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Examining the Alkaline Stability of Tris(dialkylamino)sulfoniums and Sulfoxoniums

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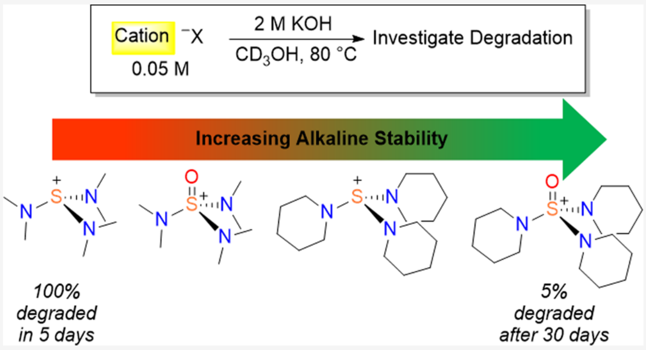
ABSTRACT: Herein, a synthetic method was developed to prepare a series of tris(dialkylamino)sulfonium and sulfoxonium cations from sulfur monochloride. Alkaline stability studies of these two cation families in 2 M KOH/CD_3OD solution at 80 °C revealed how degradation pathways change as a function of the oxidation state of the S center, as determined by ^1H NMR spectroscopy. The sulfonium cations ($^{+}S(NR_2)_3$) typically degrade by nucleophilic attack at the sulfur atom with loss of an amino group and a proton transfer reaction to produce sulfoxides, while the sulfoxoniums ($^{+}O{=}S(NR_2)_3$) tend to degrade by loss of an R group to form sulfoximines. From the group of sulfoniums and sulfoxoniums explored in this work, the tris(piperidino)sulfoxonium cation was noted to have excellent alkaline stability. This sulfoxonium should be suitable for future examination as a tethered cation in anion-exchange membranes (AEMs), or as a phase-transfer catalyst in biphasic reactions.



■ INTRODUCTION

Polymer electrolytes with covalently attached cationic groups have attracted interest for transport of hydroxide ions in alkaline fuel cells and electrolyzers.[1−12] These polymer electrolytes (known as anion-exchange membranes or AEMs) commonly have pendant ammonium cations to promote hydroxide transport, but concerns about the alkaline stability of ammoniums has led to exploration of alternatives.[1−12] The stability of any cation to hydroxide must be considered prior to use in AEMs, and a number of studies have offered insight into the alkaline stability of imidazoliums,[13−16] guanidiniums,[17−19] alkyl and aryl phosphoniums,[20−30] tetraaminophosphoniums,[31−33] cobaltoceniums,[34−36] and cationic ruthenium complexes.[37] To our knowledge, no extensive alkaline stability studies on sulfur-based cations have been conducted, and only two examples of sulfur-based cations in AEMs have appeared in the literature.[38,39]

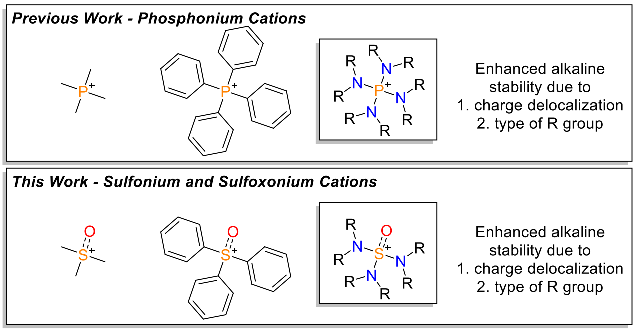


Figure 1. (Top) Phosphorus-based cations examined in AEMs. (Bottom) Sulfur-based cations explored in alkaline stability studies as part of this work for potential future use in AEMs.

Herein, we illustrate that the design principles for enhancing the stability of phosphonium cations to alkaline media are also applicable to sulfur-based cations, where a change from alkyl or phenyl substituents to more electron donating amino groups offers improved resistance to ^{-}OR and ^{-}OH (Figure 1).[32,33] The exceptional resistance of $^{+}P(NR_2)_4$ cations to alkali hydroxides is a function of charge delocalization between the central atom and attached amino groups, as well as the tunability of the substituents on the nitrogen atom.[32,33] Sulfur-based cations can be designed in nearly the same fashion, by attaching three dialkylamino groups to form the tris(dialkylamino)sulfonium cation or oxidizing further to make a tris(dialkylamino)sulfoxonium cation (Figure 1). Some precedent for the alkaline stability of tris(dialkylamino)-

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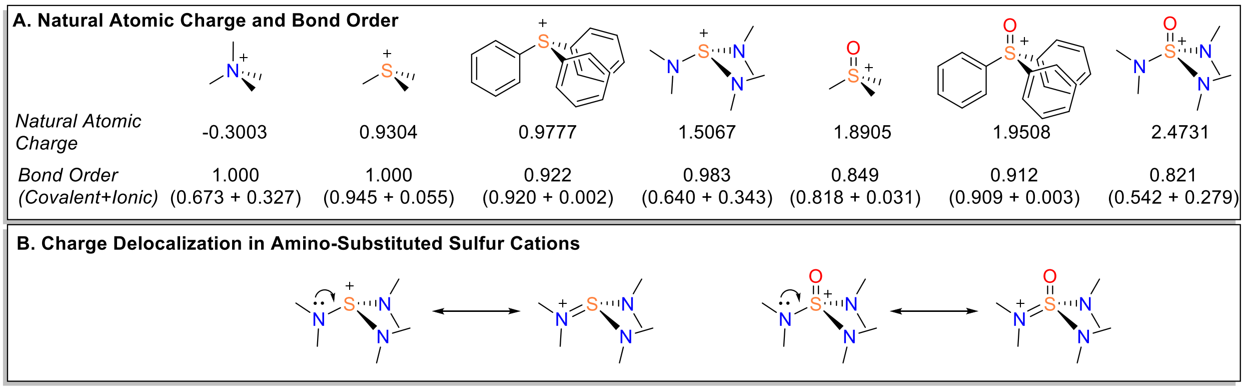
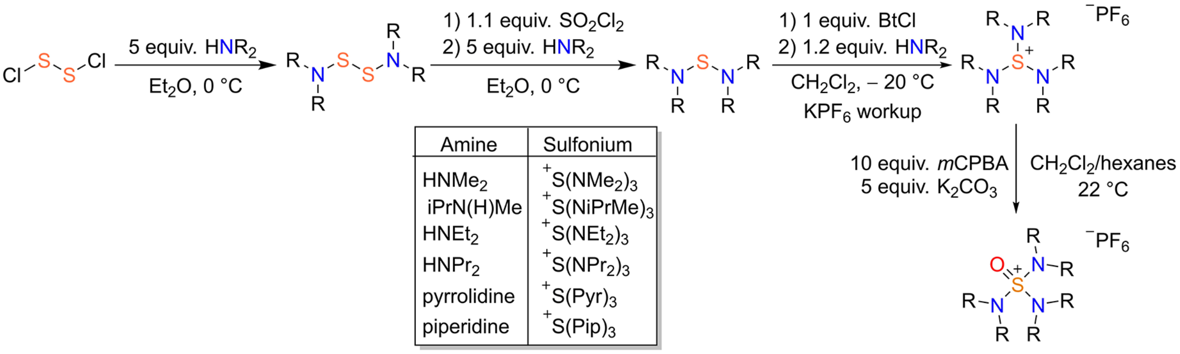


Figure 2. (A) Natural charge on the central element (either N or S) and bond orders for central element bonds (either N−C, S−C, or S−N) computed from NBO analysis. (B) Charge stabilization of sulfur-based cations through resonance with attached amino groups.

Scheme 1. Synthesis of Tris(dialkylamino)sulfoniums and Tris(dialkylamino)sulfoxoniums



Amine	Sulfonium
$HNMe_2$	$^+S(NMe_2)_3$
iPrN(H)Me	$^+S(NiPrMe)_3$
$HNEt_2$	$^+S(NEt_2)_3$
$HNPr_2$	$^+S(NPr_2)_3$
pyrrolidine	$^+S(Pyr)_3$
piperidine	$^+S(Pip)_3$

sulfoxonium cations exists, as Kobayashi and co-workers have shown that the $^+O{=}S(N\text{-morpholino})_3$ cation is particularly resistant to bases, as significant degradation with NaDMSO was noted only at 150 °C.[40]

Alkaline stability is a key factor in the selection of cations for hydroxide transport, but many alternatives to ammoniums (e.g., imidazoliums, phosphoniums, cobaltoceniums) are larger and heavier than the nitrogen derivatives.[1−12] This size difference can lead to larger occupied volumes in AEMs, limiting ion-exchange capacity (IEC) and, in some instances, increasing water uptake in the material.[1−12] Our group has focused on tetraaminophosphonium-based AEMs due to their exceptional alkaline stability,[41,42] and we envisioned that tris(dialkylamino)sulfonium/sulfoxonium cations should have improved alkaline stability relative to alkyl or aryl-substituted sulfoniums. Given the limited exploration of sulfur-based cations as AEMs,[38,39] we synthesized a series of $^+S(NR_2)_3$ and $^+O{=}S(NR_2)_3$ cations to examine their stability in alkaline media. Model studies revealed that the oxo moiety is key to enhancing the stability of these molecules, as nearly all the sulfoxonium derivatives were more stable than the corresponding sulfoniums. Moreover, the appropriate choice of dialkylamino substituents produced cations which rival the stability of ammonium and phosphonium cations currently used in AEMs.[43,44] The tris(piperidino)sulfoxonium cation was identified as a stable phase-transfer catalyst under highly alkaline conditions, and was also noted to be redox stable under neutral conditions from −2 to 2 V (versus standard hydrogen electrode or SHE). Altogether, the data suggest that amino-substituted sulfur cations have potential for future use in AEM materials.

■ RESULTS AND DISCUSSION

DFT Calculations. Prior to carrying out synthetic work, structure optimizations of sulfonium and sulfoxonium cations were carried out at the ωB97XD/6-31g(d,p) level. Natural bond orbital analysis[45−48] provided insight into the electronic differences between the different classes of sulfur cations. Specifically, the trimethyl-, triphenyl-, and tris(dimethylamino)sulfonium cations were computed, along with their corresponding sulfoxonium derivatives. The natural atomic charge (NAC) on sulfur markedly increased when substituted with dialkylamino groups, demonstrating the difference in charge distribution when compared to the alkyl and aryl derivatives (Figure 2A). These values are quite different when compared against the benchmark tetramethylammonium cation, where the NAC on the central nitrogen atom is negative.

Bond order analysis for the different sulfur cations also revealed differences between the alkyl, aryl, and amino sulfur cations. Specifically, the S−C bonds in trimethyl and triphenyl sulfur cations are largely covalent, while the S−N bonds for the amino cations have much more ionic character (>30% ionic) as shown in Figure 2A. This suggests that the amino sulfoniums and sulfoxoniums are better suited to accommodate positive charge. This mirrors the high ionic character noted in the N−C bonds of the tetramethylammonium cation (Figure 2A). In addition to the ionic character for the S−N bonds, natural resonance theory (NRT) analysis confirmed that charge delocalization in tris(dialkylamino)sulfonium and tris(dialkylamino)sulfoxonium occurs via lone pair donation from N and O to adjacent antibonding S—N and S═O orbitals (Figure 2B).

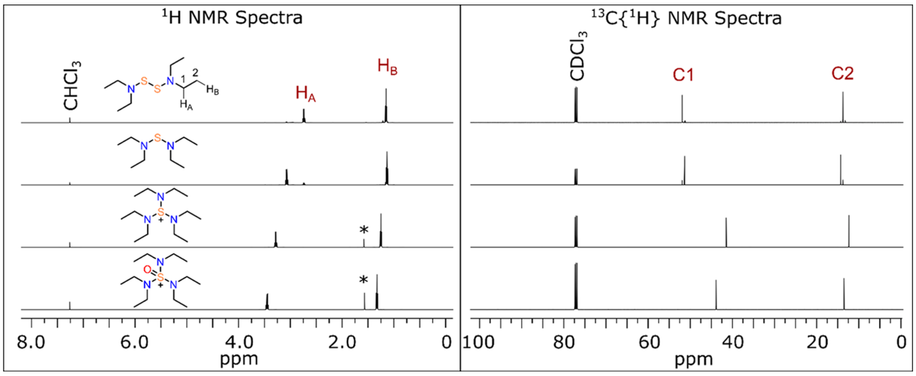


Figure 3. ^{1}H NMR spectra (left) and ^{13}C{^{1}H} NMR spectra (right) of diethylamino derivatives collected in $CDCl_3$ (500 and 126 MHz, respectively). The diaminosulfide is contaminated with ~10% of the disulfide. The asterisk signals (*) correspond to H_2O.

Synthesis of Sulfoxonium Cations. Given the expected improvements in alkaline stability for tris(dialkylamino)-sulfoxonium cations, we set out to synthesize a series of derivatives. Kobayashi and co-workers previously synthesized tris(dialkylamino)sulfonium cations via oxidation of bisaminosulfides using *N*-chlorobenzotriazole or *N*-chlorosuccinimide, followed by substitution with a secondary amine.[49] These 3-coordinate sulfur cations were then oxidized to the corresponding sulfoxonium using sodium perbenzoate in water.[40] This approach was expanded upon here, and a modular 4-step synthesis was developed to construct these cations (Scheme 1). No column chromatography was necessary for any of the synthetic steps shown in Scheme 1, and all purification was accomplished via precipitation or recrystallization.

Sodium tetrathionate has been used previously as the sulfur source for the preparation of bis(dialkylamino)sulfides.[50] Though this could be employed for the preparation of a few select bis(dialkylamino)sulfides, the method was best suited for water-soluble amines. Given this, we employed an alternative approach, where sulfur monochloride was combined with excess dialkylamine to generate a disulfide, along with some sulfide and trisulfide byproducts. The ratios of these products were determined by gas chromatography (GC) and ^{1}H NMR. In the crude form, this mixture could then be near quantitatively converted to the desired bis(dialkylamino)-sulfide through reaction with sulfuryl chloride, forming a sulfenyl chloride intermediate that was subsequently treated with excess amine.[51] Disulfide impurities were noted in the spectra for the bis(dialkylamino)sulfides, but further purification was unnecessary, as these impurities are removed in the workup of the following reaction. The bis(dialkylamino)-sulfides were oxidized using *N*-chlorobenzotriazole (BtCl) at −20 °C,[52] followed by combination with another secondary amine to produce the desired sulfonium cations. Aqueous KPF_6 workup was employed to enable manipulation in organic solvents and afford the $[S(NR_2)_3][PF_6]$ salts.

Oxidation to the sulfoxonium was attempted using *m*-chloroperoxybenzoic acid (*m*CPBA) in combination with KOH to oxidize the $[S(NR_2)_3][Cl]$ salts in water. However, only partial conversion to the desired sulfoxonium was observed in most instances. Only the tris(dimethylamino)-sulfoxonium was successfully synthesized using this approach. Since *m*-chloroperoxybenzoate can be used to oxidize electron-poor olefins in CH_2Cl_2,[53] we attempted to oxidize the $[S(NR_2)_3][PF_6]$ salts in organic solvents. Though oxidation in pure CH_2Cl_2 was incomplete, oxidization could be accomplished essentially quantitatively using excess *m*CPBA/K_2CO_3 in a 1:1 mixture of CH_2Cl_2:hexanes. We suspect that the low polarity solvents decrease the solvation of both the cation and *m*-chloroperoxybenzoate, improving reactivity. Using the methods described above, six tris(dialkylamino)-sulfonium and sulfoxonium derivatives were synthesized (Scheme 1), with ^{1}H and ^{13}C{^{1}H} NMR spectra for each compound available in the Supporting Information. The oxidation conditions could also be applied to the oxidation of $[SPh_3][BF_4]$ (Experimental Section).

In the ^{1}H NMR spectra, a progressive downfield shift of the protons nearest to the sulfur center indicates the change in chemical environment from disulfide to sulfoxonium. This is clear in the spectra for the diethylamino derivative, where the triplet signal for the CH_2 group (H_A) shifts downfield from 2.73 to 3.45 ppm upon conversion from the disulfide to the corresponding sulfoxonium (left in Figure 3). The carbon atom of the same methylene group, is shifted upfield in the ^{13}C{^{1}H} NMR spectra upon oxidation (right in Figure 3).

Single crystal X-ray diffraction was attempted to determine the bond order for the S—N and S═O bonds in these salts. Crystals suitable for X-ray diffraction were obtained for $[S(Pip)_3][PF_6]$ by vapor diffusion of diethyl ether into a CH_2Cl_2 solution of the sulfonium (Figure 4). Attempts to crystallize the corresponding sulfoxonium in a similar manner

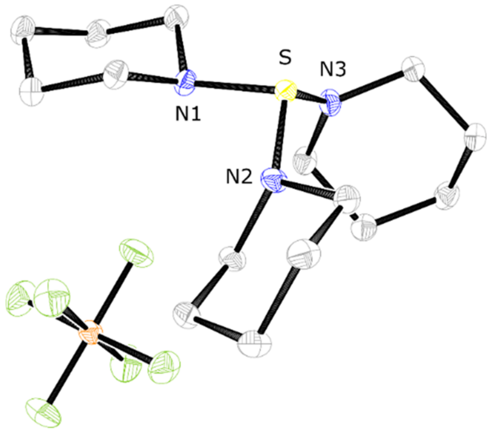


Figure 4. Solid-state molecular structure of $[S(Pip)_3][PF_6]$. Thermal ellipsoids at 50% probability. Selected bond lengths (Å) and bond angles (deg): S−N1 1.6858(9); S−N2 1.6265(10); S−N3 1.6124(10); N2−S−N1 98.03(5); N3−S−N1 99.29(5); N3−S−N2 116.29(5).

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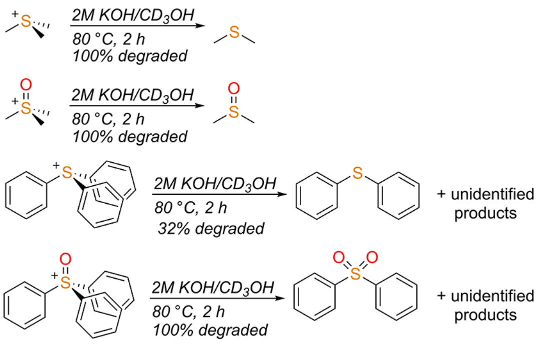
produced thin plates which did not diffract as well. The connectivity of [O═S(Pip)$_3$][PF$_6$] was confirmed from diffraction data, with the counterions on special positions (CIF file included as Supporting Information), but discussion of the bond lengths and angles for this derivative is not possible.

The solid-state molecular structure of [S(Pip)$_3$][PF$_6$] is shown in Figure 4. The S−N bond distances range from 1.6124(10) to 1.6858(9) Å. The mean S−N bond length (1.642 Å) was then used to estimate bond order in this structure (B.O. = 1.36).[54] The B.O. value suggests additional π-bonding character between the S and N atoms, as expected from the resonance forms shown in Figure 2B. While the bond lengths of O═S(Pip)$_3$[PF$_6$] cannot be discussed in extensive detail, a further increase in B.O. seems likely upon oxidation, as the S−N bond lengths are shorter in that derivative.

Degradation Studies in 2 M KOH/CD$_3$OH. Cation stability studies are generally performed in alkaline media where the concentration of base, reaction medium, and temperature all impact degradation rates. Though H$_2$O 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 long experiment times.[55,56] The use of alternative solvents such as methanol can increase anion reactivity resulting in faster degradation rates though it should also be noted that degradation can occur via the methoxide anion in this solvent. Since Coates and co-workers recently developed a standardized protocol to examine cation stability in KOH/CD$_3$OH, this approach was used here.[43,44] Stability studies were carried out in flame-sealed NMR tubes using 2 M KOH/CD$_3$OH at 80 °C as the reaction medium, and ^{1}H NMR analysis every 5 days was used to quantify degradation.[43,44]

To confirm that methyl and phenyl sulfonium and sulfoxonium derivatives are not suitable cations for AEMs, we evaluated the alkaline stability of [SMe$_3$][I], [O═SMe$_3$][I], [SPh$_3$][BF$_4$], and [O═SPh$_3$][PF$_6$] in 2 M KOH/CD$_3$OH at 80 °C (Scheme 2). The four different sulfur salts were all highly soluble in this alkaline medium, ensuring the reaction with base was homogeneous. All derivatives except triphenylsulfonium (32% degraded in 2 h) were completely degraded within 2 h. Trimethylsulfonium and trimethylsulfoxonium are known to react with base,[57,58] and in 2 M KOH/CD$_3$OH these derivatives were converted to the corresponding dimethyl sulfide and dimethyl sulfoxide, respectively (Scheme 2). Triarylsulfonium cations have been previously reported to react with hydroxide and alkoxides through either direct attack at the central sulfur or on one of the carbons attached to sulfur, with formation of diarylsulfides and other aryl byproducts.[59,60] Here, the triphenylsulfonium and sulfoxonium degraded to the diphenyl sulfide and diphenyl sulfone respectively, along with other unidentified aryl products. Formation of these sulfur products was confirmed by mass spectrometry analysis of the reaction mixtures, with observation of diphenyl sulfoxide and diphenyl sulfone in each case (Figure S106 and S107).

Scheme 2. Degradation Products of Alkyl and Aryl Sulfonium and Sulfoxonium Cations



The tris(dialkylamino)sulfoniums and sulfoxoniums have markedly improved alkaline stability when compared to the alkyl and aryl derivatives (Figure 5). None of the tris(dialkylamino)sulfoxoniums examined in this study fully degraded over 30 days at 80 °C in 2 M KOH/CD$_3$OH. Generally, the oxidized sulfoxoniums were more stable than the corresponding sulfoniums except in the case of isopropylmethylamino sulfonium and sulfoxonium. The [S(NMe$_2$)$_3$][PF$_6$] cation is the least stable of all derivatives tested, and completely degraded after ∼5 days. Oxidation to [O═S(NMe$_2$)$_3$][PF$_6$] leads to a markedly more alkaline-stable cation, with ∼18% remaining after 30 days in 2 M KOH/CD$_3$OH at 80 °C (left in Figure 5). Use of *N*-isopropylmethylamine in place of dimethylamine improves stability for both the sulfonium and sulfoxonium derivatives (left in Figure 5) but only 64% and 60% of [S(NiPrMe)$_3$][PF$_6$] and [O═S(NiPrMe)$_3$][PF$_6$] remained after 30 days, respectively. The limited stability of these derivatives with secondary alkyl groups is surprising, given that this type of substitution leads to significant stability enhancements for tetraaminophosphonium cations.[32,33] In our own work, we noted that tetraaminophosphonium stability in 2 M KOH/2-(2-methoxyethoxy)ethanol solution at 160 °C was more than doubled ($t_{1/2}$ = 1.3 to 2.8 h) by moving from diethylamino to *N*-methylisopropylamino substituents.[33]

Both [S(NEt$_2$)$_3$][PF$_6$] and [S(NPr$_2$)$_3$][PF$_6$] behaved similarly in the stability study, with roughly 58% and 56% remaining after 30 days, respectively. In both cases, oxidation leads to a significant stability enhancement, with near 90% of each cation remaining after ∼1 month (middle in Figure 5). The cyclic substituents also had a clear impact on alkaline stability. The [S(Pyr)$_3$][PF$_6$] derived from pyrrolidine was much less stable than the cation derived from piperidine ([S(Pip)$_3$][PF$_6$]). Once again, oxidation improves stability and the [O═S(Pip)$_3$][PF$_6$] proved to be the most stable cation examined in this study, with 95% remaining after 30 days in 2 M KOH/CD$_3$OH at 80 °C (right in Figure 5).

Proposed Degradation Pathways. The possible modes of degradation for the tris(dialkylamino)sulfonium and sulfoxonium cations under basic conditions are noted in Scheme 3. These mirror the modes of attack in the analogous tetraaminophosphonium cations: nucleophilic attack at the central atom and α-carbon, or deprotonation of the α-H and β-H's to form imines or alkenes, respectively.[32,33] In the case of the tris(dialkylamino)sulfonium cations, ^{1}H NMR analysis of the reaction mixture suggested the major product to be only the secondary amine in all instances (e.g., [S(NPr$_2$)$_3$][PF$_6$] had degraded nearly exclusively to HNPr$_2$). This suggested pathway A was operative but surprisingly, no signals corresponding to the sulfoxide were observed in the ^{1}H NMR spectrum. The formation of dipropylamine from [S(NPr$_2$)$_3$][PF$_6$] was confirmed by spiking an aliquot of the reaction mixture, leading to an increase in signal intensity for the degradation product (Figure S88). Further confirmation of amine formation was obtained by analysis of the reaction mixture using direct analysis in real time mass spectrometry

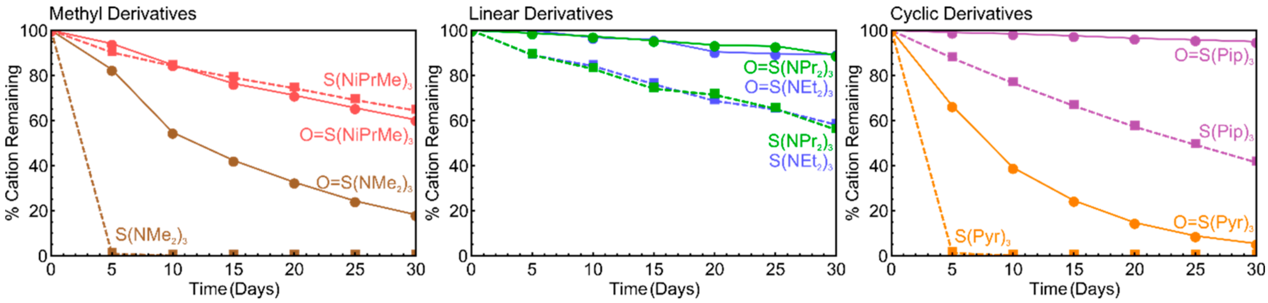
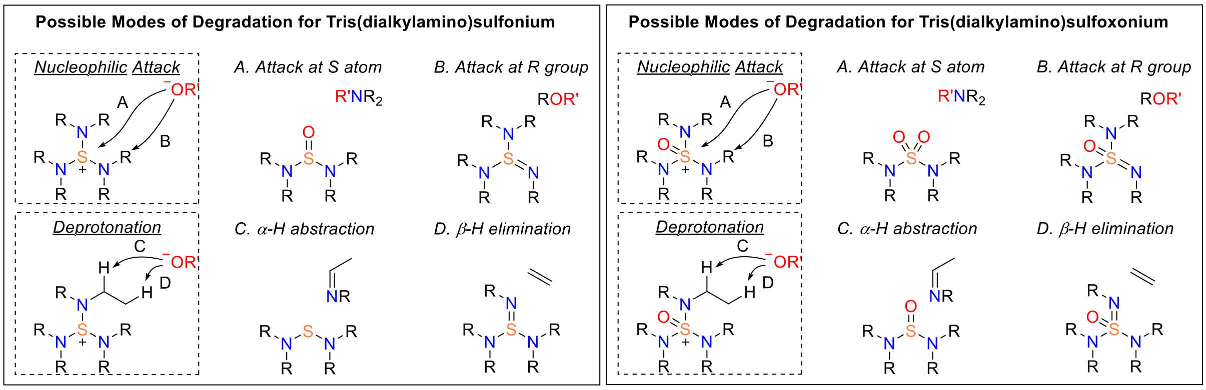


Figure 5. Degradation of sulfonium and sulfoxonium cations in 2 M KOH/CD_3OH at 80 °C over 30 days. Percent cation remaining was determined by integration of the ^1H NMR signals for the cation relative to an internal standard, every 5 days. All sulfonium degradation data are plotted using squares and dashed lines, while sulfoxonium degradation data are plotted with circles and solid lines.

Scheme 3. Degradation Pathways for Tris(dialkylamino)sulfonium and Sulfoxonium Cations



(DART-MS), with an ion signal observed corresponding to $^+H_2NPr_2$ (Figure S100), along with a weak ion signal corresponding to the protonated sulfide ($^+HS(NPr_2)_2$).

As sulfoxides are known to hydrolyze to produce amines,[61] it is reasonable to assume that the major degradation pathway of the sulfonium cation would likely be Pathway A in Scheme 3, where the anion attacks the sulfur atom and loss of an amino group with proton transfer results in the sulfoxide. To provide additional evidence for the hypothesized sulfonium degradation pathway, $[S(NPr_2)_3][PF_6]$ was reacted with 1 equiv of KOH in methanol. Upon filtration and removal of the solvent, roughly 8% of the sulfonium had been converted to $O{=}S(NPr_2)_2$. The identity of the sulfoxide was confirmed by direct synthesis via reaction of thionyl chloride with dipropylamine (Figure 6). Since all tris(dialkylamino)sulfonium cations degrade to the corresponding amine, it is likely that the first step for degradation of all sulfoniums synthesized here is Pathway A (Scheme 3), which is similar to the degradation mechanism for phosphoniums.[21−30]

The possibilities for sulfoxonium degradation (nucleophilic attack or deprotonation) are identical to those possible for the sulfoniums (Scheme 3). Both ^1H NMR and mass spectrometry revealed that sulfoxoniums degrade primarily through loss of an alkyl group to produce a sulfoximine, $RN{=}S(O)(NR_2)_2$. This suggests either attack at the R group or β-H elimination as the possible degradation pathways (B and D in Scheme 3). Attack at the R group seems to be the primary mode of degradation for the two cyclic derivatives, where ring-opened products can be clearly identified using DART-MS (Figure S103 and S105). The $O{=}S(NMe_2)_3$ seems to follow the same mechanism, as a signal appears at 3.29 ppm in the ^1H NMR spectrum which is likely attributed to methoxymethane-d_3 (CD_3OCH_3). The degradation mechanism for the unsymmetrical $^+O{=}S(NiPrMe)_3$ was more difficult to determine. Both $MeN{=}S(O)(NiPrMe)_2$ and $iPrN{=}S(O)(NiPrMe)_2$ were observed as decomposition products in DART-MS.

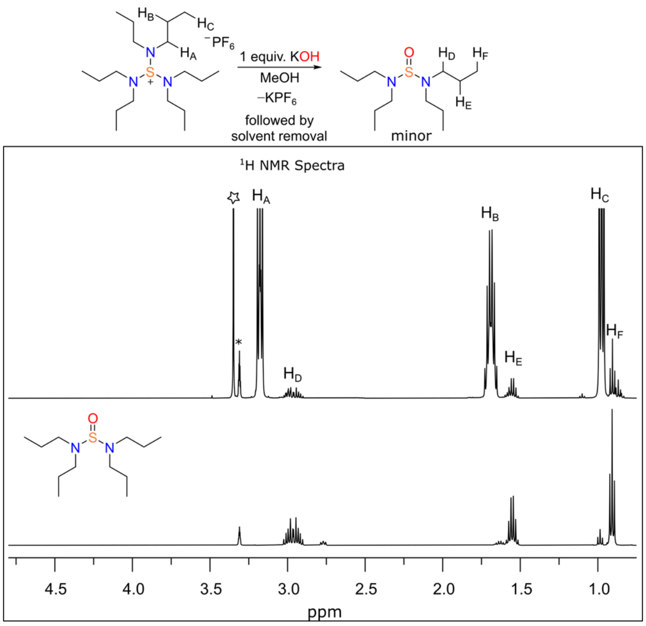


Figure 6. (Top) ^1H NMR spectrum (500 MHz, CD_3OD) of the crude reaction mixture after reaction of $S(NPr_2)_3[PF_6]$ with KOH. (Bottom) ^1H NMR spectrum (500 MHz, CD_3OD) of $O{=}S(NPr_2)_2$ prepared from thionyl chloride and dipropylamine. The asterisk (*) signal corresponds to residual protiosolvent in the CD_3OD. The star signal corresponds to CH_3OH.

Though the loss of the α-Me group is clearly occurring via nucleophilic attack, the loss of the *i*Pr group is more likely via β-H elimination, though no signals attributed to propylene were observed in the ^{1}H NMR spectrum. Since both mechanisms are likely operative, this may contribute to the limited stability of this derivative as compared to the other sulfoxoniums. Both $^+O{=}S(NEt_2)_3$ and $^+O{=}S(NPr_2)_3$ degrade to $EtN{=}S(O)(NEt_2)_2$ and $PrN{=}S(O)(NPr_2)_2$, which was clear from both ^{1}H NMR and DART-MS. We suspect that this occurs via attack at the α-position as seen in the cyclic derivatives, but it is difficult to rule out β-H elimination as a possibility.

Phase-Transfer Reactions. In addition to the 2 M KOH/CD_3OH studies, we wanted to examine the alkaline stability of $^+S(Pip)_3$ and $^+O{=}S(Pip)_3$ in biphasic $C_6H_5Cl/NaOH_{aq}$ solutions as this type of experiment can afford information rapidly.[20] Alkaline stability studies in $C_6H_5Cl/NaOH_{aq}$ have been used previously to determine whether tetraalkylammonium and tetraalkylphosphonium salts are suitable phase transfer catalysts in the presence of ^-OH.[20] In these biphasic reactions, cation degradation rate is dictated by the choice of counterion, reaction temperature, concentration of base, and stir rate.[20,62,63] Conditions used here were very similar to those employed by Landini and co-workers so that direct comparison to tetraalkylammoniums and tetraalkylphosphoniums could be made.[20]

The four onium salts examined in phase-transfer studies were $[O{=}S(Pip)_3][Cl]$, its corresponding sulfonium $[S(Pip)_3][Cl]$, the tetraaminophosphonium analogue $[P(Pip)_4][Cl]$,[64] and tetrabutylammonium chloride ($[N(n\mathrm{Bu})_4][Cl]$) for direct comparison with prior work. Each cation was dissolved in C_6H_5Cl (0.04 M) and combined with 300 equiv of 50 wt.% NaOH in H_2O at 60 °C to examine degradation with excess ^-OH. The rate constant for cation degradation by ^-OH was determined assuming a pseudo first-order process (NaOH in large excess). The percent cation remaining in each instance was determined by periodic sampling of the organic phase (C_6H_5Cl). At 60 °C, the degradation of $[S(Pip)_3][Cl]$ and $[P(Pip)_4][Cl]$ were too rapid to obtain reliable kinetics data, so their stability was examined at room temperature (Table 1, Entries 1−4). These cations had similar half-lives at 22 °C (Table 1, Entries 2 and 4). Kinetic data for both $[O{=}S(Pip)_3][Cl]$ and $[N(n\mathrm{Bu})_4][Cl]$ could be obtained reliably at 60 °C, indicating both cations are more alkaline stable than $[P(Pip)_4][Cl]$ and $[S(Pip)_3][Cl]$ (Table 1, Entries 5 and 6). In 1 h, ∼16% of the $[O{=}S(Pip)_3][Cl]$ had degraded at 60 °C, while $[N(n\mathrm{Bu})_4][Cl]$ was 50% percent degraded in only 0.33 h indicating that $[O{=}S(Pip)_3][Cl]$ was the most stable cation in the series.

Table 1. Half-Lives for Quaternary Onium Degradation in a Chlorobenzene−50% NaOH Phase Transfer Reaction

entry	cation[a]	anion	temperature (°C)	$t_{1/2}$ (h)[b]
1[c]	$^+P(Pip)_4$	^-Cl	60	<0.1
2			22	4.5
3	$^+S(Pip)_3$	^-Cl	60	<0.1
4			22	3.6
5	$^+N(n\mathrm{Bu})_4$	^-Cl	60	0.3
6	$^+O{=}S(Pip)_3$	^-Cl	60	4.3

[a] Cation degradation by ^-OH was examined by combination of the onium salt (0.04 M in C_6H_5Cl) with 50 wt % NaOH (300 equiv). Cation degradation was monitored by sampling the C_6H_5Cl phase periodically and analyzing the reaction mixture using ^{1}H NMR spectroscopy. The loss of cation was determined by comparison of the C_6H_5Cl solvent signal as an internal standard. [b] Half-lives were calculated from the pseudo-first-order rate constants (k') of cation degradation according to the equation $t_{1/2} = 0.693/k'$. [c] In the case of $[P(Pip)_4][Cl]$, ratios of the starting material to the $O{=}P(Pip)_3$ decomposition product were used to determine k'.

Both $[P(Pip)_4][Cl]$ and $[S(Pip)_3][Cl]$ appear to degrade by Pathway A as outlined in Scheme 3 (similar pathway for the phosphonium cation). This highlights the importance of bulky groups to enhance alkaline stability of tetraaminophosphoniums,[32] as it will increase the activation barrier for ^-OH attack at the central element. Tentatively, ^{1}H NMR data suggests $[O{=}S(Pip)_3][Cl]$ degrades to the sulfoximine (Figure S93), similar to the degradation pathway noted in the 2 M KOH/CD_3OH studies (nucleophilic attack at the R group, Scheme 3), but the signals for the degradation product get more complicated over time. The $[O{=}S(Pip)_3][Cl]$ half-life at 60 °C (4.3 h) is particularly striking when benchmarked against quaternary ammonium salts typically used for phase transfer catalysis, as $[NBu_4][Cl]$ only has a $t_{1/2}$ of ∼0.33 h under identical conditions, suggesting $[O{=}S(Pip)_3][Cl]$ may also be valuable for this purpose.

Redox Stability. Finally, cations for AEMs must be electrochemically stable. To test this, we conducted a cyclic voltammetry experiment using $[O{=}S(Pip)_3][PF_6]$ as the supporting electrolyte for the ferrocene/ferrocenium redox couple (Figure 7). The sulfoxonium salt was effective as the supporting electrolyte operating from approximately −2.0 to 2.0 V (referenced versus the standard hydrogen electrode or SHE). Beyond −2.0 V, an irreversible reduction for $[O{=}S(Pip)_3][PF_6]$ was observed. The wide electrochemical window of the $[O{=}S(Pip)_3][PF_6]$ salt provides evidence that this cation is suitable for use in hydrogen fuel cells, as the redox potentials for hydrogen oxidation and oxygen reduction range from −0.83−0.0 V for hydrogen oxidation and from 0.4−1.23 V for oxygen reduction, depending on pH.

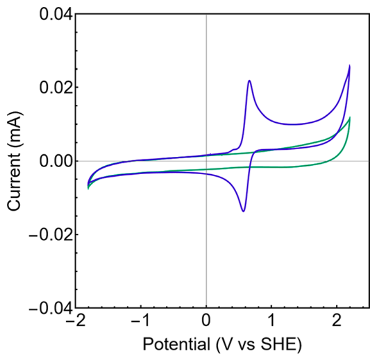


Figure 7. Cyclic voltammogram of ∼1 mM ferrocene (blue trace) recorded at 50 mV/s in degassed MeCN with $O{=}S(Pip)_3[PF_6]$ as the supporting electrolyte (0.05 M). The green trace corresponds to a voltammogram with only the supporting electrolyte. The voltammogram was referenced versus the standard hydrogen electrode (SHE) with Fc/Fc^+ as an internal standard (0.624 V vs SHE).[65]

CONCLUSION

In conclusion, the tris(dialkylamino)sulfoxonium cations have been identified as promising candidates for use in AEMs, when decorated with the appropriate amino groups. These cations can be obtained through a simple 4-step synthesis, and the $^{+}O{=}S(NEt_2)_3$, $^{+}O{=}S(NPr_2)_3$, and $^{+}O{=}S(Pip)_3$ in particular were identified as potential targets for future examination in AEMs. A phase transfer study in 50 wt % $NaOH/C_6H_5Cl$ indicated that tris(piperidino)sulfoxonium salts should also be suitable phase-transfer catalysts. Future work will focus on synthesizing novel polymers with pendant tris(dialkylamino)-sulfoxonium cations to compare with some of our prior work on AEMs derived from tetrakis(dialkylamino)phosphonium cations.[41,42,66]

■ EXPERIMENTAL SECTION

Materials and Methods. Reactions were carried out under N_2 and in anhydrous solvents unless otherwise specified. All solvents, sulfur monochloride, thionyl chloride, sulfuryl chloride, secondary amines, trimethylsulfonium iodide, trimethylsulfoxonium iodide, and triphenylsulfonium tetrafluoroborate were purchased from commercial sources and used as received. *N*-Chlorobenzotriazole was prepared according to a previous report.[67]

NMR Analysis. All NMR spectra were recorded on a 500 MHz Bruker Avance 3 Spectrometer or a 500 MHz Bruker Neo Spectrometer with Prodigy Cryoprobe. The ^{1}H NMR spectra were referenced to residual protio solvents (7.26 ppm for $CHCl_3$, 5.32 ppm for CH_2Cl_2, 3.31 ppm for CH_3OH, and 2.50 ppm for DMSO) and $^{13}C\{^{1}H\}$ NMR were referenced to the solvent signal ($CDCl_3$: 77.16 ppm).

High Resolution Mass Spectrometry (HRMS). ESI-MS and DART-MS were performed on a Thermo Scientific Exactive Plus EMR Orbitrap Mass Spectrometer operating with XCalibur software. ESI-MS samples were prepared as 10 μM solutions in methanol, and data were recorded continuously in positive mode with a scanned mass range of 50−1000 m/z using a spray voltage of 4.2 kV, a capillary temperature of 270 °C, a nitrogen sheath gas flow rate of 20, and a solvent flow rate of 10 μL/min. DART-MS data were recorded in positive mode between 200 and 400 °C with He or N_2 as the carrier gas. In some cases, $[2\ M + H]^+$ and $[M + NH_4]^+$ species were also observed.[68]

Gas Chromatography−Mass Spectrometry. GC-MS analysis was performed on a Hewlett-Packard Agilent 6890−5973 GC-MS workstation. The GC column was a Restek fused silica capillary column (RTX-5) with helium 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 (the experiment with $S_2(NMe_2)_2$ began at 50 °C with a temperature ramp of 10 °C/min and a final temperature of 170 °C). Samples were prepared by dissolving 2−3 mg of disulfide into 20.0 mL of diethyl ether (stabilized with BHT). This solution was then filtered through a 0.22 μm PTFE syringe filter into a 2 mL vial for analysis.

Cyclic Voltammetry. CV studies were carried out using a Bio-Logic SP-150 potentiostat at room temperature (∼22 °C). A 1 mm² glassy carbon working electrode (polished with diamond paste), a platinum coil counter electrode, and a silver wire pseudoreference electrode were employed for the measurements. The voltammogram was referenced versus the standard hydrogen electrode (SHE) with Fc/Fc^+ as an internal standard (0.624 V vs SHE).[65] The $O{=}S(Pip)_3[PF_6]$ supporting electrolyte (purified through vapor diffusion recrystallization in CH_2Cl_2 and diethyl ether) was used at a concentration of 0.05 M in MeCN. The MeCN solutions with the supporting electrolyte and analyte were degassed for 20 min with Ar prior to measurement. The initial potential for these measurements was $E_i = 0$ V, scanning to $E_1 \sim 2$ V and reversing to $E_2 \sim -2.0$ V with a potential sweep rate of 50 mV/s.

X-ray Crystallography. Low-temperature X-ray diffraction data for $S(Pip)_3[PF_6]$ were collected on a Rigaku XtaLAB Synergy diffractometer coupled to a Rigaku Hypix detector with Cu Kα radiation (λ = 1.54184 Å), from a PhotonJet microfocus X-ray source at 100 K. The diffraction images were processed and scaled using the CrysAlisPro software.[69] The structures were solved through intrinsic phasing using SHELXT[70] and refined against $F2$ on all data by full-matrix least-squares with SHELXL[71] following established refinement strategies.[72] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bound to carbon were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U_{eq} value of the atoms they are linked to (1.5 times for methyl groups).

Computational Studies. Density functional theory calculations were performed with Gaussian 16.[73] Geometry optimizations were performed at the ωB97XD/6-31g(d,p) level. Natural Bond Orbital and Natural Resonance Theory calculations were performed using the NBO 7 package.[74]

Sulfoxonium Cation Synthesis. *General Procedure: Diaminodisulfide.* Sulfur monochloride (1.0 equiv) in diethyl ether (0.25 M) was cooled to 0 °C in an ice bath for 30 min. Then, a secondary amine (∼5.0 equiv) was slowly added to the solution over 30 min. The reaction mixture was stirred overnight and warmed to room temperature, after which it was washed with a saturated NaCl solution (3 × 100 mL), dried with anhydrous sodium sulfate and filtered. The solvent was then removed via rotary evaporation to produce the crude diaminodisulfide which was used without further purification. Diaminosulfide and diaminotrisulfide were observed in both GC-MS and ^{1}H NMR analysis of the crude products (Supporting Information), though these did not interfere with subsequent reactions.

$S_2(NMe_2)_2$. The reaction was performed using sulfur monochloride (3.0 mL, 37.5 mmol) and dimethylamine solution (93.8 mL, 188 mmol, 2 M in THF) in diethyl ether (150 mL) to obtain the product as an orange liquid (3.81 g, 67%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.62 (s, 12H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 48.4. EI-MS $[M]^+$ calcd. for $C_4H_{12}N_2S_2$, 152.04, found 152.0.

$S_2(NiPrMe)_2$. The reaction was performed using sulfur monochloride (0.50 mL, 6.3 mmol) and *N*-isopropylmethylamine (3.3 mL, 31.7 mmol) in diethyl ether (25 mL) to obtain the product as an orange liquid (1.01 g, 78%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.10 (hept, J = 6.5 Hz, 2H), 2.75 (s, 6H), 1.15 (d, J = 6.5 Hz, 12H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 58.4, 43.3, 21.3. EI-MS $[M]^+$ calcd. for $C_8H_{20}N_2S_2$, 208.11, found 208.1.

$S_2(NEt_2)_2$. The reaction was performed using sulfur monochloride (0.50 mL, 6.3 mmol) and diethylamine (3.3 mL, 31.9 mmol) in diethyl ether (25 mL) to obtain the product as a red-orange liquid (1.20 g, 92%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.74 (q, J = 7.1 Hz, 8H), 1.15 (t, J = 7.1 Hz, 12H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 52.0, 14.0. EI-MS $[M]^+$ calcd. for $C_8H_{20}N_2S_2$, 208.11, found 208.1.

$S_2(NPr_2)_2$. The reaction was performed using sulfur monochloride (3.0 mL, 37.5 mmol) and dipropylamine (25.6 mL, 187 mmol) in diethyl ether (150 mL) to obtain the product as a yellow liquid (7.23 g, 73%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.64 (t, J = 7.1 Hz, 8H), 1.63−1.54 (m, 8H), 0.89 (t, J = 7.4 Hz, 12H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 59.9, 21.5, 11.5. EI-MS $[M]^+$ calcd. for $C_{12}H_{28}N_2S_2$, 264.17, found 264.2.

S_2Pyr_2. The reaction was performed using sulfur monochloride (0.50 mL, 6.3 mmol) and pyrrolidine (2.6 mL, 31.1 mmol) in diethyl ether (25 mL) to obtain the product as a red-purple liquid (0.91 g, 71%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.92−2.86 (m, 8H), 1.86−1.81 (m, 8H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 55.8, 25.2. EI-MS $[M]^+$ calcd. for $C_8H_{16}N_2S_2$, 204.08, found 204.1.

S_2Pip_2. The reaction was performed using sulfur monochloride (4.0 mL, 50 mmol) and piperidine (24.8 mL, 251 mmol) in diethyl ether (200 mL) to obtain the product as a yellow solid (9.20 g, 79%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.78 (t, J = 5.5 Hz, 8H), 1.64 (p, J = 5.7 Hz, 8H), 1.42−1.36 (m, 4H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 57.7, 27.2, 23.0. EI-MS $[M]^+$ calcd. for $C_{10}H_{20}N_2S_2$, 232.11, found 232.1.

Bis(piperidino)sulfide (SPip₂). Adapted from previous report.[50] In a round-bottom flask, sodium tetrathionate dihydrate (5.01 g, 16.4 mmol) in water (25 mL) was combined with piperidine (6.5 mL, 65.8 mmol) in pentane (25 mL) and stirred vigorously for 17 h at room temperature. The layers were separated, and the aqueous layer extracted with pentane (1 × 25 mL). The organic layers were combined and washed with water (1 × 25 mL) and sat. NaCl solution (2 × 25 mL). The organic layer was then dried with anhydrous sodium sulfate, filtered, and the solvent removed via rotary evaporation to produce bis(piperidino)sulfide as a pale-yellow solid (1.60 g, 24% yield). ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.30−3.22 (m, 8H), 1.53 (p, J = 5.7 Hz, 8H), 1.46−1.38 (m, 4H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 59.4, 27.7, 23.8. HRMS (DART) [M + H]$^+$ calcd. for $C_{10}H_{21}N_2S^+$, 201.1420, found 201.1419.

General Procedure: Diaminosulfide. Adapted from a previous report.[51] A diaminodisulfide (1.0 equiv) solution in diethyl ether (0.4 M) was cooled to 0 °C in an ice bath for 30 min. Sulfuryl chloride (1.1 equiv) was then added to this solution dropwise. The reaction was stirred at 0 °C for 30 min, and then warmed to room temperature for 50 min. A separate solution of secondary amine (5.0 equiv) in diethyl ether (2 M) was cooled to 0 °C. Then, the sulfide solution is slowly added to the flask containing the cooled amine and stirred at 0 °C for 1 h. The reaction mixture was then washed with saturated NaCl solution (3 × 100 mL), dried with anhydrous sodium sulfate, filtered, and the solvent removed via rotary evaporation to produce the crude diaminosulfide which was used without further purification. In some cases, a minor amount of the diaminodisulfide starting material was present in the crude product, but this did not affect subsequent reactions.

S(NMe$_2$)$_2$. The reaction was performed using dimethylaminodisulfide (3.00 g, 19.7 mmol) in diethyl ether (49 mL), sulfuryl chloride (1.75 mL, 21.6 mmol), and dimethylamine solution (49.0 mL, 2 M in THF) to obtain the product as an orange liquid (1.39 g, 29%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.01 (s, 12H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 49.8. HRMS (DART) [M + H]$^+$ calcd. for $C_4H_{13}N_2S^+$, 121.0794, found 121.0796.

S(NiPrMe)$_2$. The reaction was performed using (*N*-isopropylmethylamino)disulfide (1.01 g, 4.85 mmol) in diethyl ether (12 mL), sulfuryl chloride (0.45 mL, 5.6 mmol), and *N*-isopropylmethylamine (2.5 mL, 24.0 mmol) in diethyl ether (12 mL) to obtain the product as an orange liquid (1.50 g, 88%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.38 (sept, J = 6.6 Hz, 2H), 2.83 (s, 6H), 1.11 (d, J = 6.6 Hz, 12H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 58.5, 40.7, 21.2. HRMS (DART) [M + H]$^+$ calcd. for $C_8H_{21}N_2S^+$, 177.1420, found 177.1419.

S(NEt$_2$)$_2$. The reaction was performed using diethylaminodisulfide (5.00 g, 24.0 mmol) in diethyl ether (60 mL), sulfuryl chloride (2.13 mL, 26.3 mmol), and diethylamine (12.6 mL, 122 mmol) in diethyl ether (60 mL) to obtain the product as an orange liquid (4.16 g, 49%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.07 (q, J = 7.1 Hz, 8H), 1.13 (t, J = 7.1 Hz, 12H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 51.5, 14.5. HRMS (DART) [M + H]$^+$ calcd. for $C_8H_{21}N_2S^+$, 177.1420, found 177.1418.

S(NPr$_2$)$_2$. The reaction was performed using dipropylaminodisulfide (4.20 g, 15.9 mmol) in diethyl ether (40 mL), sulfuryl chloride (1.41 mL, 17.4 mmol), and dipropylamine (10.9 mL, 79.5 mmol) in diethyl ether (40 mL) to obtain the product as a yellow-orange liquid (6.75 g, 91%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.98 (t, J = 7.2 Hz, 8H), 1.61−1.51 (m, 8H), 0.86 (t, J = 7.4 Hz, 12H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 59.9, 22.2, 11.6. HRMS (DART) [M + H]$^+$ calcd. for $C_{12}H_{29}N_2S^+$, 233.2046, found 233.2035.

SPyr$_2$. The reaction was performed using pyrrolidinodisulfide (0.91 g, 4.45 mmol) in diethyl ether (11 mL), sulfuryl chloride (0.40 mL, 4.9 mmol), and pyrrolidine (1.8 mL, 21.8 mmol) in diethyl ether (11 mL) to obtain the product as a red-orange liquid (1.25 g, 82%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.28−3.22 (m, 8H), 1.81−1.75 (m, 8H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 56.5, 26.2. HRMS (DART) [M + H]$^+$ calcd. for $C_8H_{17}N_2S^+$, 173.1107, found 173.1106.

SPip$_2$. The reaction was performed using piperidinodisulfide (2.50 g, 10.8 mmol) in diethyl ether (27 mL), sulfuryl chloride (0.96 mL, 11.9 mmol), and piperidine (5.3 mL, 53.7 mmol) in diethyl ether (27 mL) to obtain the product as an off-white solid (3.67 g, 85%). NMR shifts match those listed above.

General Procedure: Tris(dialkylamino)sulfonium. Adapted from a previous report.[49] A diaminosulfide (1.0 equiv) solution in CH$_2$Cl$_2$ (1.5 M) was cooled to −20 °C for 20 min. *N*-Chlorobenzotriazole (~1.0 equiv) in CH$_2$Cl$_2$ (0.5 M) was slowly added to this solution and the reaction was stirred for 15 min at −20 °C. The relevant secondary amine (1.2 equiv) was then added, and the reaction was warmed to room temperature overnight. The reaction mixture was transferred to a separatory funnel and the organic phase was washed with saturated KPF$_6$ solution (3 × 50 mL) and H$_2$O (1 × 50 mL). The organic layer was then dried with anhydrous sodium sulfate, filtered, and the solvent was removed via rotary evaporation. The resultant crude product was then precipitated into diethyl ether to afford the sulfonium cation.

[S(NMe$_2$)$_3$][PF$_6$]. The reaction was performed using bis(dimethylamino)sulfide (0.63 g, 5.2 mmol) in CH$_2$Cl$_2$ (3.5 mL), *N*-chlorobenzotriazole (0.80 g, 5.2 mmol) in CH$_2$Cl$_2$ (10 mL), and dimethylamine solution (3.1 mL, 2 M in THF) to obtain the product as a white solid (0.25 g, 15%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.95 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 38.6. HRMS (ESI) [M]$^+$ calcd. for $C_6H_{18}N_3S^+$, 164.1216, found 164.1221.

[S(NiPrMe)$_3$][PF$_6$]. The reaction was performed using bis(*N*-isopropylmethylamino)sulfide (2.00 g, 11.3 mmol) in CH$_2$Cl$_2$ (7.6 mL), *N*-chlorobenzotriazole (1.74 g, 11.3 mmol) in CH$_2$Cl$_2$ (22.7 mL), and *N*-isopropylmethylamine (1.4 mL, 13.4 mmol) to obtain the product as a tan solid (2.28 g, 51%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.70 (sept, J = 6.7 Hz, 3H), 2.72 (s, 9H), 1.29 (d, J = 6.7 Hz, 18H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 53.6, 27.7, 20.2. HRMS (ESI) [M]$^+$ calcd. for $C_{12}H_{30}N_3S^+$, 248.2155, found 248.2156.

[S(NEt$_2$)$_3$][PF$_6$]. The reaction was performed using bis(diethylamino)sulfide (2.00 g, 11.3 mmol) in CH$_2$Cl$_2$ (7.6 mL), *N*-chlorobenzotriazole (1.74 g, 11.3 mmol) in CH$_2$Cl$_2$ (22.7 mL), and diethylamine (1.4 mL, 13.5 mmol) to obtain the product as a white solid (1.76 g, 40%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.28 (q, J = 7.2 Hz, 12H), 1.25 (t, J = 7.2 Hz, 18H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 41.6, 12.6. HRMS (ESI) [M]$^+$ calcd. for $C_{12}H_{30}N_3S^+$, 248.2155, found 248.2158.

[S(NPr$_2$)$_3$][PF$_6$]. The reaction was performed using bis(dipropylamino)sulfide (1.41 g, 6.07 mmol) in CH$_2$Cl$_2$ (4.0 mL), *N*-chlorobenzotriazole (0.94 g, 6.12 mmol) in CH$_2$Cl$_2$ (12 mL), and dipropylamine (1.0 mL, 7.30 mmol) to obtain the product as an orange oil (1.19 g, 41%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.15−3.07 (m, 12H), 1.70−1.59 (m, 12H), 0.96 (t, J = 7.4 Hz, 18H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 49.3, 20.9, 11.4. HRMS (ESI) [M]$^+$ calcd. for $C_{18}H_{42}N_3S^+$, 332.3094, found 332.3095.

[S(Pyr)$_3$][PF$_6$]. The reaction was performed using bis(pyrrolidino)sulfide (0.23 g, 1.3 mmol) in CH$_2$Cl$_2$ (5 mL), *N*-chlorobenzotriazole (0.21 g, 1.4 mmol) in CH$_2$Cl$_2$ (5 mL), and pyrrolidine (0.13 mL, 1.6 mmol) to obtain the product as a tan solid (0.33 g, 64%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.41−3.35 (m, 12H), 2.03−1.98 (m, 12H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 49.3, 25.3. HRMS (ESI) [M]$^+$ calcd. for $C_{12}H_{24}N_3S^+$, 242.1685, found 242.1687.

[S(Pip)$_3$][PF$_6$]. The reaction was performed using bis(piperidino)sulfide (2.88 g, 14.4 mmol) in CH$_2$Cl$_2$ (10 mL), *N*-chlorobenzotriazole (2.20 g, 14.3 mmol) in CH$_2$Cl$_2$ (29 mL), and piperidine (1.7 mL, 17.2 mmol) to obtain the product as a white solid (3.92 g, 64%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.30−3.20 (m, 12H), 1.76−1.64 (m, 18H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 48.5, 25.7, 23.6. HRMS (ESI) [M]$^+$ calcd. for $C_{15}H_{30}N_3S^+$, 284.2155, found 284.2160.

Tris(dimethylamino)sulfoxonium hexafluorophosphate [O=S(NMe$_2$)$_3$][PF$_6$]. Adapted from previous report.[40] In a round-bottom flask, *m*-chloroperoxybenzoic acid (0.93 g, 3.8 mmol, 70% in water) and potassium hydroxide (0.42 g, 7.5 mmol) were combined in water (10.0 mL) and stirred for 15 min. To this mixture, tris(dimethylamino)sulfonium chloride (0.25 g, 1.25 mmol) dissolved in water (3.5 mL) was added and stirred at room temperature for 17 h. Conversion to sulfoxonium was monitored via ^{1}H NMR in D$_2$O. Excess KPF$_6$ salt was added to the aqueous solution, which was then extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic extracts were then washed with water (1 × 10 mL), dried with anhydrous sodium sulfate and filtered. The solvent was removed via rotary evaporation, and the crude product was precipitated in diethyl ether to afford a white solid (0.11 g, 27% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.12 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 38.8. HRMS (ESI) $[M]^+$ calcd. for $C_6H_{18}N_3OS^+$, 180.1165, found 180.1162.

General Procedure: Tris(dialkylamino)sulfoxonium. To a round-bottom flask, *m*-chloroperoxybenzoic acid (10.0 equiv, 70% in water), potassium carbonate (5.0 equiv), and 50:50 CH_2Cl_2:hexanes (~0.1 M) were added and stirred vigorously under air, producing a white precipitate. To this mixture, the tris(dialkylamino)sulfonium (1.0 equiv) was added and stirred overnight. The mixture was filtered, and the precipitate was rinsed with CH_2Cl_2. Rotary evaporation of the filtrate afforded the crude product, which was redissolved in CH_2Cl_2 (50 mL) and washed with sat. KPF_6 solution (3 × 50 mL). The organic phase was then dried with anhydrous sodium sulfate, filtered, and the solvent was removed via rotary evaporation. The resultant crude product was then precipitated into diethyl ether to afford the tris(dialkylamino)sulfoxonium.

[O═S(NiPrMe)$_3$][PF$_6$]. The reaction was performed using tris(*N*-isopropylmethylamino) sulfonium (0.10 g, 0.25 mmol), *m*CPBA (0.63 g, 2.6 mmol), and K_2CO_3 (0.18 g, 1.3 mmol) in CH_2Cl_2 (14 mL) and hexanes (14 mL) to obtain the product as a white solid (0.055 g, 54%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.08 (sept, *J* = 6.7 Hz, 3H), 2.93 (s, 9H), 1.32 (d, *J* = 6.7 Hz, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 52.2, 29.7, 20.1. HRMS (ESI) $[M]^+$ calcd. for $C_{12}H_{30}N_3OS^+$, 264.2104, found 264.2106.

[O═S(NEt$_2$)$_3$][PF$_6$]. The reaction was performed using tris(diethylamino)sulfonium (0.10 g, 0.25 mmol), *m*CPBA (0.63 g, 2.6 mmol), and K_2CO_3 (0.18 g, 1.3 mmol) in CH_2Cl_2 (14 mL) and hexanes (14 mL) to obtain the product as a white solid (0.044 g, 43%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.45 (q, *J* = 7.1 Hz, 12H), 1.33 (t, *J* = 7.2 Hz, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 44.0, 13.7. HRMS (ESI) $[M]^+$ calcd. for $C_{12}H_{30}N_3OS^+$, 264.2104, found 264.2107.

[O═S(NPr$_2$)$_3$][PF$_6$]. The reaction was performed using tris(dipropylamino)sulfonium (0.10 g, 0.21 mmol), *m*CPBA (0.52 g, 2.1 mmol), and K_2CO_3 (0.15 g, 1.1 mmol) in CH_2Cl_2 (12 mL) and hexanes (12 mL) to obtain the product as a white solid (0.045 g, 0.09 mmol, 44%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.31−3.23 (m, 12H), 1.75−1.65 (m, 12H), 0.98 (t, *J* = 7.4 Hz, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 51.4, 22.0, 11.1. HRMS (ESI) $[M]^+$ calcd. for $C_{18}H_{42}N_3OS^+$, 348.3043, found 348.3042.

[O═S(Pyr)$_3$][PF$_6$]. The reaction was performed using tris(pyrrolidino)sulfonium (0.10 g, 0.26 mmol), *m*CPBA (0.64 g, 2.6 mmol), and K_2CO_3 (0.18 g, 1.3 mmol) in CH_2Cl_2 (14.5 mL) and hexanes (14.5 mL) to obtain the product as a white solid (0.055 g, 53%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.57−3.51 (m, 12H), 2.12−2.06 (m, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 49.7, 25.8. HRMS (ESI) $[M]^+$ calcd. for $C_{12}H_{24}N_3OS^+$, 258.1635, found 258.1637.

[O═S(Pip)$_3$][PF$_6$]. The reaction was performed using tris(piperidino)sulfonium (0.10 g, 0.23 mmol), *m*CPBA (0.57 g, 2.3 mmol), and K_2CO_3 (0.16 g, 1.2 mmol) in CH_2Cl_2 (13 mL) and hexanes (13 mL) to obtain the product as a white solid (0.062 g, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.51−3.43 (m, 12H), 1.81−1.65 (m, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 48.8, 25.5, 23.1. HRMS (ESI) $[M]^+$ calcd. for $C_{15}H_{30}N_3OS^+$, 300.2104, found 300.2100.

[O═SPh$_3$][PF$_6$]. The reaction was performed using triphenylsulfonium tetrafluoroborate (0.25 g, 0.71 mmol), *m*CPBA (1.75 g, 7.10 mmol), and K_2CO_3 (0.49 g, 3.5 mmol) in CH_2Cl_2 (11 mL) and hexanes (11 mL) to obtain the product as a white solid (0.12 g, 46%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01−7.93 (m, 9H), 7.87 (m, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 138.0, 131.6, 129.2. HRMS (ESI) $[M]^+$ calcd. for $C_{18}H_{15}OS^+$, 279.0838, found 279.0840.

Degradation Studies in 2 M KOH/CD$_3$OH. Solutions of base in methanol were prepared by dissolving potassium hydroxide (2 M) and 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (0.025 M) in CD_3OH (0.5 mL). The tris(dialkylamino)sulfonium or sulfoxonium salt in the PF_6^- form (0.05 M) was dissolved in this solution and added to an NMR tube. The NMR tube was flame-sealed and then heated to 80 °C for 30 min in an oil bath, after which it was analyzed by ^{1}H NMR spectroscopy for the initial time point. The NMR tube was heated to 80 °C in an oil bath for the duration of the study and removed once every 5 days, cooled to room temperature, and ^{1}H NMR spectroscopy was used to assess cation degradation. Solvent impurities associated with the CD_3OH can be seen between 1.85−2.55 ppm. Each proton signal for the cation was integrated against a 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt signal, and divided by the t_0 integration value to give the percent cation remaining (values were averaged). After 30 days, the tubes were broken and the solution inside was analyzed using DART-MS.

Phase Transfer Experiments. Both [S(Pip)$_3$][PF$_6$] and [O═S(Pip)$_3$][PF$_6$] were exchanged to the chloride form by dissolution in 1:1 acetone/methanol. To this solution was added an Amberlite exchange resin. The solution was left for 24 h and disappearance of the PF_6^- signal was monitored via ^{31}P NMR spectroscopy. Once complete, the resin was filtered off and all solvent removed. The relevant cation was then dissolved in chlorobenzene (0.04 M) and separately, an equal volume of 50% w/w NaOH in deionized water was prepared. The two solutions were combined in a round-bottom flask and stirred rapidly at room temperature for 30 s, after which a 50 μL aliquot was removed from the organic layer and diluted with DMSO-d_6 or CD_2Cl_2 to record an initial NMR spectrum (t_0). The flask was then submerged in an oil bath at 60 °C and the reaction mixture was stirred rapidly. The flask was removed from heat and the stirring was stopped at specific time intervals, to allow the layers to separate before removal of a 50 μL aliquot from the organic layer for NMR analysis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.2c01289.

NMR spectra of all compounds (^{1}H and ^{13}C{^{1}H}), stack plots of ^{1}H NMR spectra for degradation studies carried out in 2 M KOH/CD_3OH and HRMS data, Cartesian coordinates and total energies for all DFT optimized structures (PDF)

FAIR data, including the primary NMR FID files, for compounds S$_2$(NMe$_2$)$_2$, S$_2$(NiPrMe)$_2$, S$_2$(NEt$_2$)$_2$, S$_2$(NPr$_2$)$_2$, S$_2$Pyr$_2$, S$_2$Pip$_2$, S(NMe$_2$)$_2$, S(NiPrMe)$_2$, S(NEt$_2$)$_2$, S(NPr$_2$)$_2$, SPyr$_2$, SPip$_2$, [S(NMe$_2$)$_3$][PF$_6$], [S(NiPrMe)$_3$][PF$_6$], [S(NEt$_2$)$_3$][PF$_6$], [S(NPr$_2$)$_3$][PF$_6$], [S(Pyr)$_3$][PF$_6$], [S(Pip)$_3$][PF$_6$], [O═S(NMe$_2$)$_3$][PF$_6$], [O═S(NiPrMe)$_3$][PF$_6$], [O═S(NEt$_2$)$_3$][PF$_6$], [O═S(NPr$_2$)$_3$][PF$_6$], [O═S(Pyr)$_3$][PF$_6$], [O═S(Pip)$_3$][PF$_6$], [O═SPh$_3$][PF$_6$] and all the degradation studies (ZIP)

Connectivity of [O=S(Pip)$_3$][PF$_6$] (CIF)

Accession Codes

CCDC 2173580 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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