LA-UR- *11-04791*

Title: Decomposition Pathways of Tetraalkylammonium Cations via Evolved Gas Analysis: Implications for Hydroxide Ion Conducting Fuel Cell Membranes

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Intended for: Presentation talk at the American Chemical Society (ACS) national meeting.

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Form 836 (7/06)

Decomposition Pathways of Tetraalkylammonium Cations via Evolved Gas Analysis: Implications for Hydroxide Ion Conducting Fuel Cell Membranes

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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 cells (AMFCs) can offer some advantages over the PEMFC counterparts. The basic media allows for the use of non-precious electrode catalysts made from inexpensive metals such as Fe/Co/Ni/Ag versus the use of precious and expensive Pt or Ru used in PEMFCs. The primary limitation of AMFCs is the stability of the membrane at high pH necessary for good hydroxide ion conductivity.

Early studies on membrane development have focused on the use of ammonium cations $[NR_4]^+$ tethered to a polymer backbone for hydroxide ion transport.[2-5] Previous work has shown that the hydroxide ion in the membrane can react with such 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 that offers another reaction pathway for decomposition.[6-8]

In this study the degradation of ammonium cations bearing β-hydrogen atoms was investigated. Specifically the mechanism of thermal decomposition of ethyltrimethyl ammonium deuteroxide, $[EtNMe_3][OD] \cdot xD_2O$, *n*-propyltrimethyl ammonium deuteroxide, $[n\text{-}PrNMe_3][OD] \cdot xD_2O$, and *iso*-butyltrimethyl ammonium deuteroxide, $[i\text{-}BuNMe_3][OD] \cdot xD_2O$ was studied using thermogravimetric analysis (TGA) and evolved gas analysis (EGA) due to the importance of these and related ions in AMFCs.

Experimental

Ethyltrimethylammonium deuteroxide $([EtNMe_3][OD] \cdot xD_2O)$: Reaction of Ethyltrimethylammonium iodide with silver (I) oxide in water furnished ethyltrimethylammonium hydroxide. Deuteroxide exchange was accomplished by dissolution of the ethyltrimethylammonium hydroxide in D_2O followed by removal of the excess D_2O via lyophilization. This process was repeated twice more to ensure complete deuteroxide exchange.

n-Propyltrimethylammonium deuteroxide $([n\text{-}PrNMe_3][OD] \cdot xD_2O)$: Reaction of 1-bromopropane with trimethylamine in acetonitrile furnished *n*-propyltrimethylammonium bromide. Subsequent reaction with silver (I) oxide in water followed by deuterium exchange in D_2O furnished $[n\text{-}PrNMe_3][OD] \cdot xD_2O$.
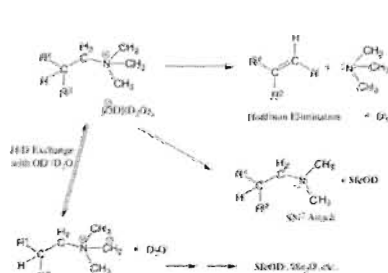
*iso-*butyltrimethylammonium deuteroxide $([i\text{-}BuNMe_3][OD] \cdot xD_2O)$: Reaction of 1-bromo-2-methylpropane with trimethylamine in acetonitrile furnished *iso*-butyltrimethylammonium bromide. Subsequent reaction with silver (I) oxide in water followed by deuterium exchange in D_2O furnished $[iso\text{-}BuNMe_3][OD] \cdot xD_2O$.

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, 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). 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). At the outlet to the gas cell a Pfeiffer Thermo-Star mass spectrometer (TG-MS) sampled the gas via a stainless steel capillary in addition to a Varian 4-channel CP-4900 gas chromatograph (GC) via a stainless steel capillary as well. Non-isothermal temperature ramp rates consisted of 0.25 and 0.15°C min^{-1} starting from 30 and an endpoint of 260°C and 160°C respectively. Isothermal experiments initiated with a rapid ramp from 30 to 120°C and were followed by an isothermal segment at 120°C for 30 min. Samples sizes were approximately 25mg.

Results and Discussion

Scheme 1 illustrates a number of viable decomposition pathways for the thermal decomposition of the tetraalkylammonium deuteroxides studied. Specifically one can envision decomposition occurring through 3 potential pathways. The presence of β-hydrogen atoms in $[EtNMe_3][OD] \cdot xD_2O$ would suggest that decomposition through Hoffman elimination to form ethylene and trimethylamine would be the primary pathway for the thermal decomposition. Previous studies on the thermal decomposition of tetramethylammonium deuteroxide $[Me_4N][OD] \cdot 5D_2O$ illustrated that formation of a nitrogen ylide species through reversible deprotonation/protonation of $[Me_4N]^+$ prior to any decomposition was observed.[6] Thus, one cannot rule out the formation of similar ylide species in the decomposition of $[EtNMe_3][OD] \cdot xD_2O$. Furthermore, direct nucleophilic attack of the deuteroxide ion on the cation are certainly possible. In order to understand the thermal decomposition process, the identity of the gases evolved during the decomposition of $[EtNMe_3][OD] \cdot xD_2O$ were analyzed by a combination of FTIR spectroscopy, mass spectrometry, and gas chromatography.

Scheme 1. Thermal decomposition pathways of tetraalkylammonium deuteroxides

A thermal curve (TGA) of the decomposition of $[EtNMe_3][OD] \cdot xD_2O$ when heated at 0.15 °C min^{-1} starting at 30 °C is shown in Figure 1. In stark contrast to prior decomposition studies of $[Me_4N][OD] \cdot 5D_2O$ where the onset of decomposition is not observed until some water of hydration is lost (2 molecules) and the temperature is above 110 °C,[6] the decomposition of $[EtNMe_3][OD] \cdot xD_2O$ begins immediately upon heating from 30 °C. Complete decomposition of the material is observed by 68 °C under the given heating rate. This drastic difference can be attributed to a number of factors. Namely, the exact extent of the solvation level of the $[EtNMe_3][OD] \cdot xD_2O$ starting material could not be determined. Whereas $[Me_4N][OD] \cdot 5D_2O$ is a commercially available crystalline stable solid, $[EtNMe_3][OD] \cdot xD_2O$ had to be prepared via synthetic methods and all attempts to crystallize the material proved in vain. Furthermore, an analysis of the gases produced by FTIR spectroscopy and GC showed the formation of only ethylene and trimethylamine as reaction products

(Figure 1) in equal concentrations. This is consistent with Hoffmann elimination as the only decomposition pathway. However, analysis of the trimethylamine given off via mass spectrometry revealed that above 40°C, the presence of deuterium scrambling occurs indicating the barrier to nitrogen ylide formation is rather low (Figure 2). The deuterium scrambling above 40°C can be corroborated with the appearance of C-D stretches in the FTIR spectrum.
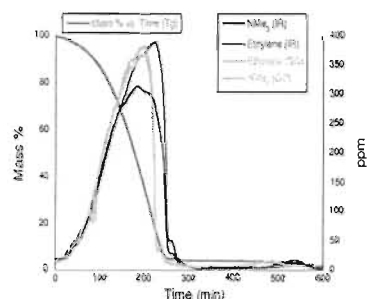

Figure 1. Evolved gas analysis (EGA) of [EtNMe₃][OD]·xD₂O thermal decomposition.

The thermal decomposition of [n-PrNMe₃][OD]·xD₂O was carried out in a similar fashion. In this case the material began to decompose immediately from heating at 30°C and is completely decomposed by 85°C under the given heating rate (0.15°C min⁻¹). The reaction products produced are only propylene and trimethylamine, consistent with Hoffmann elimination as the only decomposition pathway. In this case deuterium scrambling in the trimethylamine was observed immediately indicating essentially a barrier less pathway and the resultant MS spectrum is similar to that observed from the decomposition of [EtNMe₃][OD]·xD₂O.

Figure 2. Mass spectrum of the trimethylamine produced in the ramped decomposition of [EtNMe₃][OD]·xD₂O.

The thermal decomposition of [iso-BuNMe₃][OD] · xD₂O was carried out at a heating rate of 0.25°C min⁻¹. This material again begins to decompose immediately starting at 30 °C. However, in this case at 95°C the TGA curve levels off until approximately 110 °C at which point the material ra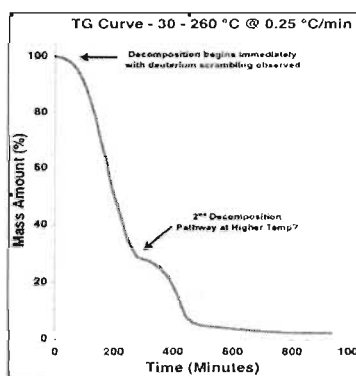pidly decomposes (Figure 3). Analysis of the reaction products below 95°C show only the formation of Hoffmann elimination products (isobutylene and trimethylamine). Again, deuterium scrambling is observed immediately at 30°C with the mass spectrum of the trimethylamine showing a similar isotopic scrambling as seen in Figure 2. However, above 100°C the appearance of isobutyldimethylamine is observed in the mass spectrum, which can only be produced via nucleophilic attack of the hydroxide ion on the methyl group of the ammonium cation, or via direct further decomposition from the nitrogen ylide species, which are indistinguishable.

When the reaction was performed at such a heating rate (0.15°C min⁻¹) that the material completely decomposed before reaching 100°C the only reaction products were isobutylene and trimethylamine. However, if the reaction was performed isothermally by ramping the TGA from 30°C to 120°C immediately and held at 120°C the material decomposes in 10 minutes and the formation of isobutyldimethylamine is again observed in the mass spectrum (along

Figure 3. Thermal curve of the decomposition of [i-BuNMe₃][OD] ·xD₂O.

with trimethylamine and isobutylene). Looking at a slice of data near the end of decomposition one can observe extensive formation of isobutyldimethylamine (up to 25%), which shows a consistent deuterium isotopic scrambling pattern (Figure 4). Furthermore, this deuterium isotopic scrambling pattern is observed in each of the daughter fragmentation species arising from methyl group loss.
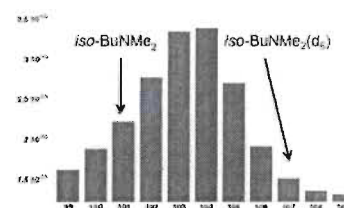
The overall picture that emerges from these studies is that while Hoffman elimination is the preferred decomposition pathway for ammonium cations bearing β-hydrogens, and ylide formation scrambles protons from water (or D₂O) into the trimethylamine that is formed. Blocking the β-hydrogen positions by successively adding methyl groups increases the stability of the cation, but in the case of [i-BuNMe₃][OD]·xD₂O, a second decomposition pathway is observed (nucleophilic attack or ylide decomposition). These results represent the extreme conditions of potential fuel cell operability (effectively zero percent relative humidity). Further studies will focus on decomposition of these materials under controlled humidity conditions.

Figure 4. Mass spectrum of the isobutyldimethylamine produced in the ramped decomposition of [iso-BuNMe₃][OD]·xD₂O.

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