] and loss of some of the water of hydration (as measured by the ~20% mass loss). The compound then melts at 68°C, consistent with the value reported in the literature [10]. As the temperature rises past 110°C, decomposition of the material occurs as evidenced by the large mass loss. This mass loss is associated with the broad endotherm that peaks at ~130°C with an onset temperature of 112°C and accounts for approximately 97% of the mass loss associated with decomposition. Complete decomposition occurs by 150°C with essentially quantitative formation of volatile products leaving no solid behind.

In order to understand the thermal decomposition process, the identity and quantities of the gases that are evolved upon decomposition were analyzed by a combination of FTIR spectroscopy and mass spectrometry. Figure 3 shows a thermal curve that was measured at a heating rate of 0.25°C min^{-1} and an evolved gas analysis via FTIR of the gases that are generated during the decomposition reaction. The observed gas phase products were water, trimethylamine, dimethyl ether and methanol. A mass spectrum of the evolved gases during decomposition also confirmed the presence of these compounds. The observation of water loss at low temperatures prior to further reaction of the cation itself suggests that partial dehydration of the material is necessary for cation decomposition to occur. The mass loss is consistent with the removal of 2 moles of H_2O per tetramethylammonium hydroxide formula unit before any significant cation decomposition occurs. As the sample is heated to temperatures above 110°C, the thermal data shows that the reaction proceeds in two distinct steps (note that the separation of these two processes is not resolved at the faster heating rate that was used in Fig. 2). From 110–125°C, methanol and DME are formed along with trimethyl amine and a large quantity of water is also formed/released. In the second stage of the reaction (125–130°C), only the formation of DME, trimethylamine and a small amount of water are observed. Because the concentrations of the evolved gases were measured in ppm vol/vol, the ratios of the peaks in the EGA analysis represent the molar stoichiometric ratios of products of the decomposition reaction.

When the reaction was performed isothermally at 90°C, the material decomposes over the course of one week as shown in Fig. 4. Initially, the majority of the gas released is water and then the decomposition accelerates noticeably after ca. 60 h once the first 20–40% of the mass has been lost. This correlates well with the observation in the ramped temperature decomposition where the initial mass loss corresponds to loss of waters of hydration and only when the water reaches a critical level do the cations decompose as shown by the release of methanol, DME and trimethylamine. The observed decomposition temperature is lower than that reported in the literature [5] and lower than that observed in the ramped experiment.

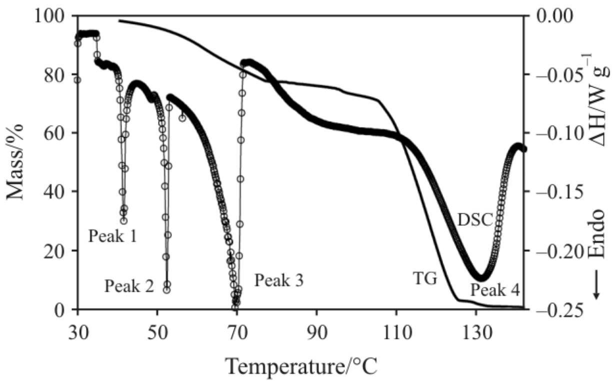


Fig. 2 Thermal curve of the decomposition of [NMe_4][OH]·$5H_2O$. Temperature ramp, 0.50°C min^{-1}. Peak 1 – polymorph of the original crystal, C3 reorientation of the CH_3 groups. Peak 2 – polymorph relates to C3 and C2 reorientations of the cation as a whole. Peak 3 – melting point of $(CH_3)_4NOH·5H_2O$ [5, 6]. Peak 4 – endothermic reaction of the material

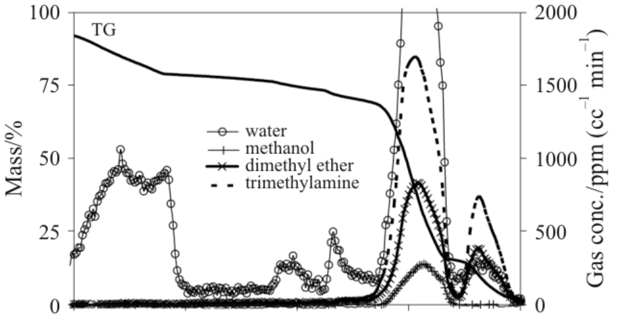


Fig. 3 TG-EGA via infrared spectroscopy of the ramped thermal decomposition of $(CH_3)_4NOH·5H_2O$. Temperature ramp is 0.25°C min^{-1}

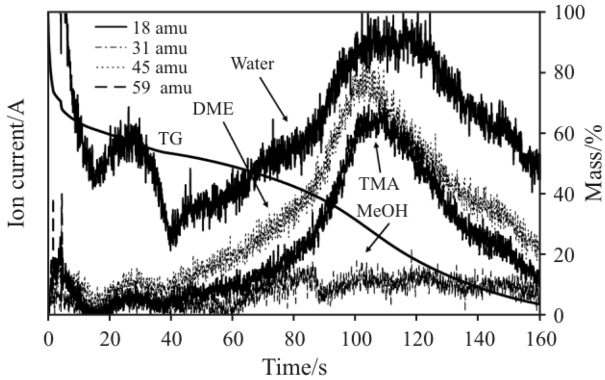


Fig. 4 EGA via mass spectrometry of the isothermal decomposition of $(CH_3)_4NOH·5H_2O$ at 90°C

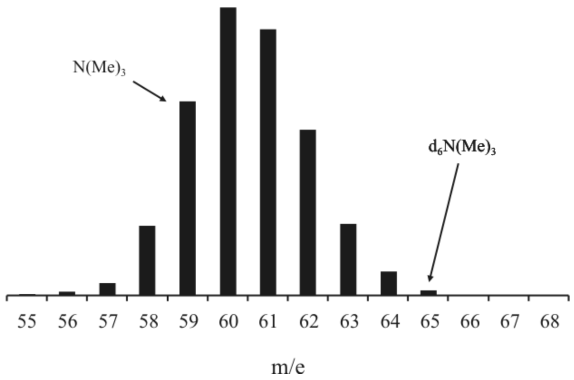
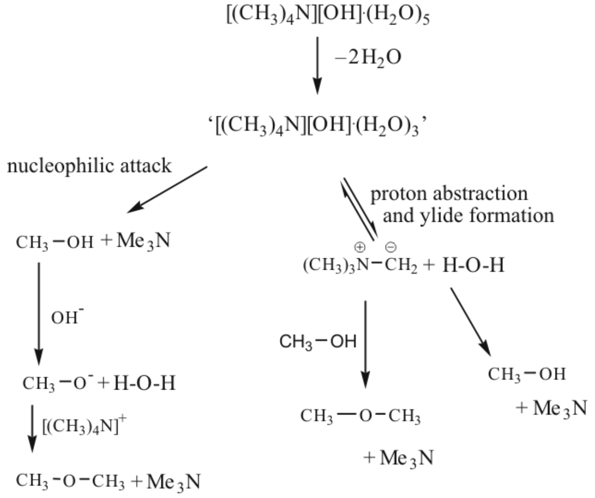


Fig. 5 Mass spectrum of the trimethyl amine produced in the ramped decomposition of $(CH_3)_4NOD{\cdot}5D_2O$. The most abundant peak in the mass spectrum of $N(CH_3)_3$ appears at 58 amu with the parent peak at 59 amu being 70% of the intensity of M-1 peak

Figure 5 shows the mass spectrum of the trimethyl amine (TMA) that is produced when $(CH_3)_4NOD{\cdot}5D_2O$ decomposes. The molar mass of undeuterated trimethyl amine is 59 with 58 amu being the major signal in its spectrum. The 59 amu peak is 70% of the intensity of the major peak at 58 amu. It is obvious from the data that heavier mass isotopomers make up the majority of the species that are observed. These species arise from the exchange of deuterium from the D_2O in the sample with the protons of the methyl groups of the tetramethyl ammonium ions as the material is decomposing. Both the methanol and DME signals show that deuterium from D_2O scrambles with the protons of the methyl groups of these species during the decomposition reaction. When the isotopic composition of the trimethyl amine produced was analyzed as a function of the temperature that it was produced, the ratio was determined to be invariant. This suggests that the isotopic scrambling was complete prior to the generation of any trimethyl amine in the gas phase.

The results from the thermal analysis experiments described above allow us to propose a mechanism for the decomposition of solid $(CH_3)_4NOH{\cdot}5H_2O$ shown in Scheme 1. It is clear that the first process that occurs upon heating is loss of some of the water of hydration. Gravimetric analysis suggests that 2 water molecules per formula unit are removed from the material prior to reaction of the cation with hydroxide. This observation is consistent with simulations of the reactivity of $[Me_4N]^+[OH]^-$ in the presence of water [11, 12]. In these studies, if the hydroxide ion is solvated with more than 3 water molecules, it does not react readily with $[Me_4N]^+$. Our experimental results demonstrate that the hydration level of the hydroxide ion determines its reactivity. Once the $[OH]^-$ is activated by removal of the stabilizing water from the lattice, it can react with $[Me_4N]^+$ via two paths. It can behave as a nucleophile via an S_N2 type mechanism generating methanol and trimethyl amine directly, or it can behave as a Bronsted base and deprotonate the $[Me_4N]^+$ generating a nitrogen ylide species that subsequently undergoes further reaction also giving methanol and DME.



Scheme 1

The result of the isotopic labeling experiment in which $(CH_3)_4NOD{\cdot}5D_2O$ was observed to decompose giving a mixture of deuterated trimethylamines (as well as deuterated DME and methanol) is consistent with the formation of an ylide species via reversible deprotonation/protonation of $[(CH_3)_4N]^+$. Because trimethyl amine formation does not occur until two water molecules have been driven from the solid, the extent of H/D scrambling is consistent with nearly statistical scrambling of the 7 deuterium atoms that are left in the sample (the stoichiometry becomes $(CH_3)_4NOD{\cdot}3D_2O$ following loss of $2D_2O$ at low temperatures) with the 12 protons in $[Me_4N]^+$. Once the first two waters of hydration are lost, the sample melts, and that the decomposition reaction that ensues, occurs from the liquid-state. The observation that the initial trimethyl amine that is formed has complete deuterium scrambling is consistent with scrambling by the ylide mechanism prior to any irreversible cation degradation. While the presence of the ylide mechanism in the decomposition of methylated ammonium hydroxides has been recognized, this is the first experimental evidence that such a mechanism is the first step in the decomposition reaction. These results are also consistent with computational results that show that the ylide mechanism has a lower activation barrier associated with it than the nucleophilic attack of hydroxide on the cation [11].

Our data demonstrate that abstraction of the α-proton to generate a nitrogen ylide is a very important degradation mechanism for methyl ammonium species. As shown in Scheme 1, the formation of methanol can occur by direct nucleophilic attack of hydroxide on a methyl group of $[Me_4N]^+$ or by insertion of the methylene group of the ylide into the OH bond of water. This latter reaction is well precedented in the chemistry of carbenes [13]. Dimethyl ether can also be formed in two ways. The reaction of methanol with the ylide via insertion of the methylene group into the O–H bond of methanol, or by nucleophilic attack of methoxide ion (formed by deprotonation of methanol) on a methyl group of $[Me_4N]^+$. Thus, both reaction sequences involve the initial formation of methanol which is then converted to DME. The stoichiometry of the reaction demands that whenever a carbon oxygen bond is formed an equivalent of trimethyl amine must also be formed. This leads to a ratio of one trimethyl amine produced for every methanol produced and two trimethyl amines produced for every DME that is formed regardless of the mechanism. The evolved gas analysis data shown in Fig. 3 is consistent with the stoichiometry of the reaction described above and is consistent with the mechanism proposed in Scheme 1.

A question arises as to why there are two distinct thermal regions associated with the decomposition of the $[NMe_4]^+$ cations. In the data shown in Fig. 3, the onset temperature of the first region is 106°C and the second onset occurs at 120°C. In the lower temperature process, methanol and DME as well as significant quantities of water are being eliminated from the sample. This contrasts with the higher temperature process in which DME is the sole oxygenated organic that is formed along with the required two equivalents of trimethyl amine and one equivalent of water. If we assume that by 125°C all the water of hydration has been removed from the sample, then the water that is generated in the higher temperature process must come from the reaction alone. The only way that water can be produced in the decomposition of $[Me_4N][OH]$ is by the deprotonation of methanol by hydroxide. The methoxide formed in this way then reacts with $[Me_4N]^+$ via an S_N2 process to generate DME. The methanol that is dehydrated in this fashion could be formed by either the ylide or S_N2 mechanisms. Because the original water of hydration of the sample is still being lost during the lower temperature process, it is impossible to determine unequivocally which mechanism(s) may be operating in this temperature range.

Conclusions

The overall picture of the degradation of tetramethylammonium hydroxide that emerges from these studies is that the extent of hydration of the $[Me_4N][OH]$ is critical in determining the stability of the material. As long as there is sufficient water present to solvate and thereby attenuate the reactivity of the hydroxide ion, the material is significantly more resistant to thermal degradation. While it has been suggested that the stability of the alkyl ammonium cation might allow membranes using these cations as counter ions to hydroxide to survive to only limited temperatures (up to 60°C) [1], the results reported here suggest that under the correct conditions, these cations actually possess reasonable stability at higher temperatures. Our results stress the importance of hydration as a method to attenuate the reactivity of the hydroxide ion and suggest that controlled humidification of the membrane may present a viable strategy that could enable the construction of useful AMFCs from ammonium cations or any other cation that could be degraded by reaction with hydroxide. Future work will address the decomposition of alkyl ammonium hydroxides under controlled humidity conditions.

Acknowledgements

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