DOI: 10.1002/chem.200901217

Ionic Liquid-Based Routes to Conversion or Reuse of Recycled Ammonium Perchlorate

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Abstract: New, potentially green, and efficient synthetic routes for the remediation and/or re-use of perchlorate-based energetic materials have been developed. Four simple organic imidazolium- and phosphonium-based perchlorate salts/ionic liquids have been synthesized by simple, inexpensive, and nonhazardous methods, using ammonium perchlorate as the perchlorate source. By appropriate choice of the cation, perchlorate can be incorporated into an ionic liquid which serves as its own electrolyte for the electrochemical reduction of the perchlorate anion, allowing for the regeneration of the chloride-based parent ionic liquid. The electrochemical degradation of the hazardous perchlorate ion and its conversion to harmless chloride during electrolysis was studied using IR and ^{35}Cl NMR spectroscopies.

Keywords: ammonium perchlorate · electrochemistry · energetic materials · ionic liquids · remediation

Introduction

Many modern energetic materials, even though highly advanced, and understood in terms of their performance and behavior, suffer from safety issues and environmental concerns.[1,2] Organic salts are potential replacement energetic materials, and as such, interest in their synthesis has been growing rapidly in recent years.[3,4] The reasons for this are manifold, but some of those most commonly expressed relate to their advantageous properties such as greater density and low or negligible vapor pressure under common operating conditions.

One of the most common oxidizers used, both in multi-component energetic systems[5] and in energetic salts, is the perchlorate anion. Moreover, one of the recent approaches to new liquid energetic salts has been to combine perchlorate with nitrogen-rich heterocyclic cations such as triazolium, tetrazolium, and more recently, bicyclic azolium salts.[4] Many of these salts use highly modified heterocyclic cations, with amino, nitro, and azo substitution of the heterocyclic ring that often results in the formation of products with melting points <100 °C, referred to as ionic liquids (ILs). By utilizing a common feature of ILs, that is, their broad liquidus ranges, many of the problems associated with energetic materials may be overcome. Recent developments in energetic ionic liquids (EILs) research have been reviewed[3c,6] and the initial results for many of these salts are promising as energetic materials.

A number of simpler heterocyclic perchlorate salts have also been prepared previously, with imidazolium,[7] 1-methylimidazolium,[8] 1-butyl-3-methylimidazolium,[9] 1,3-dibutylimidazolium,[10] and 1-hexyl-3-methylimidazolium cations.[11] The two predominant routes to such perchlorate-containing materials have been either through the protonation of a ring nitrogen using perchloric acid, resulting in the formation of

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thermally unstable, protonated salts, or by metathesis of an IL precursor with a perchlorate salt, most commonly $AgClO_4$. $LiClO_4$ also has been described as starting material for 1-butyl-3-methylimidazolium perchlorate.[12]

Both of these methods have disadvantages, with concentrated perchloric acid requiring careful handling, and $AgClO_4$, as well as, $LiClO_4$, being more expensive than would be ideal for large scale preparations, in addition to the environmental hazard inherent in the use of perchlorate. We have thus considered direct reuse or recycle of ammonium perchlorate (AP) in the synthesis of new energetic materials as an interesting option taking into account the two main advantages of this material: i) higher thermal stability, and thus ease of handling in comparison to other perchlorate salts and the free acid, and ii) the relative ease of handling or removal of the associated ammonium cation after the completion of the reaction. Additionally, AP is available in large quantities from demilitarization of rocket fuels. By using AP from such sources for the production of new perchlorate-based materials, the use of perchloric acid (with the hazards associated with its use) or $AgClO_4$ (with its higher cost) can be avoided.

In order to effectively utilize AP in the synthesis of perchlorate-based energetic materials, new synthetic protocols for the formation of such products are required which allow for fast and benign (in terms of byproducts) synthesis of the target materials. Here, we present three potential routes to incorporate the perchlorate anion into potentially energetic 1-methylimidazolium and phosphonium salts, using AP as the perchlorate source, including: 1) the reaction of a neutral amine (1-methylimidazole) with AP in aqueous solution, resulting in the formation of a protonated imidazolium perchlorate ([Hmim][ClO_4], **1**) and ammonia gas; 2) decarboxylation of 1,3-dimethylimidazolium-2-carboxylate[13] by reaction with AP to form 1,3-dimethylimidazolium perchlorate ([C_1mim][ClO_4], **2**), ammonia, and CO_2; and 3) metathesis of 1-butyl-3-methylimidazolium chloride with AP in water, forming the insoluble 1-butyl-3-methylimidazolium perchlorate ([C_4mim][ClO_4], **3**) and water soluble NH_4Cl. Using this same metathesis methodology but with methanol as solvent, trihexyl(tetradecyl)phosphonium perchlorate ([P_{66614}][ClO_4], **4**) was also prepared. Due to the relative hydrophobicity of these new salts, one could even envision recycle of aqueous perchlorate waste streams (for example, from water washout of rocket engines) by forming an IL and separating the anhydrous IL phase.

It must also be pointed out here, that perchlorate is considered to be environmentally and toxicologically hazardous. This anion has been identified to interfere with the human thyroid glands and hence to suppress the formation of several iodine-containing hormones.[14] The U.S. Environmental Protection Agency (EPA) set a limit of 15 ppb perchlorate for drinking water;[15] however, the discussions on that topic are controversial.[16] We have thus considered that our approach to reuse AP could also be utilized as a remediation strategy for AP.

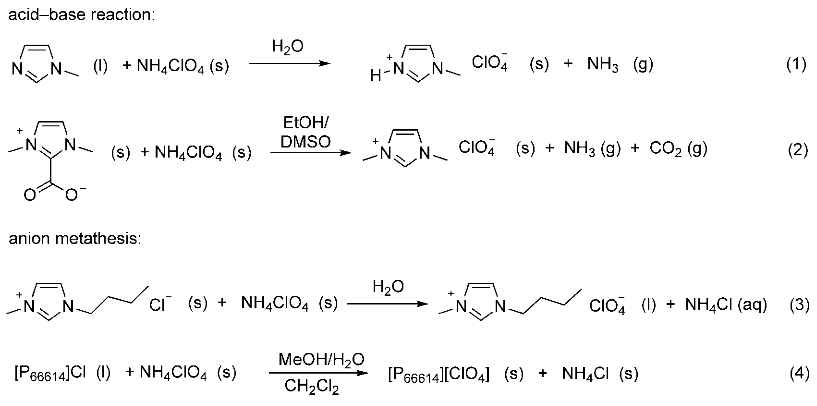
The electrochemical remediation of perchlorate ions is one of the best ways of converting the toxic perchlorate to the non-toxic chloride ion efficiently. There are several reports on the electro-reduction of perchlorate at various electrodes, for example, Rh,[17–22] Pt,[23–26] tungsten carbide,[27] Al,[28] Ti,[29] Ir,[30] Ru,[31] Re,[32] Tc,[33] and Sn.[34] The literature in this area has recently been reviewed.[35] In most of the above papers, perchlorate reduction is carried out in aqueous systems, and to our knowledge, there are no reports on the electrochemical reduction of the perchlorate anion using an IL approach.

Given the wide exploration of ILs in electrochemistry, we felt it was appropriate to study the reduction of perchlorate in a medium which was both the reagent and the electrolyte. With such a strategy the perchlorate anion could be reduced to non-hazardous chloride, regenerating the starting salt which in return could be exchanged to a perchlorate anion again, thus creating a regenerative cycle for the remediation of perchlorate. The advantages of this approach would include the potentially improved electrochemical stability of ILs compared to water, no hydrogen/oxygen evolution during electrolysis if the IL is wisely chosen, good conductivity, and, most importantly, no requirement for volatile organic solvents and supporting electrolytes.

Results and Discussion

Syntheses of perchlorate salts: Using three different routes [see Equations (1)–(4)] and AP as the perchlorate source, we have prepared 1-methylimidazolium perchlorate, ([Hmim][ClO_4], **1**), 1,3-dimethylimidazolium perchlorate, ([C_1mim][ClO_4], **2**), 1-butyl-3-methylimidazolium perchlorate, ([C_4mim][ClO_4], **3**), and trihexyl(tetradecyl)phosphonium perchlorate, ([P_{66614}][ClO_4], **4**). All four of these salts were formed in high yields, requiring little purification; **3** and **4** are ILs by definition, while **1** and **2** melt at temperatures above 100 °C.

The first, and simplest method involves the reaction of a neutral amine (1-methylimidazole) with AP in aqueous solution, resulting in the formation of **1** and ammonia gas which due to its volatility and thus easy removal, allows a shift in the reaction equilibrium to completion. Ultimately, the ammonia generated by this process could be recovered and reused, making this reaction very atom efficient. The reaction was conducted in water followed by evaporation to yield a colorless crystalline hygroscopic solid. Protonation of the imidazole ring was shown to be quantitative both by the presence of the NH peak, and the shift in position of all the 1-methylimidazole peaks in the ^{1}H NMR spectrum. The IR spectrum showed one peak in the $[ClO_4]^-$ stretching region, a strong and broad peak at 1044 cm^{-1}, with a shoulder at 1005 cm^{-1}, consistent with the symmetry of the $[ClO_4]^-$ anion being slightly altered,[37] probably by hydrogen-bonding. An additional peak was observed at 3081 cm^{-1} indicative of the protonation of the imidazole ring.[36]



The second method involves utilization of a previously reported protocol for the formation of a permanent cation, that is, the preparation of imidazolium-based salts via the decarboxylation reaction of 1,3-dimethylimidazolium-2-carboxylate.[13] When reacted with AP, this compound is transformed to [C_1mim][ClO_4], **2**, and easily removable gaseous by-products ammonia and CO_2. The Krapcho decarboxylation of 1,3-dimethylimidazolium-2-carboxylate was carried out in a mixture of EtOH and DMSO. Evaporation of the solvents gave **2** as a colorless, crystalline, extremely hygroscopic solid, in quantitative yield. The decarboxylation of the zwitterion was confirmed by both the ^{1}H and ^{13}C NMR spectra; the ^{1}H NMR showing a resonance for the C2 proton, and the ^{13}C NMR showing neither R-COO$^-$ nor $[HCO_3]^-/[CO_3]^{2-}$ species. Production of pure **2** was confirmed by single crystal X-ray diffraction (Figure 1).

The compounds **3** and **4** were prepared by metathesis of NH_4ClO_4 with [C_4mim]Cl in water or with [P_{66614}]Cl in methanol, respectively. The IL products phase separated from the corresponding solution to give **3** as a pale yellow viscous liquid and **4** as a clear liquid that transformed into a white solid at around 20 °C. AgCl precipitation tests were negative indicating the absence of Cl^- in each product to the limit of detection. The lack of an absorption band for water in the IR spectra after drying and the measured water contents of 0.17 % w/w (**3**) and 0.12 % w/w (**4**) indicated the materials to be quite hydrophobic. The IR spectra showed a strong and broad peak in the $[ClO_4]^-$ stretching region (1068 cm^{-1}, **3**; 1081 cm^{-1}, **4**) for each compound consistent with the symmetry of the $[ClO_4]^-$ anion being unbroken.[37]

Thermal investigations: All four salts were examined by DSC and TGA using a standard protocol. From the DSC of **1**, a melting point of 148 °C (lit. 154–158 °C)[38,39] was observed, with an additional transition observed at 2 °C. This melting point is a bit lower than the one found in the literature, and we assume that this may be caused by the compound's high hygroscopicity and thus fast absorption of water from the atmosphere. However, no detailed information on the methods used to determine the melting-point range was provided in the literature. From its appearance, the transition at 2 °C was identified as a solid-state polymorph transition, and its reversibility indicated it to be polytrophic.

Compound **2** proved to be comparably unstable and the TGA experiment resulted in an energetic decomposition at 262 °C. DSC runs were therefore not conducted past 150 °C, up to which temperature no thermal transitions were observed. In **3**, only a glass transition at $T_g = -77$ °C was observed. The DSC of **4** showed a melting point at 24.7 °C and from this standpoint it can be classified as an IL.

In TGA investigations, all salts showed stability at lower temperatures with almost no mass loss observed below 200 °C. Compound **1** exhibited a two-step decomposition with $T_{5\%\,\mathrm{decomp}} = 241$ °C, and an onset temperature for the second decomposition step of 495 °C. Salt **2** showed a more violent decomposition with $T_{5\%\,\mathrm{decomp}} = 244$ °C, after which a steady rate of decomposition was observed until 262 °C when it underwent extremely rapid, energetic decomposition. Compound **3** exhibited $T_{5\%\,\mathrm{decomp}} = 282$ °C. Above this temperature the IL showed a steady rate of decomposition up to 310 °C, when it underwent very rapid, total decomposition. Compound **4** decomposes in one step with $T_{5\%\,\mathrm{decomp}} =$ 254.5 °C.

In contrast to these materials, AP itself generally shows a more controllable thermal decomposition,[40] which begins around 130 °C, but below its phase-transition temperature of ~240 °C, does not undergo complete decomposition. While it is regarded as more generally thermally stable than NH_4NO_3, the stability of AP does depend on a variety of factors, including method of crystallization, preliminary treatment of crystals, how long they have been stored, and the purity of the salt.

X-ray structure: Crystals suitable for X-ray crystallographic analysis of **2** were obtained by the vapor diffusion of diethyl ether into a dry ethanol solution of **2**. Despite the use of perfluorinated oil, **2** showed signs of rapid absorption of water from the air, and likely recrystallized once placed in the liquid nitrogen stream on the diffractometer. However, no water was found in the crystal structure.

The compound crystallizes in the monoclinic space group $P2_1/c$ where the asymmetric unit of the salt contains one full cation and anion, unusual given the symmetry of both ions. The closest contact is through the C2 proton in the cation to O3 in the perchlorate anion (Figure 1). Close contacts about each ion reveal that the cation interacts with five anions, three of which are via the three hydrogen atoms on C1, each to separate perchlorate anions. The anion similarly interacts with five cations, two of which are to O3. O1, O2, and O4 each interact with one cation. Additionally, the imidazolium cations stack in parallel pairs that alternate in ori-

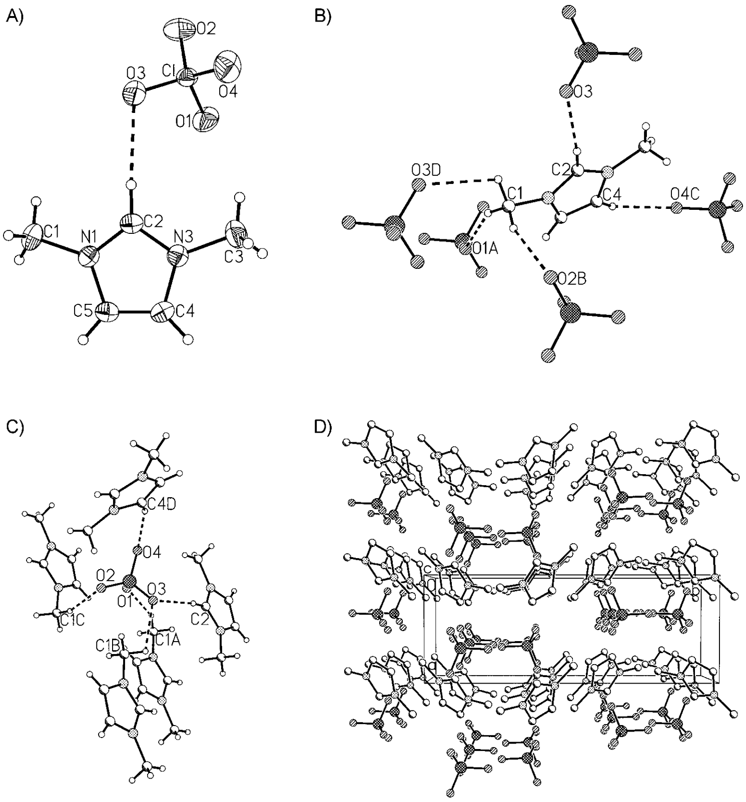


Figure 1. Crystal structure of [C$_1$mim][ClO$_4$] (**2**) showing (A) the asymmetric unit with the dominating interaction of the most acidic proton in the cation (C2-H) with the perchlorate anion indicated; the interactions (distances less than the sum of the van der Waals' radii minus 0.1 Å) to the (B) cation and (C) anion; and (D) the packing down the crystallographic *c* axis showing the distinct cationic and anionic layers (hydrogen atoms were omitted).

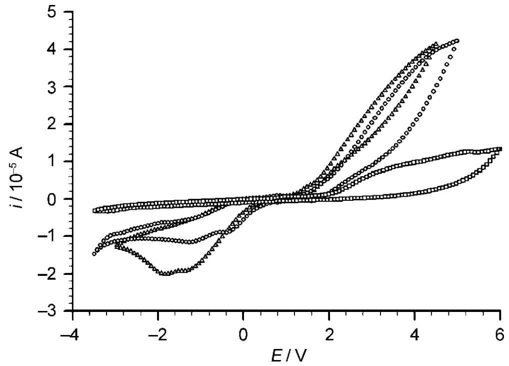


Figure 2. Electrochemical behavior of [P$_{66614}$][ClO$_4$] on a Au electrode vs. Ag/Ag$^+$ at 50 °C and 100 mV s^{-1}; △ = −3.0 to 4.5 V, ○ = −3.5 to 5 V, □ = −3.5 to 6 V.

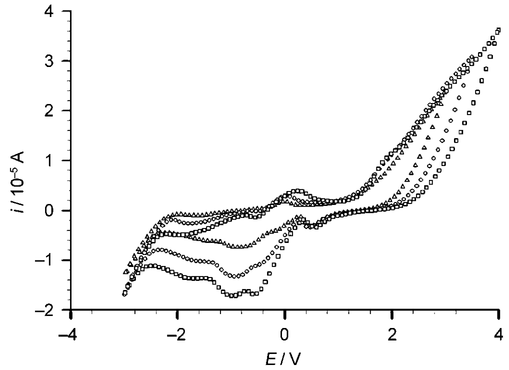


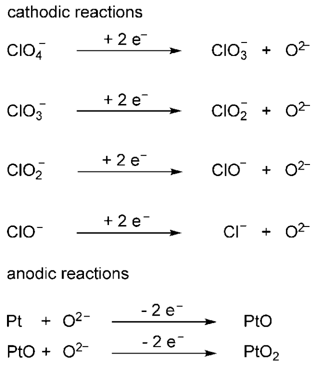
Figure 3. Electrochemical behaviour of [P$_{66614}$][ClO$_4$] on a Pt electrode vs. Ag/Ag$^+$ at 50 °C and 100 mV s^{-1}; △ = −3.0 to 3 V, ○ = −3 to 3.5 V, □ = −3 to 4 V.

entation with other pairs of cations. Distinct cationic and anionic layers are found to form in the (0 −1 1) plane. The combination of these various interactions gives rise to a skewed NaCl-type of packing arrangement for the salt.

Electrochemical reduction of perchlorate: To test the ability of a perchlorate-based IL to serve as reagent and electrolyte, we chose [P$_{66614}$][ClO$_4$] (**4**) since the phosphonium cation is electrochemically more stable than imidazolium cations,[41] and this provides a wider electrochemical window. The cyclic voltammetry (CV) experiments carried out with neat **4** indicated that the perchlorate anions can be reduced on both gold (at −1.3 and −2 V vs Ag/Ag$^+$) and on platinum (at −0.5 and −1 V with a hump at −1.8 V) electrodes (see Figures 2 and 3). When the potential range was increased (−3.5 to 6 V) while using the gold electrodes, the perchlorate ions were adsorbed on the gold electrode surface which passivated the electroactive area and eventually reflected on the electrochemically inert behavior at both anodic and cathodic sides of the CV. Using platinum electrodes, when the potential window was increased, the current increased on the reduction peaks, showing that the electroreduction of perchlorate was progressing.

The electrocatalytic reduction of perchlorate on Pt follows the mechanism depicted below,[42] where desorption of the intermediates is negligible and platinum acts as a sacrificial anode. Perchlorate is reduced stepwise to chloride, while the platinum counter electrode is simultaneously oxidized by the oxygen produced. The formation of PtO$_2$ (a dark-brown solid that is soluble in aq. KOH) in the anode chamber was observed.

This is, to the best of our knowledge, the first report of the electro-reduction of perchlorate from a system using



ILs. In aqueous systems, the reduction of perchloric acid leads to the evolution of hydrogen which may significantly reduce the amount of perchlorate being transformed to chloride.[43] In our study, there are no acidic protons present and consequently no hydrogen evolution, allowing the electro-reduction of perchlorate to proceed uninterrupted.

Based on this success, Pt was chosen as the material for the working electrode for subsequent bulk electrolysis experiments. As platinum is a very expensive material, nickel could be used as a sacrificial anode in bulk studies as shown by Rusanova et al., for aqueous systems.[43]

The bulk electrolysis experiment was carried out at -2 V versus Ag/Ag^+ by chronoamperometry for 120 min on a Pt electrode at room temperature. During this bulk electrolysis of **4**, the electrochemical degradation of the perchlorate ions and their conversion into chloride ions was studied using IR (Figure 4) and ^{35}Cl NMR (Figure 5). Samples were taken from the electrolytic cell periodically after 15, 30, 45, 90, and 105 min of electrolysis for analyses, and were also tested with $AgNO_3$ for the presence of chloride. The observed precipitation level of AgCl increased with the time of electrolysis, suggesting an increase in the chloride ion concentration in the electrolyte with time.

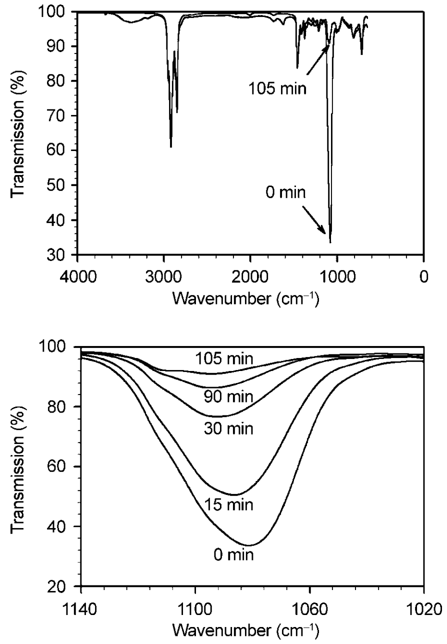


Figure 4. IR spectra of $[P_{66614}][ClO_4]$ in acetonitrile before (0 min) and after (105 min) electrolysis (top) and magnification of the perchlorate peak recorded during the electrolysis to monitor the degradation of perchlorate ions (bottom).

In the IR spectra (1 mM solutions of electrolyte, $[P_{66614}][ClO_4]$, in acetonitrile), the intensity of the perchlorate peak at 1081 cm^{-1} decreased with time of electrolysis, reflecting the reduction of the $[ClO_4]^-$ ions. In the ^{35}Cl NMR spectra, the peak around 1000 ppm was assigned to the $[ClO_4]^-$ anion, and the peak at 50 ppm was assigned to the Cl^- ion.

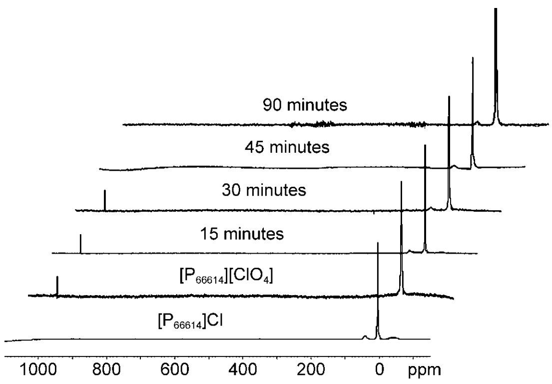


Figure 5. ^{35}Cl NMR spectra recorded during the electrolysis of $[P_{66614}][ClO_4]$ to determine the degradation of perchlorate ions and accumulation of chloride ions. The peak at ~0 ppm is attributed to the external standard 1.0 M NaCl in D_2O. The peak at ~50 ppm is attributed to the presence of $[Cl]^-$ anions formed over time by electrolysis.

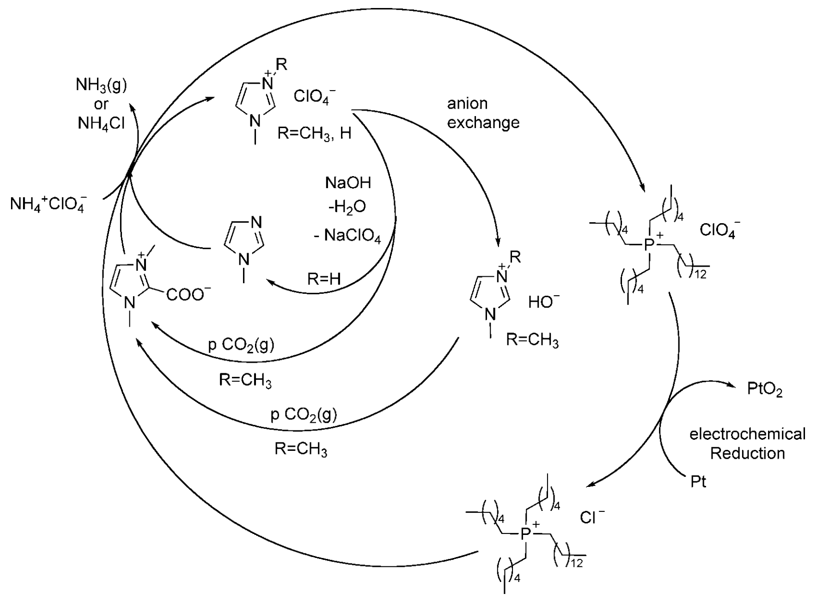
As electrolysis time increased, the peak for perchlorate was diminished and the peak for chloride became prominent.

The complete disappearance of the perchlorate peak in the ^{35}Cl NMR does not, however, support that all perchlorate anions have been converted to chloride during this short period of time. It is because the resolution of the perchlorate peak even in pure **4** was very poor when compared to that in AP, perhaps because of the rather high viscosity of the sample, or due to the lower symmetry of the phosphonium cation, compared to NH_4^+.[44] However, the substantial decrease of the size of this peak in comparison to the increasing size of the Cl^- peak allows us to speculate that substantial conversion is taking place.

To the best of our knowledge we are the first to report the electrochemical degradation of perchlorate ions using an IL strategy while simultaneously recycling back the parent IL. It is conceivable that due to the simplicity of the system and ability to recover the starting material $[P_{66614}]Cl$, that can later be reconverted back to **4**, using up further AP, the developed system could be used in a continuous fashion in the process of perchlorate removal and conversion to innocuous chloride (Scheme 1).

Conclusions

Three new routes have been shown for the synthesis of organic perchlorate salts of simple nitrogen heterocycles and a quaternary phosphonium compound, using AP as the source of perchlorate. Specifically, new preparative routes have been determined for the easy preparation of 1-methylimidazolium perchlorate, 1,3-dimethylimidazolium perchlorate, 1-butyl-3-methylimidazolium perchlorate, and trihexyl(tetradecyl)phosphonium perchlorate. The synthetic routes proceed in a single step from the chosen precursors, and produce the desired products in high yield and purity. Most importantly, the electrochemical remediation of the perchlo-



Scheme 1. Possible AP IL reuse/remediation strategies.

rate ion from an ionic liquid leading to a potential perchlorate removal/remediation cycle was achieved. This could lead to a continuous process for converting perchlorate to chloride ions using a strategy where an IL serves as both reagent and electrolyte. A few such strategies based on the results reported here are illustrated in Scheme 1.

Experimental Section

CAUTION! Although no problems were encountered in the synthesis or characterization of these salts, all perchlorate salts should be treated as potentially explosive, and should be prepared in small amounts under good control. Energetic decomposition of perchlorate-based systems can be initiated by a variety of external stimuli (e.g., impact, electrostatic discharge), and care should be taken during all handling of such materials.

General: All chemicals unless otherwise stated were purchased from Aldrich Chemical Company (Milwaukee, WI) and used without further purification. Water was deionized (DI) in house above 18 MΩ cm using a Barnstead (Dubuque, IA) deionization system. Infrared spectra for compounds **1**–**3** were recorded as neat samples from 4000–650 cm^{-1} on a Perkin–Elmer (Waltham, MA) Spectrum 100 FT-IR spectrometer fitted with a Universal ATR Sampling Accessory; spectra for compound **4** were measured as neat samples for the characterization of the pure compound, and as 1 mM solutions in acetonitrile for the monitoring of the perchlorate degradation, from 4000–650 cm^{-1} on a Perkin–Elmer (Dublin, Ireland) Spectrum 100 FT-IR Spectrometer. The solvent signals were subtracted (as background) from the spectra.

NMR data for compounds **1**–**3** were recorded in [D$_6$]DMSO at 25 °C on a 500 MHz Bruker (Billerica, MA) AX500 spectrometer, with tetramethylsilane (TMS) as the internal standard for ^{1}H (500 MHz) or the solvent as the internal standard for ^{13}C (125 MHz). NMR data of compound **4** were collected from the neat sample, on a Bruker (Coventry, UK) 500DRX spectrometer with capillary [D$_6$]DMSO as the external standard for ^{1}H (500 MHz) and ^{13}C NMR (125 MHz). No standard was used to record the ^{31}P NMR (202 MHz). A solution of 1.0 M NaCl in D$_2$O served as external standard for the ^{35}Cl NMR (49 MHz) experiments.

Water content of compound **3** was measured by Karl-Fischer titration with an EM Science Aquastar V1b Titrator (Hiranuma Sangyo, Japan). The water content of compound **4** was determined using a Cou-Lo Aquamax from GRScientific (Bedfordshire, UK) Karl-Fischer titrator. Electrospray mass spectrometry and elemental analysis were performed on an LCT Premier from Waters using an Advion nanomate injection system (Manchester, UK), and a PerkinElmer 2400 Series II CHNS/O Elemental Analyser (Shelton, CT), respectively.

Thermogravimetric analyses: Decomposition temperatures for compounds **1**–**3** were measured in the dynamic heating regime using a TA Instruments (New Castle, DE) TGA 2950 Thermogravimetric Analyzer under dried air. Samples were heated from room temperature to 600 °C under constant heating at 5 °C min^{-1} in 10 mm platinum sample pans (Instruments Specialists Inc., Twin Lakes, WI) that were flame treated before each data collection. Compound **4** was analyzed with the same procedure but using a TA Instruments (West Sussex, UK) TGA Q 5000 analyzer. Decomposition temperatures ($T_{5\%\,\mathrm{decomp}}$) were determined from the onset to 5 wt% mass loss in an isocratic TGA experiment.

Differential scanning calorimetry: DSC scans for compounds **1**–**3** were conducted on a TA Instruments Model 2920 Modulated DSC calorimeter (New Castle, DE) cooled with a liquid nitrogen cryostat. Data were collected at constant atmospheric pressure. Samples between 8 and 13 mg were placed in fresh aluminum pans (PS1007, hermetic sample pans, Instrument Specialists Inc., Twin Lakes, WI) and massed using a Cahn C-35 microbalance (Thermo Electron Corp., Waltham, MA). An empty pan was used as a reference in the DSC. The dry box of the DSC was flushed with dry nitrogen to prevent condensation and crystallization from ambient moisture upon cooling of the sample. The following protocols were used on all samples. For solids; an initial heating rate of 5 °C min^{-1} to 50 °C below the $T_{5\%\,\mathrm{decomp}}$ determined by TGA was followed by a 5 min isotherm. A cooling rate of 5 °C min^{-1} to −30 °C was followed by a 5 min isotherm, with the cycle repeated twice. For liquids; an initial cooling rate of 5 °C min^{-1} to −110 °C was followed by a 5 min isotherm. A heating rate of 5 °C min^{-1} to 120 °C was followed by a 5 min isotherm, with the cycle repeated twice. Compound **4** was analyzed following a similar procedure but using a TA instruments (West Sussex, UK) DSC Q 2000 analyzer.

X-ray crystallography

Crystal data: [C$_1$mim][ClO$_4$] (**2**); $C_5H_9N_2O_4Cl$; 196.59 g mol^{-1}; monoclinic, $P2_1/c$; $T=173$ K; $a=6.2666(6)$, $b=17.0452(17)$, $c=7.8173(8)$ Å, $\beta=92.580(2)°$; $Z=4$; $V=834.16(14)$ Å^3; $\rho=1.565$ g cm^{-3}; R_1, wR_2 [$I>2\sigma(I)$, 1550 flections] = 0.0302, 0.0809; R_1, wR_2 (all data, 5110 reflections, 1703 unique) = 0.0335, 0.0832; GooF = 1.070. Data were collected on a Bruker CCD area detector-equipped diffractometer (Madison, WI) using graphite monochromated Mo$_{K\alpha}$ radiation ($\lambda=0.71073$ Å). The single crystal was coated in Paratone-N (Hampton Research, Laguna Niguel, CA) perfluorinated oil, mounted on a glass fiber and transferred to the goniometer for data collection. The crystal was cooled to −100 °C using a cold nitrogen gas stream. The structures was solved and refined using the SHELXTL software package[45] and absorption corrections were made using SADABS.[46] The structure was refined by full-matrix least squares on F^2. All non-hydrogen atoms were readily located and their positions refined anisotropically, while all hydrogen atoms were found from difference Fourier maps and isotropically refined without restraint. CCDC 730659 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Electrochemistry: All electrochemistry experiments were carried out at room temperature unless stated otherwise, using a computer controlled Autolab PGSTAT (Eco Chemie B.V., The Netherlands) potentiostat. A conventional three electrode electrochemical system consisting of a platinum disc as a working electrode, platinum coil as a counter electrode, and Ag/Ag$^+$ as the reference electrode was used. The counter and reference electrode compartments were filled with the same electrolyte as the bulk ([P_{66614}][ClO_4]), but were separated from the bulk electrolyte by a glass frit. This reduces the contamination of the bulk electrolyte by the by-products from the counter electrode during electrolysis. For voltammetric measurements, working electrodes purchased from BioAnalytical Systems (Warwickshire, UK) were used. Prior to each experiment, the electrodes were polished on soft lapping pads with alumina slurry of size 1 and 0.3 μm and then washed with distilled water and dried by compressed air. All samples were degassed with Ar prior to measurement.

Synthesis of [Hmim][ClO$_4$] (1): NH_4ClO_4 (0.50 g, 4.3 mmol) was dissolved in DI water (3 mL). *N*-Methylimidazole (0.44 mL, 0.35 g, 4.3 mmol) was dissolved in DI water (1 mL), the solutions were mixed and stirred overnight. The water was evaporated under a N_2 gas stream to give an off-white solid. A further portion of DI water was added and the evaporation repeated. The solid material was dried under high vacuum at room temperature to give the desired product as a white hygroscopic solid in quantitative yield (0.76 g). M.p. (DSC) 148 °C, onset for 5 % decomposition $T_{5\%\,\text{decomp}}=241\,°C$, second decomposition $T_{\text{decomp}}=495\,°C$; ^{1}H NMR (500 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta=8.51$ (s, 1 H, NC*H*N), 7.48 (s, 1 H, NC*H*CHN), 7.38 (s, 1 H, NCHC*H*N), 7.07 ppm (br s, 1 H, N*H*), 3.78 ppm (s, 3 H, NC*H*$_3$); ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta=136.48$ (N*C*HN), 122.72 (NCH*C*HN), 122.18 (N*C*HCHN), 34.45 ppm (*C*H$_3$) ; selected IR (neat sample): $\tilde{\nu}$ = 3154, 3116, 3081, 3022, 2976, 2880, 1587, 1550, 1439, 1308, 1280, 1044 ([ClO$_4$]$^-$), 1005 ([ClO$_4$]$^-$), 931, 914, 856, 747 cm^{-1}; MS: *m*/*z* (%): 83.06 (100) [Hmim]$^+$, 265.06 (90) [Hmim$_2$ClO$_4$]$^+$, 82.9 (35) [ClO$_3$]$^-$, 98.9 (100) [ClO$_4$]$^-$.

Synthesis of [C$_1$mim][ClO$_4$] (2): 1,3-Dimethylimidazolium-2-carboxylate was prepared according to the literature method.[47] NH_4ClO_4 (0.50 g, 4.3 mmol) was dissolved in DMSO/EtOH 3:1 (2.5 mL) and added to a warmed solution of 1,3-dimethylimidazolium-2-carboxylate (0.60 g, 4.3 mmol) dissolved in EtOH (2 mL). The mixture was heated to 70 °C and then stirred for 3 d. The solvent was removed under high vacuum to leave the desired product as a white and extremely hygroscopic solid in quantitative yield. X-ray quality crystals were grown by the diffusion of diethyl ether vapor into a solution of **2** in dry EtOH. The melting point was not determined. Due to the discovered instability of the investigated compound (the TGA experiment resulted in an energetic decomposition), the DSC experiment was not conducted above 150 °C, to which temperature no thermal transition was recorded. Onset temperature for 5 % decomposition $T_{5\%\,\text{decomp}}=244\,°C$ (followed by explosive decomposition); ^{1}H NMR (500 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta=8.99$ (s, 1 H, NC*H*N), 7.65 (s, 2 H, NC*H*C*H*N), 3.84 ppm (s, 6 H, NC*H*$_3$); ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta=136.93$ (N*C*HN), 123.34 (N*C*H*C*HN), 35.58 ppm (*C*H$_3$).

Synthesis of [C$_4$mim][ClO$_4$] (3): NH_4ClO_4 (0.50 g, 4.3 mmol) was dissolved in DI water (3 mL). [C$_4$mim]Cl (BASF, Ludwigshafen, Germany) (0.74 g, 4.3 mmol) was dissolved in DI water (1 mL) and added with initial mixing. The mixture was left to stand for 2 h. The water was evaporated under a N_2 gas stream to give a mixture of solid and liquid residue. The liquid was separated from the solid by extraction with CH_2Cl_2, and the solvent removed in vacuo. The resulting viscous liquid was taken up in CH_2Cl_2 and extracted with DI water until the washing water did not form a precipitate when tested with a solution of $AgNO_3$. The CH_2Cl_2 was removed in vacuo and the resulting pale yellow viscous liquid dried under high vacuum at room temperature to give the desired product (0.91 g, 89 %). No melting point was detected in the compound's DSC trace, but a glass transition was observed at $T_g=-77\,°C$; onset for 5 % decomposition $T_{5\%\,\text{decomp}}=282\,°C$; ^{1}H NMR (500 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta=9.10$ (s, 1 H, NC*H*N), 7.77 (s, 1 H, NC*H*CHN), 7.70 (s, 1 H, NCHC*H*N), 4.16 (t, 2 H, ^3J(H,H)$=7.0$ Hz, NC*H*$_2$), 3.85 (s, 3 H, NC*H*$_3$), 1.77 (m, 2 H, NCH$_2$C*H*$_2$), 1.27 (m, 2 H, C*H*$_2$CH$_3$), 0.91 ppm (t, 3 H, ^3J(H,H)$=7.5$ Hz, CH$_2$C*H*$_3$); ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta=136.45$ (N*C*HN), 123.57 (NCH*C*HN), 122.22 (N*C*HCHN), 48.47 (N*C*H$_2$), 35.71 (N*C*H$_3$), 31.29 (CH$_2$*C*H$_2$CH$_2$), 18.72 (*C*H$_2$CH$_3$), 13.21 ppm (*C*H$_3$); selected IR (neat sample): $\tilde{\nu}$ = 3156, 3116, 2962, 2933, 2874, 1572, 1464, 1168, 1068 ([ClO$_4$]$^-$), 842, 751 cm^{-1}; MS: *m*/*z* (%): 83.07 (25) [Hmim]$^+$, 139.1 (100) [C$_4$mim]$^+$, 239.2 (30) [*M*+H]$^+$, 82.9 (5) [ClO$_3$]$^-$, 97.0 (15) [dimim]$^-$, 98.9 (100) [ClO$_4$]$^-$. The compound appears to be slightly hygroscopic, as the elemental analysis suggests that a substoichiometric hydrate formed after several days with contact to the atmosphere: elemental analysis calcd (%) for $C_8H_{15}N_2ClO_4\times0.25\,H_2O$ (243.2): C 39.52, H 6.42, N 11.52; found: C 39.41, H 6.23, N 11.32.

Synthesis of [P$_{66614}$][ClO$_4$] (4): A mixture of [P$_{66614}$]Cl (Cytec, Niagara Falls, Canada) (4.07 g, 7.8 mmol) and NH_4ClO_4 (0.922 g, 7.8 mmol) in MeOH (10 mL) containing a few drops of water was stirred at room temperature. A phase separation was observed after 15 min (precipitation of NH_4Cl), but the stirring was continued overnight to ensure the completion of the reaction. The product was extracted using CH_2Cl_2. The organic phase was washed until chloride free, and the solvent was removed in vacuo. The product was dried under high vacuum at 35 °C overnight to give a colorless liquid that slowly crystallized (91 %). M.p. (DSC) 24.7 °C, single decomposition $T_{5\%\,\text{decomp}}=254.5\,°C$; ^{1}H NMR (500 MHz, [D$_6$]DMSO, 25 °C): $\delta=2.17$ (m, 8 H, PC*H*$_2$), 1.34 (m, 48 H, C*H*$_2$), 0.88 ppm (m, 12 H, C*H*$_3$); ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C): $\delta=$ 31.27 (*C*H$_2$), 30.36 (*C*H$_2$), 30.02 (*C*H$_2$), 29.81 (*C*H$_2$), 29.61 (*C*H$_2$), 29.01 (*C*H$_2$), 28.93 (*C*H$_2$), 28.68 (*C*H$_2$), 28.61 (*C*H$_2$), 28.05 (*C*H$_2$), 22.06 (*C*H$_2$), 21.77 (*C*H$_2$), 20.48 (d, *C*H$_2$), 17.46 (d, *C*H$_2$), 13.89 (*C*H$_3$), 13.80 ppm (*C*H$_3$); ^{31}P NMR (202 MHz, [D$_6$]DMSO, 25 °C): $\delta=34.96$ ppm; ^{35}Cl NMR (49 MHz, D$_2$O, 25 °C, NaCl): $\delta=1010.80$ ppm; selected IR (neat sample): $\tilde{\nu}$ = 2955, 2923, 2854, 1465, 1412, 1378, 1215, 1081 ([ClO$_4$]$^-$), 812, 720 cm^{-1}; MS: *m*/*z* (%): 483.5 (100) [P$_{66614}$]$^+$, 82.9 (5) [ClO$_3$]$^-$, 98.9 (100) [ClO$_4$]$^-$, 202.9 (95) [P$_{66}$H]$^-$; elemental analysis calcd (%) for $PC_{32}H_{68}ClO_4$ (583.3): C 65.89, H 11.75; found: C 66.32, H 11.88.

Acknowledgements

This research was supported by a grant from Amtec Corporation and the Air Force Office of Scientific Research (Grant F49620-03-1-0357).

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Received: May 7, 2009