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Rapid Analysis of Tetrakis(dialkylamino)phosphonium Stability in Alkaline Media

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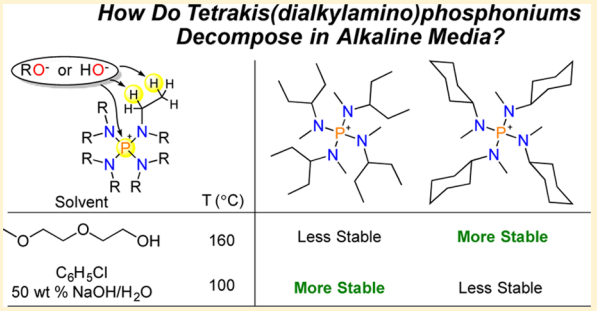
Supporting Information

ABSTRACT: Hydroxide-stable organic cations are crucial components for ion-transport processes in electrochemical energy systems, and the tetrakis(dialkylamino)phosphonium cation is a promising candidate for this application. These phosphoniums are known to be highly resistant to alkaline media; however, very few investigations have systematically evaluated how these cations decompose in the presence of hydroxide or alkoxide anions. The excellent stability of several tetraaminophosphoniums in 2 M KOH/CH_3OH at 80 °C led us to design experiments for the rapid assessment of phosphonium degradation in homogeneous solution and under phase-transfer conditions. The analysis illustrated how substituents around the cation core affect both degradation pathways and rates. β-H elimination and direct attack at the phosphorus atom are the most common degradation pathways observed in an alcoholic solvent, while α-H abstraction and direct attack are observed under phase-transfer conditions (PhCl and 50 wt % NaOH/H_2O). The collected data provided a relative stability comparison for this family of cations to enable future design improvements and illustrated the utility of using multiple tests for degradation studies.



INTRODUCTION

Materials that enable selective ion transport under a wide range of conditions (temperature, pH, oxidative stress) are necessary for chemical separation processes and electrochemical energy systems (e.g, redox-flow batteries and fuel cells).[1] Solid polymer electrolytes are a natural choice for these applications, since polymers can be easily decorated with various ionic groups to provide pathways for charge movement. While polymers with pendant anions have been employed extensively as proton conductors for ion transport,[1a] anion-exchange membranes (AEMs) with pendant cations to conduct hydroxide often suffer from limited chemical stability.[2]

Preparation of hydroxide-stable AEMs has attracted significant attention for fuel cell devices,[3−5] since non-noble metals can be used for O_2 reduction under alkaline conditions.[2] The limited chemical durability of most AEMs is often directly related to the cation appended to the polymer chain.[2] A number of model compound studies have appeared on organic cations in an effort to better understand decomposition pathways and improve alkaline stability (e.g., ammonium,[6] imidazolium,[7] guanidinium,[8] and arylphosphonium[9]). These studies offer a direct means to determine how cations decompose before they are appended to a polymer chain.

Tetrakis(dialkylamino)phosphonium cations have attracted our attention as candidates for AEMs[10] due to their impressive resistance to hydroxide. These cations have already been explored as counterions for anion delivery, including F^-, Cl^-, and OH^-.[11] Additionally, these cations are derived from a class of organic superbases known as phosphazenes.[12] Though the utility of these phosphoniums has been well documented, few reports have detailed the limits of stability for these cations in the presence of hydroxide anions (Figure 1). Marchenko and

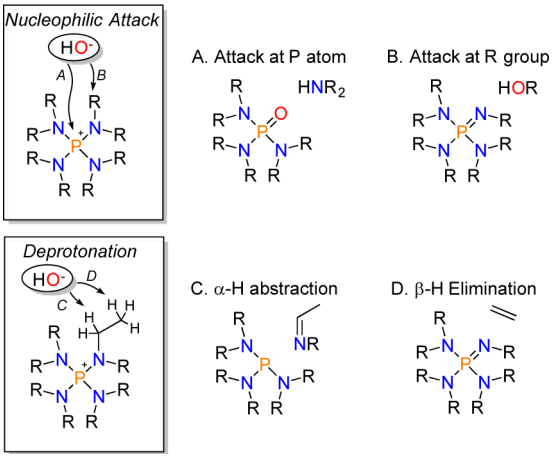


Figure 1. Decomposition pathways of $[P(NR_2)_4]^+$ cations.

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co-workers first identified the potential decomposition pathways of $[P(NR_2)_4]^+$ cations with linear alkyl substituents (R = Me, Et, ^{n}Pr, ^{n}Bu).[13] Schwesinger significantly expanded on this work and investigated the nature of the R group and the size of the phosphorus−nitrogen framework for phase-transfer catalysis.[14] Both studies established a clear link between molecular structure and alkaline stability; however, decomposition pathways were only determined for a few select systems.[13,14]

Herein, we systematically evaluated how a series of tetrakis(dialkylamino)phosphoniums degrade in homogeneous solution and under phase-transfer conditions. The experiments were designed to enable rapid screening of decomposition pathways for these systems and inform future molecular design. The utilization of harsh conditions and short experiment times are key to accelerated discovery, ensuring that the best cations are targeted for membrane applications.

RESULTS AND DISCUSSION

A number of factors must be considered when evaluating cation degradation under alkaline conditions. The reaction medium, the concentration of the reactants, and the temperature all significantly affect degradation rates for these ions. Subtle changes in any of these parameters can dramatically influence the rate of decomposition and the pathway by which the cation degrades. Consequently, direct comparisons between independent studies are difficult, as reaction setups are rarely identical.[6b,c] Most stability investigations of model compounds are conducted in H_2O as the solvent: with a concentration of cation between 0.01 and 1 M, a concentration of hydroxide between 1 and 6 M, and temperatures between 60 and 160 °C.[6c] While H_2O is the most relevant solvent for H_2-based fuel cells, the solvating power of water limits the nucleophilicity and basicity of the hydroxide anion and leads to longer experiment times.[6b,h] Rather than explore stability over periods of days or months, rapid screening (hours to minutes) could enable molecular design improvements much more quickly. This approach would be complementary to longer-term stability studies in H_2O but help delineate how different cations degrade much more quickly.

Changing the reaction medium to solvents with lower dielectric constants will result in more aggressive reaction conditions. Methanol has already been used in a number of stability studies, since it accelerates degradation and the data are relevant for direct methanol fuel cells (DMFCs).[6a,7b,9,10b] When investigating tetrakis(dialkylamino)phosphoniums, we initially selected CH_3OH as the solvent for decomposition studies; however, it did not facilitate rapid screening. We have previously reported that $[P(N(Me)Cy)_4]^+$ exhibits no signs of degradation in NaOD/CD_3OD over a period of 20 days.[10b] For comparison, we explored $[P(N\text{-pyrrolidinyl})_4]^+$ under similar conditions and found that this much smaller cation also shows no signs of change in 30 days (Figure 2).

Much harsher conditions were necessary to bring about $[P(NR_2)_4]^+$ degradation on a fast time scale; therefore, methyl carbitol (2-(2-methoxyethoxy)ethanol) was selected as a solvent. It has a low dielectric constant (14.8), is miscible with water, and has a boiling point of 194 °C. This alcohol, combined with KOH, was selected to access higher reaction temperatures for screening.

Eight tetrakis(dialkylamino)phosphoniums were synthesized to systematically probe decomposition with different amino groups. Decomposition pathways for these structures are summarized in Figure 3. Degradation was achieved by dissolving KOH (2 M) and the phosphonium (0.05 M) in degassed 2-(2-methoxyethoxy)ethanol followed by heating at 160 °C (Scheme 1). Aliquots were removed from the mixture after 4 h and analyzed to determine which phosphorus species had formed (**P-imide**, **P-oxide**, and **Phosphine**, Scheme 1). Three types of dialkylamino groups were evaluated: cyclics, straight-chain alkyls, and branched alkyls.

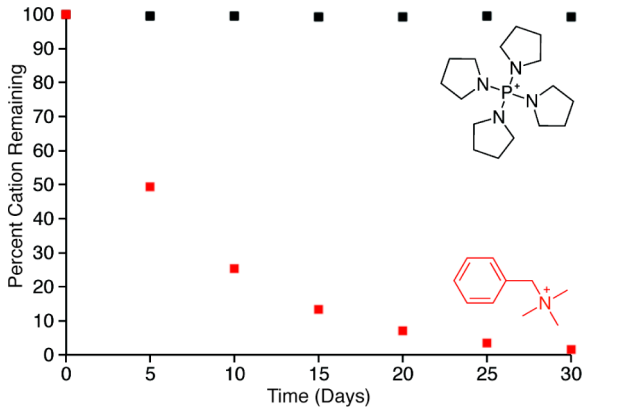

Figure 2. Alkaline stability studies of **1** in 2 M KOH/CD_3OH at 80 °C (experimental setup according to ref 7b).

Cyclic Substituents. The first class of phosphonium compounds investigated included cyclic amino groups on phosphorus (compounds **1** and **2** in Figure 3). These two systems were the least stable of all tetraaminophosphoniums investigated in this study, and temperatures below 160 °C could bring about decomposition. Compound **1** degraded completely within several hours at 120 °C with formation of a single phosphorus species in the $^{31}P\{^1H\}$ NMR spectrum (Figure S24 in the Supporting Information). Mass spectrometry confirmed that this signal corresponds to the tris(*N*-pyrrolidinyl)-phosphine oxide (**P-oxide**). Two decomposition pathways are possible to form the **P-oxide**: direct attack of the hydroxide at the P atom (pathway A, Figure 1) and subsequent formation of the phosphine oxide or α-H abstraction and oxidation of the three-coordinate phosphine (pathway C, Figure 1). Since no three-coordinate phosphine was observed in the NMR spectrum, direct nucleophilic attack at the phosphorus atom by the anion is most likely.

Direct attack is commonly postulated for decomposition of phosphonium hydroxides ($[PR_4]OH$) with alkyl or aryl groups.[15] Initial attack of OH^- occurs at phosphorus (R_4POH), and a second equivalent of OH^- deprotonates this species to form an oxyanion (R_4PO^-). The rate-determining step is loss of a carbanion (R^-) to produce the neutral phosphine oxide (with rapid protonation of R^-). This mechanistic interpretation is consistent with a reaction that is second order in OH^- and first order in phosphonium.[15] In our case, the large excess of base (2 M) in comparison to the tetraaminophosphonium (0.05 M) did not permit determination of the reaction order for the hydroxide. However, we were able to ensure that phosphine oxide formation from the phosphonium species is a pseudo-first-order process, as evidenced by a series of spectra collected over 2 h at 120 °C (Figure 4).

We synthesized compound **2** with *N*-piperidinyl substituents[16] and subjected it to the similar harsh conditions applied to compound **1**. Slightly higher temperatures were needed to bring about decomposition of **2** in comparison to **1**, suggesting

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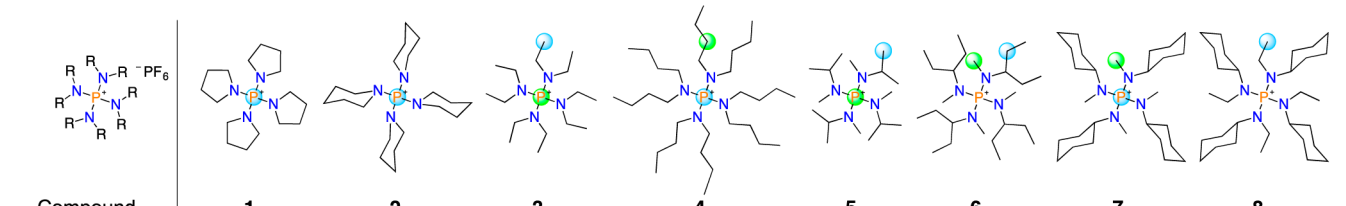
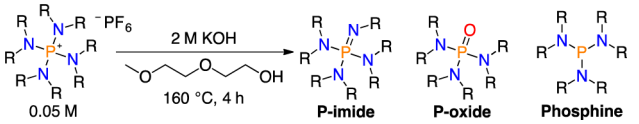


Compound	1	2	3	4	5	6	7	8
Temperature	120 °C	160 °C	160 °C	160 °C	160 °C	160 °C	160 °C	160 °C
Major Degradation Pathway (●)	Direct Attack	Direct Attack	β-H Elimination	Direct Attack	β-H Elimination	β-H Elimination	Direct Attack	β-H Elimination
Minor Degradation Pathway (●)	N/A	N/A	Direct Attack	β-H Elimination	Direct Attack	α-H Abstraction	α-H Abstraction	N/A

Figure 3. Summary of the decomposition pathways observed for the $[P(NR_2)_4]^+$ cations in 2 M KOH/2-(2-methoxyethoxy)ethanol.

Scheme 1. Possible Decomposition Products of Tetrakis(dialkylamino)phosphoniums in Alkaline Media



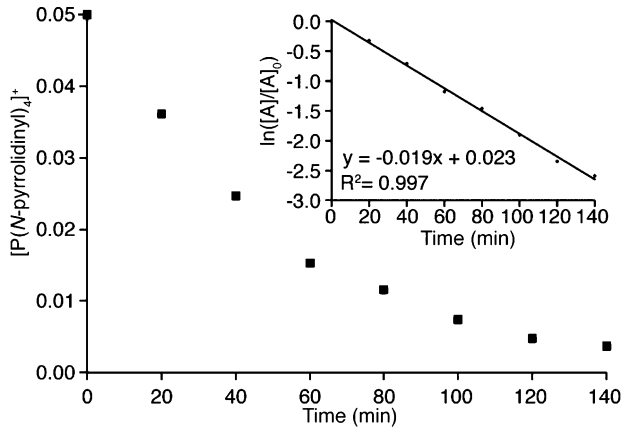


Figure 4. Plot of phosphonium decay (compound **1**) versus time in 2 M KOH/2-(2-methoxyethoxy)ethanol at 120 °C. Inset: pseudo-first-order kinetic analysis.

an increase in steric shielding around phosphorus. At 140 °C, some loss of **2** was detected, but 160 °C was used to ensure complete decomposition, also by direct attack (Figure S25 in the Supporting Information).

Straight-Chain Substituents. The diethylamino and dibutylamino derivatives **3** and **4** had both been synthesized previously.[13,17,18] Decomposition of these compounds was nearly complete after 4 h at 160 °C. Combination of **3** with KOH in methyl carbitol (Figure S26 in the Supporting Information) produced the **P-imide** as the major decomposition product (loss of an ethyl group). Some concurrent **P-oxide** formation was also observed with an ~3:1 ratio of the phosphazene to the phosphine oxide (Table 1). Loss of the ethyl group from the structure was confirmed by analysis of the reaction mixture using mass spectrometry (ESI). Interestingly, the formation of these two products, as well as their ratios, are consistent with the observations of Marchenko and co-workers. They explored decomposition of **3** by reaction of the bromide salt with anhydrous metal hydroxide under vacuum at high temperature.[13] Extension of the alkyl chains to butyl groups afforded nearly exclusive formation of **P-oxide** (Table 1), also

Table 1. Ratios of the Different Phosphorus Species after 4 h in 2 M KOH/2-(2-Methoxyethoxy)ethanol

Cpd	Cation Remaining	P-imide	P-oxide	Phosphine	U[a]	T (°C)	$t_{1/2}$ (h)
1	0	0	>99	0	0	120	0.6
2	0	0	>99	0	0	160	0.2[b]
3	12	66	21	0	1	160	1.3
4	5	14	80	1	0	160	0.9
5	37	57	5	0	1	160	2.8
6	57	34	0	6	3	160	4.8
7	76	1	16	5	2	160	10.5
8	52	48	0	0	0	160	4.3

[a]Percentage of unidentified signals in the $^{31}P\{^1H\}$ NMR spectrum. [b]Half-life for compound **2** was estimated after 0.5 h.

consistent with Marchenko's observations.[13] Elimination is likely the preferred pathway for compound **3** with the *β*-Me groups. The longer alkyl chains in compound **4** provide shielding to slow *β*-H elimination but cannot prevent direct attack at phosphorus.

Branched Substituents. Branched groups offer a greater degree of steric shielding around the central atom in these cationic structures. The combination of compound **5** with KOH in methyl carbitol at 160 °C produced the **P-imide** as the major decomposition product by loss of an isopropyl group, supporting the *β*-H elimination hypothesis (confirmed by ESI). Only a minor amount of **P-oxide** is formed in the decomposition of compound **5** (Table 1). A plot of the reaction progress for **5** revealed that pseudo-first-order behavior is still observed when the elimination pathway is operational (Figure 5).

Extension of the branched alkyl group to a 3-pentyl (**6**) rather than an isopropyl group impeded the rate of elimination but did not completely prevent it (Table 1). *β*-H elimination is minimal for compound **7**, as expected from the work of Schwesinger and co-workers.[14] Compound **8**, with the ethyl substituents, exclusively forms the **P-imide**, as these groups promote the elimination pathway.

A summary of all the collected data is included in Table 1. The relative amounts of phosphorus products were determined by integration of the final NMR spectrum for each reaction mixture. In some of the spectra, minor unassigned signals were

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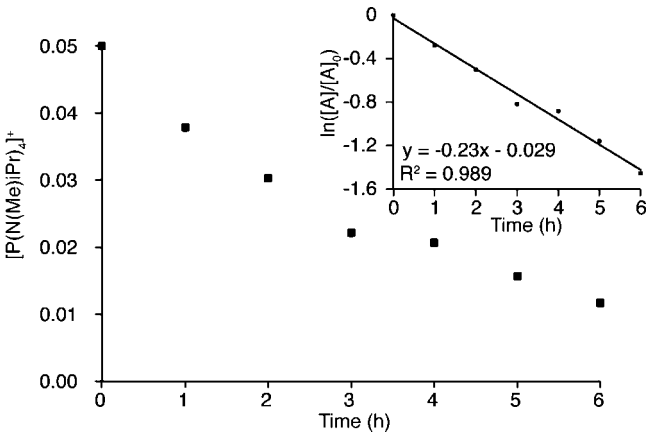


Figure 5. Plot of phosphonium decay (compound **5**) versus time in 2 M KOH/2-(2-methoxyethoxy)ethanol at 160 °C. Inset: pseudo-first-order kinetic analysis.

observed, which were also given a percentage (less than 5% in all cases). The two most common decomposition pathways are direct attack at phosphorus and β-H elimination. The trends are clear: direct attack of the anion at the P atom occurs with cyclic substituents such as pyrrolidine and piperidine. With linear alkyl chains on the amino group, the predominant decomposition pathways are β-H elimination and direct attack at phosphorus. Branched alkyl groups can enhance steric shielding, but β-H elimination tends to dominate as the mode of decomposition with these derivatives unless substituents (e.g, cyclohexyl groups) are employed to block this pathway. Considering pseudo-first-order decay was observed for both **1** and **5**, the half-lives of all cations were estimated from the 4 h time point on the basis of the relative ratios of different phosphorus species in the mixture. This information was used to provide a relative stability comparison for the different derivatives (Table 1).

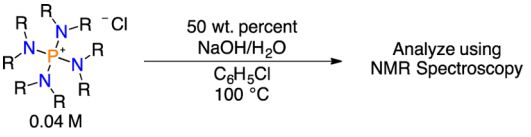
Linear alkyls on the amino group provide some measure of protection in alkaline media, as compounds **3** and **4** do not completely decompose after 4 h under the harsh conditions employed (12% and 5% remaining, respectively). However, branched substituents substantially improve the stability of tetrakis(dialkylamino)phosphonium salts (higher $t_{1/2}$ observed for compounds **5**−**8**). The branching offers increased steric protection, impeding direct attack at phosphorus. Compound **7**, first synthesized by Schwesinger, exhibited the highest degree of alkaline resistance in methyl carbitol due to the cyclohexyl group. The role of this substituent is 2-fold: first, it imparts steric bulk around the central atom and limits attack at P. Second, the preferred conformation of the cyclohexyl group will have the substituent in an equatorial position, impeding β-H elimination.[14] The decomposition of compound **7** was much slower than that for all the other derivatives with a half-life greater than 10 h in 2 M KOH/2-(2-methoxyethoxy)ethanol at 160 °C, a testament to its excellent alkaline resistance.

Phase-Transfer Reactions. In alcoholic solvents, the mixture of OR^- and OH^- is likely affecting decomposition pathways and degradation rates. Researchers have already observed differences in products from $[PR_4]^+$ decomposition depending on reaction conditions, solvents, and anions.[19] To ensure only hydroxide promotes decomposition in solution, water must be used as the reaction medium. While decomposition studies in H_2O can be slow, phase-transfer reactions can be used to obtain strongly alkaline solutions in low-polarity solvents while ensuring only OH^- is present.[20] We explored phase-transfer reactions as a possible means of decomposition for **5**−**7** using a method similar to that of Landini and co-workers.[21] We focused on the branched systems due to their performance in the alcoholic KOH studies.

Phase-transfer catalysis is typically used to accelerate reactions between an organic substrate and a reactive anion. The anion (insoluble in organic solvents) and the substrate (insoluble in aqueous) are combined in a two-phase system. A catalytic amount of a lipophilic transport reagent facilitates extraction of the reactive anion into the organic phase, where the reaction takes place. Interestingly, researchers have noted previously that transport agents such as quaternary ammoniums and phosphoniums display limited stability under strongly alkaline conditions and degrade by Hofman elimination and direct attack, respectively.[22] Landini and co-workers extensively explored the decomposition of these quaternary onium salts using two-phase reaction systems (chlorobenzene and NaOH/H_2O).[21] Consequently, phase transfer should serve as an effective tool to evaluate the stability of lipophilic cations.

Four parameters are extremely important for carrying out these phase-transfer reactions, and each variable affects the decomposition rate. First, the counterion selected for the organic cation has a dramatic effect on the amount of OH^- extracted into the organic phase ($K_{OH/X}^{sel}$).[21] To maximize the concentration of OH^- in the organic phase for decomposition, if a halogen counterion is used, then Cl^- is best.[21] This will result in accelerated tests in comparison to other halides, since extraction of anions in low-polarity solvents follows the sequence $OH^- \ll Cl^- < Br^- < I^-$.[20] Second, higher temperatures will result in faster decomposition with more extraction of OH^- into the chlorobenzene.[21] Third, as the concentration of NaOH is increased in the aqueous phase, hydration of the OH^- in the organic phase is diminished, increasing its reactivity.[22c] Finally, high stirring rates are necessary to ensure rapid extraction of the reactive anion into the organic phase.[21] To compare directly with prior work from Schwesinger, we exposed compounds **5**−**7** with a Cl^- counterion to 50 wt % NaOH/H_2O in chlorobenzene at 100 °C (Scheme 2). Decomposition reactions proceeded rapidly

Scheme 2. Phase-Transfer Conditions Employed for Decomposition



under these conditions.[23] Interestingly, significant changes in the major decomposition pathways were observed in comparison to our data obtained in methyl carbitol (Table 2). For compounds **5** and **7**, only phosphine oxide was formed, indicating direct attack, while, for compound **6**, α-H abstraction is predominant.

In stark contrast to the alcohol study where β-H elimination is dominant, this pathway was not observed in the two-phase system. In methyl carbitol, the bulkier alkoxide is present and thus elimination is favored.[24] Under phase-transfer conditions, the smaller hydroxide is the only anion present, and direct attack dominates. For alkaline fuel cells (AFCs), this information is relevant, since fuel choices (ROH versus H_2) will likely influence which anions are present in the electro-

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Table 2. Ratios of the Different Phosphorus Species in PhCl (0.04 M) with 50% NaOH/H_2O at 100 °C

Cpd	Cation Remaining	P-imide	P-oxide	Phosphine	U[a]	Time (h)
5	6	0	94	0	0	1
6	39	0	13	43	5	2
7	10	0	90	0	0	2

[a]Percentage of unidentified signals in the $^{31}P\{^1H\}$ NMR spectrum.

chemical cell and could promote different decomposition pathways.

Interestingly, we observed rapid degradation of phosphonium salts **5** and 7 in comparison to the prior report.[14] Nearly complete degradation of **5** occurred within 1 h (94%) and 90% degradation of 7 within 2 h (the previously reported $t_{1/2}$ value for 7 was 67 h[14]). A slightly lower concentration of cation (0.04 M versus 0.07 M) was used in our study, along with larger amounts of NaOH in the aqueous layer, but the change in half-life is dramatic. We suspect the large difference can be traced back to different stir rates and the counterion exchange procedures. We used an anion-exchange resin to obtain phosphonium chlorides, while Schwesinger conducted a BF_4^- to Cl^- anion exchange using methanol as a solvent. Landini's report indicated how critical the Cl^- counterion is to maximize extraction of the hydroxide into the organic phase.[21] If anion exchange to the Cl^- were incomplete, this would affect decomposition rates.

We completed phase-transfer studies on [7]PF_6 and compared it to a 50/50 mixture of [7]PF_6 and [7]Cl to illustrate how counterions can alter decomposition rates. The percent cation remaining was determined after 2 h, and the differences are remarkable (Figure 6). No degradation is

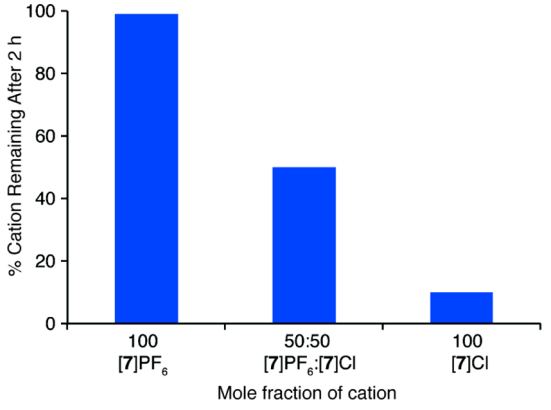

Figure 6. Change in decomposition rate as a function of counterion choice for compound 7 in PhCl (0.04 M) and 50% NaOH/H_2O.

observed at all with only PF_6^- as the counterion, while a 50/50 mixture of the chloride and hexafluorophosphate forms produced 50% loss of 7 in only 2 h. If only [7]Cl is present, 90% loss of the cationic structure is observed. Consequently, counterion exchange is an important consideration when stability is investigated.

Another interesting feature was the lower stability of compound 7 in comparison to **6** under phase-transfer conditions. This is in contrast to the study in methyl carbitol, where 7 is more stable. We suspect in the alcohol that the bulkier alkoxide anions favor elimination, which the cyclohexyl groups prevent. In the phase-transfer reaction with only hydroxide anions present, **6** has improved steric shielding (limiting direct attack) due to the increased conformational flexibility provided by the 3-pentyl group.[25] This enhances the stability of **6** in comparison to 7. Space-filling structures of the computed cations (Figure 7) illustrate the steric constraints

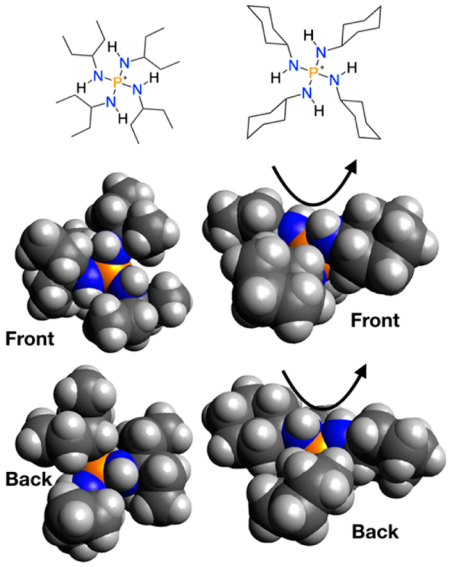

Figure 7. Space-filling structures of the computed (B3PW91/6-31G(d,p)) phosphonium cations with 3-pentyl and cyclohexyl substituents.

imposed by the two branched substituents on P and highlight the limited accessibility of the N–H groups for the 3-pentyl substituent in comparison to the cyclohexyl precursor.

Another indicator of the steric crowding imposed by this substituent is clear in the attempted ethylation of $[P(N(H)3\text{-}Pent)_4]^+$. To date, we have been unable to achieve complete ethylation, whereas $[P(N(Et)Cy)_4]^+$ could be synthesized at higher temperatures. This suggests that substitution reactions with cyclohexyl substituents on the aminophosphonium are more facile. This analysis is also indicative that further optimization around the amino phosphonium core can lead to improvements in stability.

Redox Stability. Finally, phosphonium cations for AFCs must exhibit good electrochemical stability in addition to alkaline stability. To ensure this, we conducted a cyclic voltammetry experiment with [7]PF_6 as the supporting electrolyte (Figure 8). Compound 7 was selected, since it has been used in polyolefin AEMs previously.[10b] Compound 7 functioned as an excellent supporting electrolyte for the ferrocene/ferrocenium redox couple, rivaling the behavior of $[NBu_4]PF_6$. The redox stability of [7]PF_6 provides further support for use of these cations in AEMs.

CONCLUSION

The promise of tetrakis(dialkylamino)phosphoniums for AEMs led us to explore the possible decomposition pathways of these cations in the presence of oxyanions. This family of cations required extremely harsh conditions to bring about decomposition, which is a strong indicator of their stability.

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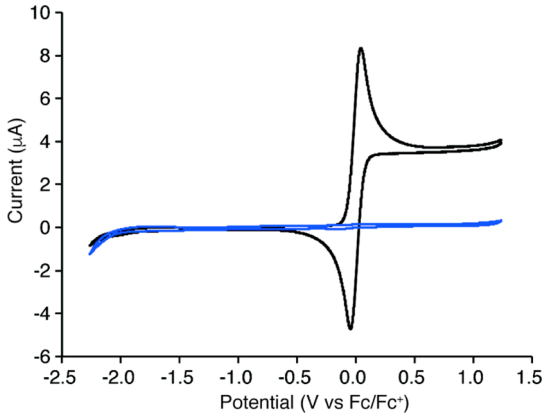

Figure 8. Cyclic voltammogram of 5 mM ferrocene (black trace) recorded at 100 mV/s in degassed MeCN with [7]PF_6 as the supporting electrolyte (0.05 M). The blue trace is a voltammogram with only the supporting electrolyte ([7]PF_6).

Degradation studies were conducted in methyl carbitol with KOH at high temperatures to better understand the modes of decay for these cationic structures. In this alcoholic solvent, the predominant decomposition pathways were direct attack at phosphorus and β-H elimination. The observed decomposition pathways changed when degradation studies were carried out under phase-transfer conditions. This is attributed to the oxyanion driving decomposition (OR^- versus OH^-) in the different reaction media. These studies indicate that both steric bulk and conformational flexibility play a role in ion stability. The different fuels employed in AFCs will affect cation stability, a feature to consider when preparing AEMs.

There is tremendous difficulty comparing degradation rates between individual studies. This study was meant to provide a relative comparison for the tetrakis(dialkylamino)phosphonium salts and determine their decomposition pathways to inform cation design. Model studies using water have been employed in the past for ammoniums, but more lipophilic cations (e.g., phosphoniums and imidazoliums) are often insoluble in water, making comparisons difficult. Phase-transfer studies offer a means to directly compare lipophilic cations while using the base concentration and temperature as parameters to tune the basicity of the reaction mixture. Phase transfer does require the cation to be soluble in chlorobenzene, which may not be suitable for all AEM cation candidates.

Future work will evaluate degradation in more depth for these aminophosphoniums: particularly, the oxidation process and how OR^- or OH^- interacts with the phosphonium to bring about **P-oxide** formation. In the future, other systematic changes to the substituents on the tetraaminophosphoniums will be explored to further optimize these structures. Other phosphonium cations will also be evaluated using the above methods, as the different alkaline conditions and electrochemical measurements are crucial to assess potential AEM compounds.

EXPERIMENTAL SECTION

General Methods. Salts of compounds **1**−**5** and **7** were prepared according to previous literature reports and washed with saturated KPF_6 solutions to furnish the expected products (^1H and $^{31}P\{^1H\}$ NMR spectra are included in the Supporting Information).[14,16,18] Benzyltrimethylammonium bromide ([BTMA]Br) was prepared according to a previous report.[7b] Tetrakis(cyclohexylamino)-phosphonium hexafluorophosphate(V) ([$P(N(H)Cy)_4$]PF_6) was synthesized according to a previous report.[14]

NMR Analysis. All NMR spectra were recorded on either a 300 or 500 MHz Bruker Avance spectrometer. The ^1H NMR spectra were referenced to residual protio solvents ($CHCl_3$, 7.26 ppm; $CHDCl_2$, 5.32 ppm; CHD_2OH, 3.31 ppm; DMSO-d_5, 2.50 ppm; acetone-d_5, 2.05 ppm), and $^{13}C\{^1H\}$ NMR were referenced to the solvent signal ($CDCl_3$, 77.23 ppm; CD_2Cl_2, 54.00 ppm; DMSO-d_6, 39.51 ppm; acetone-d_6, 29.92 ppm). The $^{31}P\{^1H\}$ NMR spectra were electronically referenced using internal Bruker software according to a universal scale determined from the precise ratio, Ξ, of the resonance frequency of the ^{31}P nuclide to the ^1H resonance of TMS in a dilute solution (φ < 1%).[26] Quantitative $^{31}P\{^1H\}$ NMR spectra were recorded using inverse-gated decoupling for the decomposition studies (compounds **5** and **7** required 256 and 2000 scans, respectively, due to limited solubility, and spectra were recorded at 65 °C). A relaxation delay of 20 s was employed to ensure accurate integrations for the final time points. The percent cation remaining was determined by integration of all phosphorus signals present in the mixture and calculating a ratio (the PF_6^- signal was excluded from the analysis).

Mass Spectrometry (MS). High-resolution MS was performed in the School of Chemical Sciences Mass Spectrometry Laboratory at the University of Illinois, Urbana−Champaign, IL. Low-resolution ESI-MS to determine decomposition products was performed on an LCQ Classic (ThermoFisher Scientific Corp., San Jose, CA) APCI quadrupole ion trap mass spectrometer operating with the XCalibur software (Version 1.3). Data were recorded continuously with a scanned mass range of 150−1000 m/z using a spray voltage of 3.0 kV, a capillary temperature of 200 °C, and nitrogen as the carrier gas.

GC-MS Analysis. GC-MS analysis was performed on a Hewlett-Packard Agilent 6890-5973 GC-MS workstation. The GC column was a Hewlett-Packard fused silica capillary column cross-linked with 5% phenylmethylsiloxane. Helium was used as the carrier gas. The following conditions were used for all GC-MS analyses: injector temperature, 250 °C; initial temperature, 70 °C; temperature ramp, 10 °C/min; final temperature, 280 °C.

Synthesis of Tetrakis(pentan-3-ylamino)phosphonium Hexafluorophosphate(V) ([P(N(H)3-Pent)$_4$]PF_6). A 250 mL Schlenk flask was evacuated and back-filled with N_2 three times. The flask was charged with 150 mL of dry dichloromethane, 3-aminopentane (5.0 mL, 43 mmol), and triethylamine (6.0 mL, 43 mmol). The reaction vessel was then cooled to 0 °C using an ice bath. The rubber septum was removed from the top of the flask, and under a stream of N_2, solid PCl_5 (2.13 g, 10.2 mmol) was added slowly to the reaction mixture over a period of 5 min. After complete addition of the PCl_5, the ice bath was removed, the reaction mixture was warmed to room temperature, and the mixture was stirred for 17 h. An aliquot was removed and analyzed using $^{31}P\{^1H\}$ NMR spectroscopy to ensure complete conversion to the desired product (δ ~23 ppm). The reaction mixture was transferred to a separatory funnel, and the organic solution was washed twice with a saturated KPF_6 solution (2 × 100 mL) and once with water (50 mL). The organic layer was subsequently dried over anhydrous sodium sulfate and concentrated using rotary evaporation. The crude solid was dissolved in a minimal amount of dichloromethane and precipitated into 200 mL of diethyl ether. The white solid was collected using vacuum filtration and recrystallized from hot water/ethanol (2.42 g, 45% yield). ^1H NMR (500 MHz, CD_2Cl_2): δ 3.13−3.01 (m, 4H), 2.83 (t, J = 11.0 Hz, 4H), 1.60 (dtd, J = 14.5, 7.4, 6.0 Hz, 16H), 0.94 (t, J = 7.4 Hz, 24H). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2): δ 22.2 (s), − 143.4 (sep, $^1J_{PF}$ = 711.8 Hz). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 55.8 (d, $^2J_{PC}$ = 1.4 Hz), 28.4 (d, $^3J_{PC}$ = 4.8 Hz), 9.9. HRMS (EI) (m/z): calculated $[M]^+$ for $C_{20}H_{48}N_4P$, 375.3617; found, 375.3609.

Synthesis of Tetrakis(methyl(pentan-3-yl)amino)-phosphonium Hexafluorophosphate(V) (Compound 6). [P(N-(H)3-Pent)$_4$]PF_6 (0.197 g, 0.38 mmol), chlorobenzene (0.64 mL), 0.64 g of 50% (w/w) KOH_{aq}, and methyl iodide (0.25 mL, 4 mmol) were placed in a 25 mL flask. The flask was placed in an oil bath set at 60 °C, and the reaction mixture was stirred for 17 h. An aliquot from the organic layer was removed and analyzed by $^{31}P\{^1H\}$ NMR

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spectroscopy to ensure complete conversion to the desired product (δ ~47 ppm). The mixture was transferred to a separatory funnel and diluted with 15 mL of water and 20 mL of dichloromethane. The layers were separated, and the aqueous layer was extracted twice more with dichloromethane (2 × 20 mL). The organic extracts were combined and washed once with saturated KPF_6 solution (15 mL) and once with water (15 mL). The combined organic extracts were dried over anhydrous sodium sulfate and then concentrated using rotary evaporation. The residue was precipitated into 150 mL of diethyl ether, and the solids were collected using vacuum filtration. The product was isolated as a white powder (0.147 g, 67% yield). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 3.03 (qt, J = 8.3, 5.2 Hz, 4H), 2.65 (d, J = 10.0 Hz, 12H), 1.83 (dp, J = 15.1, 7.5 Hz, 8H), 1.64−1.50 (m, 8H), 1.01 (t, J = 7.5 Hz, 24H). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ 46.6, − 143.6 (sep, $^1J_{PF}$ = 709.5 Hz). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 59.5 (d, $^2J_{PC}$ = 4.2 Hz), 30.6 (d, $^3J_{PC}$ = 3.8 Hz), 26.4 (br s), 11.9. HRMS (EI) (m/z): calculated $[M]^+$ for $C_{24}H_{56}N_4P$, 431.4243; found, 431.4240.

Synthesis of Tetrakis(cyclohexyl(ethyl)amino)phosphonium Hexafluorophosphate(V) (Compound 8). $[P(N(H)Cy)_4]PF_6$ (0.198 g, 0.35 mmol), chlorobenzene (1.1 mL), 1.12 g of 50% (w/w) KOH_{aq}, and ethyl iodide (1.60 mL, 20 mmol) were placed in a 25 mL round-bottomed flask equipped with a reflux condenser. The flask was placed in an oil bath at 115 °C, and the reaction mixture was stirred for 48 h. An aliquot from the organic layer was removed and analyzed by ^{31}P{^{1}H} NMR spectroscopy to ensure complete conversion to the desired product (δ ~56 ppm). The reaction mixture was transferred to a separatory funnel and diluted with 15 mL of water and 20 mL of dichloromethane. The layers were separated, and the aqueous layer was extracted twice more with dichloromethane (2 × 20 mL). The organic extracts were combined and washed once with saturated KPF_6 solution (15 mL) and once with water (15 mL). The combined organic extracts were dried over anhydrous sodium sulfate and then concentrated using rotary evaporation. The residue was precipitated into 150 mL of diethyl ether, and the solids were collected using vacuum filtration. The product was isolated as a white powder and recrystallized from hot water/acetone (0.211 g, 89% yield). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 3.30 (qq, J = 11.7, 4.0 Hz, 4H), 3.13 (p, J = 7.3 Hz, 8H), 1.91 (dt, J = 13.4, 3.3 Hz, 8H), 1.85−1.67 (m, 20H), 1.39 (t, J = 7.1 Hz, 12H), 1.30 (qt, J = 12.8, 3.7 Hz, 8H), 1.17 (qt, J = 13.2, 3.5 Hz, 4H). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ 56.5, − 143.6 (sep, $^1J_{PF}$ = 709.8 Hz). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 56.5 (d, $^2J_{PC}$ = 4.3 Hz), 41.1 (d, $^2J_{PC}$ = 4.6 Hz), 33.2, 27.1, 25.8, 17.4 (d, $^3J_{PC}$ = 6.0 Hz). HRMS (EI) (m/z): calculated $[M]^+$ for $C_{32}H_{64}N_4P$, 535.4869; found, 535.4870.

Stability Investigation in CD_3OH. This study was conducted according to a published report.[7b] Stock solutions of basic methanol were prepared by dissolving KOH (1 or 2 M) and 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt standard (0.025 M) in CD_3OH. Compound **1** (0.05 M in 1 M KOH or 0.03 M in 2 M KOH) was dissolved in 1 mL of the methanol stock solution and transferred to an NMR tube. The NMR tube was flame-sealed and analyzed by ^{1}H NMR spectroscopy for the t = 0 h point. Integration of a selected signal relative to a signal for the standard provided the initial concentration of phosphonium salt. The tube was heated in an 80 °C oil bath, and every 5 days, the tube was removed, cooled to 22 °C, and analyzed by ^{1}H NMR spectroscopy to determine the percent cation remaining. A very small signal was observed at 8.6 ppm in some of the ^{1}H NMR spectra, which we believe corresponds to a formate (confirmed using a spiking experiment). This forms due to some carbon monoxide from flame-sealing the NMR tubes. For a representative example calculation and photographs of the experimental setup, see the Supporting Information.

General Procedure for Degradation Experiments in 2 M KOH/2-(2-Methoxyethoxy)ethanol. A 20 mL scintillation vial with a septum-sealed cap was charged with a phosphonium salt (0.1 g) and KOH. The contents were evacuated and back-filled with Ar or N_2 seven times. Degassed 2-(2-methoxyethoxy)ethanol was syringed into the vial (phosphonium concentration 0.05 M, KOH concentration 2 M), and the reaction mixture was placed into an aluminum block at a predetermined temperature (either 120 or 160 °C). An aliquot was removed for an initial time point after the solution became homogeneous (within a few minutes). The reaction mixture was stirred at the above temperature for 4 h, and aliquots were removed at 2 and 4 h for analysis using ^{31}P{^{1}H} NMR spectroscopy. We have noted some variation in the PF_6^- counterion signal, which we suspect is due to solubility in the solvent when the mixture is cooled for NMR analysis. We ensured that the mixtures are homogeneous at the desired decomposition temperature. For photographs of the experimental setup, see the Supporting Information.

After 4 h, characterization was completed as follows: a 0.5 mL aliquot was removed for NMR analysis, and percent cation remaining was determined by integration of all phosphorus signals present in the mixture and calculation of a ratio (excluding the PF_6^- signal). A 0.5 mL aliquot was also removed, neutralized with 10% HCl (v/v), extracted with ethyl acetate (15 mL), and analyzed using GC-MS. Finally, mixtures which contained **P-imide** were analyzed using ESI-MS. Samples were prepared by removing a 0.5 mL aliquot and neutralizing with 10% HCl (v/v). The mixture was extracted with dichloromethane (3 × 5 mL), and the organic layer was concentrated via rotary evaporation. The residue was diluted with 200 mL of acetonitrile and analyzed.

Example Procedure for Degradation of Compound 1. A 20 mL scintillation vial with a septum-sealed cap was charged with **1** (100 mg, 0.22 mmol) and KOH (490 mg, 8.7 mmol). The vial was evacuated and back-filled with Ar or N_2 seven times, and then degassed 2-(2-methoxyethoxy)ethanol (4.4 mL) was added via syringe. The vial was placed in an aluminum block set to 120 °C. Aliquots were removed after 2 and 4 h for analysis by ^{31}P{^{1}H} NMR spectroscopy. After 4 h, an aliquot was removed and analyzed using GC-MS.

Pseudo-first-order kinetic analysis for compound **1** and **5** were conducted in an identical manner, except a series of ^{31}P{^{1}H} NMR spectra were collected at periodic intervals and analyzed.

General Procedure for Degradation Using a Two-Phase Reaction Mixture. The $[P(NR_2)_4]PF_6$ salts were converted to the $[P(NR_2)_4]Cl$ salts by dissolution in MeOH and stirring in the presence of Amberlite IRA-400 Cl^- Exchange Resin (8 g of resin per 1 g of phosphonium salt). The mixture was gently stirred for 17 h, and the resin beads were removed by filtration. ^{31}P{^{1}H} NMR spectroscopy was used to ensure loss of the PF_6^- counterion. MeOH was removed by rotary evaporation, and the slightly brown residue was dissolved in 20 mL of dichloromethane and washed with saturated NaCl solution (2 × 10 mL) and water (1 × 5 mL). The organic layer was concentrated by rotary evaporation, and the salt was further dried in vacuo at 70 °C. The compounds were obtained as white solids.

The two-phase method employed was similar to prior reports (an example procedure is included below).[14,21] A phosphonium chloride salt (0.1 g) was placed in a 20 mL scintillation vial and dissolved in chlorobenzene (0.04 M). A 50% w/w solution of NaOH in deionized water was prepared and placed in the vial. The weights of NaOH and H_2O (in grams) were matched to the number of milliliters of chlorobenzene. This ensured a minimum of 300-fold excess of OH^- in the water layer to the phosphonium cation in the organic layer. The vial was capped (septum-seal), and 50 μL was removed from the chlorobenzene layer via syringe. This aliquot was diluted with 0.6 mL of DMSO-d_6 for an initial NMR analysis. The vial was placed in an aluminum block set to 100 °C, with a stirring rate of 800 rpm. After the specified times, the reaction mixture was cooled and a 50 μL aliquot was removed, diluted with 0.6 mL DMSO-d_6, and analyzed using NMR spectroscopy. ^{1}H NMR spectroscopy was conducted using a 30° tip angle, 64 scans, and 1 s delay. ^{31}P{^{1}H} NMR spectroscopy was conducted using a 30° tip angle, 1000 scans, and 2 s delay. The percent cation remaining was determined by integration of all phosphorus signals present in the mixture and calculation of a ratio. For photographs of the experimental setup, see the Supporting Information.

Example Procedure for Degradation of Compound 5. A 20 mL scintillation vial was charged with [**5**]Cl (100 mg, 0.28 mmol) and chlorobenzene (7.0 mL). A 50% w/w NaOH/H_2O solution was prepared by dissolving 3.5 g of NaOH in 3.5 g of deionized water, and this alkaline solution was placed in the vial (equal grams of 50%

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NaOH solution to milliliters of chlorobenzene). The vial was capped, and a 50 μL aliquot was removed from the organic layer and then diluted with 0.60 mL of DMSO-d_6 for an initial NMR analysis. The vial was placed in an aluminum block set to 100 °C, with a stirring rate of 800 rpm. The reaction mixture was stirred for 1 h, and the vial was removed from the aluminum block and cooled (5 min) before removing a 50 μL aliquot from the organic layer, diluting with DMSO-d_6, and analyzing using NMR spectroscopy.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00663.

NMR and mass spectra, kinetic data, and sample calculations (PDF)

All computed molecule Cartesian coordinates (XYZ)

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Notes

The authors declare no competing financial interest.

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