

Synthesis and Conductivity Studies of Tetraarylphosphonium Salts As Potential Electrolytes in Advanced Batteries.

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Abstract:

*The purpose of this study was to synthesize polysubstituted tetraarylphosphonium/tetrakis (pentafluorophenyl) borate salts **3**, also known as TAP^R/TFAB where R is a substituent, and to measure their conductance/conductivity in low-polarity media such as tetrahydrofuran (THF) and dichloromethane (DCM). Such determination was to provide a rationale to the question of whether these compounds, and other weakly coordinating cations/anions combinations are suitable electrolytes for advanced batteries which are energized in safer, low-polarity organic solvents.*

Introduction

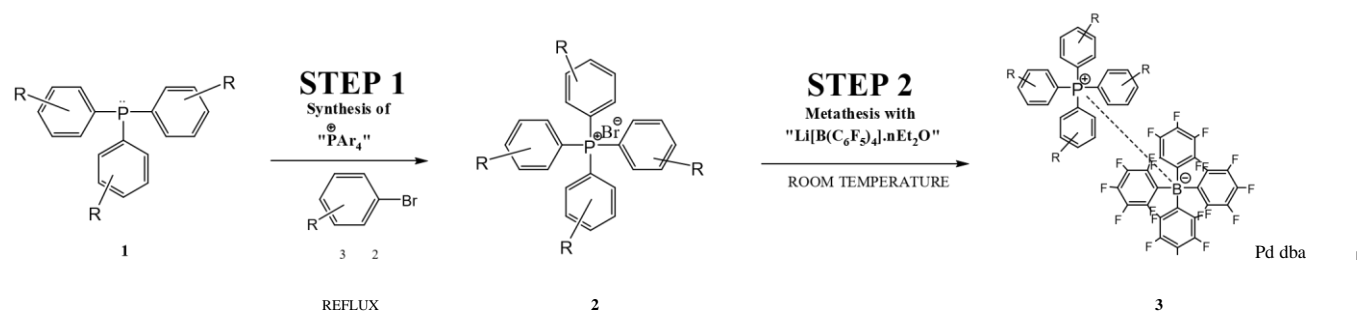
Battery technology is one of the important components in renewable energy to store produced energy. Li-ion battery has become a prominent technology while its use of metals could pose the problem of long-term stability, disposal, and handling.¹⁻⁴ In order to address the pressing issue of battery safety, other alternatives are actively being considered.⁵⁻⁶ Potential solutions include organic radical battery (ORB) and organic redox flow battery (ORFB).⁷⁻⁹ ORB uses organic radical polymers and electrolytes, which has a potential to be more environmentally friendly and more flexible than conventional metal-based batteries while maintaining or theoretically surpassing the capacity and charge density of Li-ion batteries. In pure ORB, organic radical polymers act as anodes and cathodes, which are separated by a porous membrane and submerged in electrolytes. ORFB consists of redox active molecules such as quinones and electrolytes dissolved in aqueous or non-aqueous solvents, which could achieve high energy density and good cyclability. Nonaqueous solvents with electrolytes can offer a wide window of electrochemical stability with higher cell voltage. In both ORB and ORFB, electrolytes act as a key component that allows the transport of ions between electrodes and enables charge balance. To date, a variety of electrolytes has been tested with varying ionic conductivity, but testing has been limited to readily available electrolytes.¹⁰⁻¹¹ Fewer efforts were made to explore other types of electrolytes that could achieve high ionic conductivity and stability in ORB and ORFB. In addition, only polar solvents are used generally due to reduced solubility of electrolytes and redox active materials in non-polar solvents. We hypothesize that electrolytes that can be used in non-polar solvents could expand the ability to test other redox active materials, which may help improve the performance of batteries. For instance, weakly coordinating anions (WCAs) and cations (WCCs) have potentials to improve the efficiency and stability of batteries over the existing and commonly used electrolytes by increasing and optimizing conductivity tailored to the redox active

molecules. WCAs and WCCs are a loose association of anions and cations where minimal interaction exists between ions. This can be achieved by building large and bulky cations and anions. Such loosely held ion-pairs may thus lead to increased conductivity even in low polarity solvents because of their high solubility. At the same time, larger and bulkier ions, such as $[B\{C_6H_3(CF_3)_2\}_4]^-$ or TFAB, travel more slowly in a viscous medium than do smaller ions, which could limit conductivity while the association constants of TFAB-containing salts are much lower than salts containing smaller conventional anions such as hexafluorophosphate. WCAs are widely studied in catalysis and in electrochemistry although reports of their electrochemical usage as supporting electrolytes in non-polar environments and batteries are scarce.¹²⁻¹³ Recently, Mullen and Floudas have developed a novel class of WCAs and WCCs by polyphenylene-dendrimerizing of tetraaryborate ions and tetraphenylphosphonium ions, respectively.¹⁴⁻¹⁸ While these rigid compounds have not been tested yet as supporting electrolytes for electrochemistry, the association constants of these electrolytes are lower than those of conventional electrolytes reported earlier. In the case of WCCs, higher generation dendrimers have been found to lower the association constants, presumably by shielding the core phosphonium cations from the periphery rather than delocalizing charges over the dendrimers. Dendrimerization works to make weakly coordinating anions/cations more conductive, but conductivity is only moderately improved in higher generation dendrimers. Thus, the choice of an adequate supporting electrolyte is paramount since the salt affects both mass transport and solution resistance in the aforementioned batteries.

Materials and Method:

Preparation of these salts followed a modified procedure by Charette et al.²³ As depicted in the general **Scheme 1**, substituted aryl halides underwent a palladium-catalyzed coupling reaction with corresponding triarylphosphines **1** in boiling *o*-xylene in order to yield novel substituted tetraarylphosphonium ylides **2** (STEP 1). The insoluble phosphonium halides precipitated in the *o*-xylene and were isolated from the reaction mixture by simple filtration. The subsequent metathesis reaction allowed an exchange of ions between the phosphonium ylide **2** and the lithium tetrakis boron pentafluorobenzene (Li^+ TFAB⁻) salt, which resulted in the formation of lithium halide and the desired ion-pair tetraarylphosphonium-tetrakis boron pentafluorobenzene $TAP^{R+} TFAB^-$ **3** (STEP 2). Synthesized compounds were characterized by various NMR spectroscopic methods.

Scheme 1: Synthesis of $TAP^{R+} TFAB^-$.



Conductivity Measurements were made with a YSI 3200 conductivity bridge utilizing a YSI 3256 dip probe with a cell constant of 0.091 (0.004 cm^{-1}). The cell constant was calculated by repeat measurements

of aqueous KCl solutions at two concentrations. The test solution was contained in a conductivity cell made by “sawing off” the top half of a 100-mL graduated cylinder. The diameter of this cell is normally set slightly larger than that of the YSI 3256 dip probe, thus minimizing the amount of solvent necessary for the experiment. Typically, 30 mL of solution were added to the conductivity cell and then stirred. The YSI 3256 contains a thermistor, and the temperature of the solution was recorded during each experiment. The temperature throughout an experiment remained consistent while the average temperature throughout the entire set of data was set to 22.45 (0.95 °C). Ten 100- μ L aliquots of a nominally 3 mM stock solution of the electrolyte were added to the conductivity cell resulting in concentrations ranging from 10^{-5} to 10^6 M. After measurement of the final solution, the volume of solution in the conductivity cell was determined via the graduations on the graduated cylinder. In the case of tetrahydrofuran, the volume of stock solution added (1 mL) was compensated for by solvent evaporation. We were able to perform conductivity measurements on both newly synthesized electrolytes (R= *p*OCH₃ and R= *p*CH₃) for comparison with the automotive industry standards electrolyte salts: TBA-TFAB and TBA-PF₆.

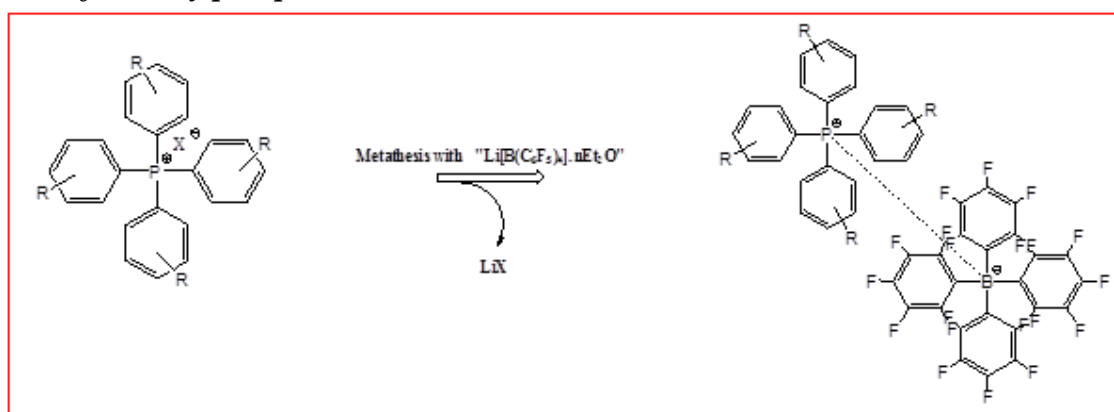
Results and Discussion:

The central hypothesis of this study is that novel weakly coordinating cations (WCCs) salts, combined with [TFAB] as a WCA, are much more highly dissociated than the traditional electrolytes [BF₄]⁻ or [PF₆]⁻ in low-polarity solvents while at the same time retaining good transport properties.¹⁹ This increased solubility of new salts in low-polarity solvents can provide the impetus to explore alternative cations as new, high performance, less toxic electrolytes for ORB and OFRB. Although we are looking at cation sides specifically, our knowledge in dissociation constants of WCCs and WCAs in general and redox potential determinations in non-polar environments can be applied to a wider range of fields, including organic synthesis, energy, and even biology as mentioned. The energy community will benefit from the comprehensive results of this project. A new series of electrolytes could help us explore furthermore the effect of electrolytes and solvents, especially non-polar solvents, in ORFB and ORB, and it might be even possible to find some that work in actual batteries. The first requirement for electrochemistry of any kind, including those in batteries and common potentiostat measurements, is a conductive solution. Non aqueous solvents have become increasingly attractive as alternatives to aqueous media in the fields of metal deposition²⁰ and non-aqueous electrolyte batteries.²¹ Ion pairing was shown to be prevalent in such media and this necessitated the use of microelectrodes. The attractive energy E of the cation-anion interaction is related to the dissociative energy of the thermal motion $k_B T$ (where k_B is the Boltzman constant while T is the absolute temperature) by the Bjerrum theory. This theory predicts that *ions might exist separately only if their size σ_{ion} exceeds a certain value, the so-called Bjerrum radius σ_B .*²² Otherwise they would build cation-anion pairs as the thermal motion would not be able to prevent their association at small distances. This condition can be satisfied in two different ways: 1) soluble molecules that can dissociate into large ions; 2) disassociation of small molecules with further solubilization of ions into larger micelles. In this project, we consider the first approach by preparing salts or “ion pairs” that, due to the bulkier sizes and the electronic properties of their constitutive ions, will disassociate into large cation and anion. Electrostatic

attraction pulls these cations and anions together creating the so-called ion pairs. They exist in dynamic balance between electrostatic attraction and destructive thermal motion. Enlarged ions size can prevent their [re]association into pairs of ions, creating disassociated “free” ions.

As depicted in the general **Scheme 1**, substituted aryl halide underwent a palladium-catalyzed coupling reaction with corresponding triarylphosphine **1** in boiling *o*-xylene in order to yield novel substituted tetraarylphosphonium ylide **2**. The insoluble phosphonium bromide precipitated in the *o*-xylene and was isolated from the reaction media by simple filtration. The subsequent metathesis reaction allowed an exchange of ions between the phosphonium ylide **2** and lithium tetrakis boron pentafluorobenzene, resulting in the formation of lithium bromide and the desired ion-pair tetraarylphosphonium **3**.

Scheme 2: Metathesis of tetraarylphosphonium halides with LiTFAB



Conductivity Measurements: We, then, performed electrochemical experiments to probe the effect of both the solvent and the synthesized electrolytes ($\text{TAP}^{\text{R}+} \text{TFAB}^-$ ion-pairs) on conductivity. Indeed, non- and low-polar solvents can be made sufficiently conducting when these weakly coordinating anions/cations (i.e. the electrolytes) are dissolved in the solvent. Our goal was to determine the association/disassociation constants of these ions in solution. Ions associate in solution to form a stable entity in media of low permittivity because Coulombic interactions are greater than the thermal energies of the “separated” ions.²⁴ Molar conductivity was measured and plotted versus the concentration to show that: 1) At low concentrations, the conductivity decreased proportionally to the concentration, 2) At high concentration in low polarity solvents, a minimum was obtained, and 3) Weak electrolytes displayed a more rapid decrease in conductivity. Disassociation constants (K_d) were measured and limiting conductivity calculated for the different synthesized salts, with greater value obtained for $\text{R} = \text{OCH}_3$, and generally, electron-donating groups enhanced conductivity by promoting disassociation of ion-pairs according to **Table 1**.

Table 1. Preliminary conductivity data for TAP^R-TFAB salts.

TAP ^R -TFAB Substituents	Disassociation Constant (K _d)	Limiting Conductivity (Λ ₀)	Association Constant (K _A)
R= pOCH ₃	2.29 x 10 ⁻⁴	90.1 Scm ² /mole	4.37 x 10 ³
R= pCH ₃	2.03 x 10 ⁻⁴	68.80 Scm ² /mole	4.92 x 10 ³
TBA-TFAB TBA-PF ₆	1.20 x 10 ⁻⁴	83.3 Scm ² /mole	8.33 x 10 ³
	2.68 x 10 ⁻⁶	121.0 Scm ² /mole	373.13 x 10 ³

Conclusion:

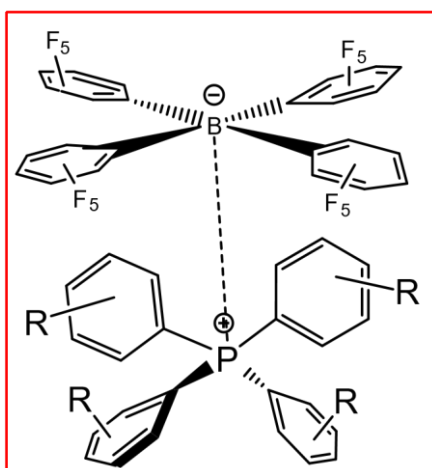
The long term goal of this project is to address issues related to renewable energy and its safe and sustainable conversion and storage in batteries for use in appropriate devices. The lithium-ion battery is plagued by issues either at the electrodes or the electrolytes. Organic Radical Batteries (ORBs) and Organic Redox Flow Batteries (ORFBs) are attractive because they present the possibility of fabricating lightweight and flexible devices with better safety and comparable or possibly better performance than lithium-based batteries for which increasing demands exist already.²⁵ The next decade will be characterized by an increase in use of grid-independent, portable electrical devices that are slim, with tunable potentials such as a battery-on-the package that would be easy and “green” to manufacture and to process, being made of resource-abundant organic material and environmentally friendly to dispose of.²⁶ We have designed a series of WCAs/WCCs which can offer in addition to the above-mentioned advantages, improved ions’ mobility in nonpolar solvents for electrolytes that would enhance the specific capacity of ORBs and ORFBs. We expect to perform electrochemical measurement in non-polar solvents with electrolytes that are soluble in those solvents. We plan to use them to conduct pulse radiolysis studies to determine redox potentials of redox-active molecules such as those used in ORBs and ORFBs in non-polar solvents and, possibly to measure redox potentials in an electrolyte-free environment for the first time.

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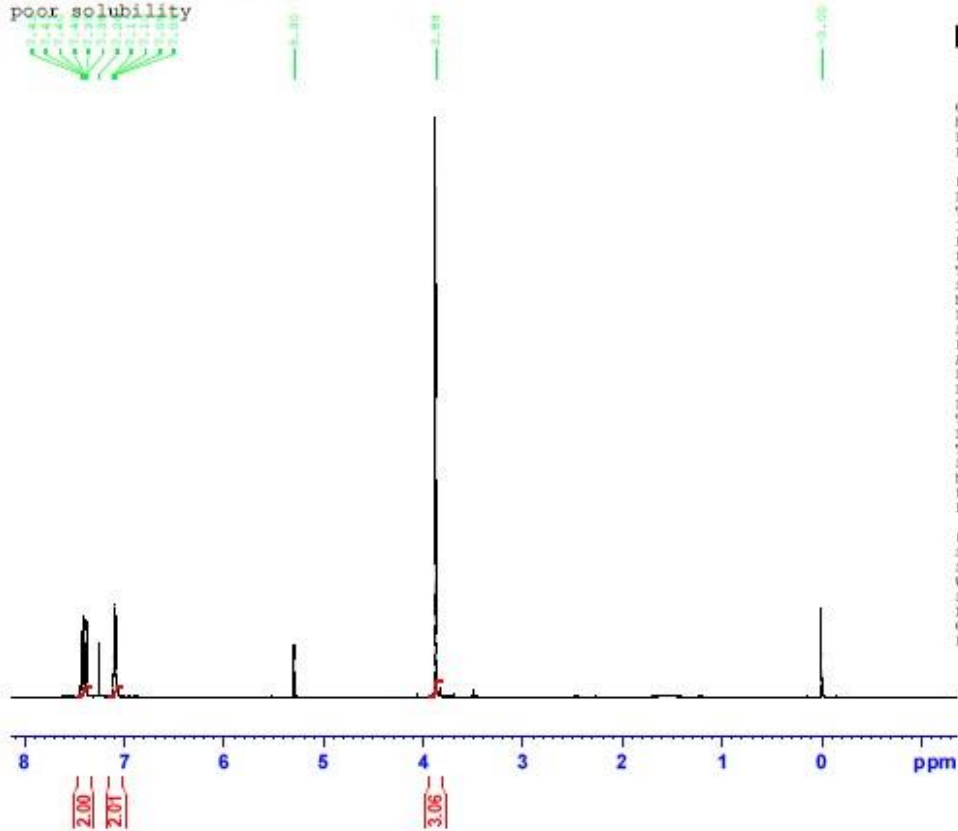
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Supplemental Data ¹H NMR:



With R= *p*OCH₃

WCC01 in CDCl₃ 1H NMR
poor solubility



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PROCNO   1

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NUC1     1H
F1       15.25 usec
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¹⁹F NMR:

