

Total Synthesis of Ionic Liquid Systems for Dissolution of Lunar Simulant

Robert J. Sharpe

Marshall Space Flight Center

August 6, 2010

Reviewed by NASA Mentor

Dr. Laurel J. Karr

EM10

Signature Here

Total Synthesis of Ionic Liquid Systems for Dissolution of Lunar Simulant

Robert J. Sharpe¹

The University of Alabama Department of Chemistry, Tuscaloosa, Alabama, 35486

Dr. Laurel J. Karr²

National Aeronautics and Space Administration Marshall Space Flight Center, Marshall Space Flight Center, Alabama, 35808

Dr. Mark S. Paley³

AZ Technology, Huntsville, Alabama, 35812

Abstract

For purposes of Space Resource Utilization, work in the total synthesis of a new ionic liquid system for the extraction of oxygen and metals from lunar soil is studied and described. Reactions were carried out according to procedures found in the chemical literature, analyzed via Thin-Layer Chromatography and ¹H Nuclear Magnetic Resonance Spectroscopy and purified via vacuum distillation and rotary evaporation. Upon final analysis via ¹H NMR, it was found that while the intermediates of the synthesis had been achieved, unexpected side products were also present. The mechanisms and constraints of the synthesis are described as well as the final results of the project and recommendations for continued study.

Nomenclature

| | |
|------------|----------------|
| <i>Br</i> | = bromine |
| <i>C</i> | = carbon |
| <i>Cl</i> | = chlorine |
| <i>Et</i> | = ethyl |
| <i>F</i> | = fluorine |
| <i>H</i> | = Hydrogen |
| <i>I</i> | = iodine |
| <i>IL</i> | = ionic liquid |
| <i>Mhz</i> | = megahertz |
| <i>mL</i> | = milliliter |
| <i>N</i> | = nitrogen |
| <i>O</i> | = oxygen |
| <i>P</i> | = phosphorous |
| <i>S</i> | = sulfur |

I. Introduction

First referenced in chemical literature in 1914, ionic liquids have become of great interest to Organic Chemists due to their remarkable physical properties such as chemical stability, molecular design flexibility, abilities as solvents, low vapor-pressure, recyclability, and properties as electrolytes.^{1,2} Ionic liquids are room temperature liquid salts composed of large organic molecules featuring at least one anionic and cationic center. Such properties have not only allowed for a completely new branch of research in Organic Chemistry to emerge, but they have also caused scientists to look back to former research topics with hopes of using ILs to improve older processes. Since their discovery, a large variety of IL systems have been synthesized. Figure 1 depicts a sample of reported IL anions and cations.

¹ Undergraduate Research Assistant, EM10, Marshall Space Flight Center, The University of Alabama

² Materials Engineer, EM10, Marshall Space Flight Center

³ Senior Scientist for Organic Chemistry, EM40, Marshall Space Flight Center

The rate and effectiveness of the rearrangement is affected by the steric hindrance of the alkyl halide according to the following sequence: Primary>Secondary>Tertiary. Furthermore, the identity of the leaving halide impacts the reaction's effectiveness according to the following sequence: I>Br>Cl.

The Michaelis-Arbusov Rearrangement can also be used to selectively substitute one halide on a molecule containing more than one reactive site. According to the procedure reported by Stock, by heating to reflux a fourfold excess of dibromoalkane with triethyl phosphite, the monosubstituted product can be recovered after leftover starting materials are removed under vacuum⁵.

B. Acid Catalyzed Hydrolysis

Hydrolysis is used to cleave ester functional groups to their corresponding acids and alcohols. The transformation is catalytic in acid and proceeds through 4 intermediate steps prior to the synthesis of the final product. However, while the Arbuzov Rearrangement is said to go to "completion," the products and reactants of hydrolysis exist in varying equilibrium with each other according to Le Chatelier's Principle. The mechanism (as shown in figure 3) proceeds first by protonation of the carbonyl oxygen by acid, making water a strong enough nucleophile to attack the electrophilic carbon center, thus forming the tetrahedral intermediate. Following a proton transfer, an alcohol leaving group is generated, which can be removed via reformation of the carbonyl species. The final step involves the reprotonation of water to reform the acid present in the first step.

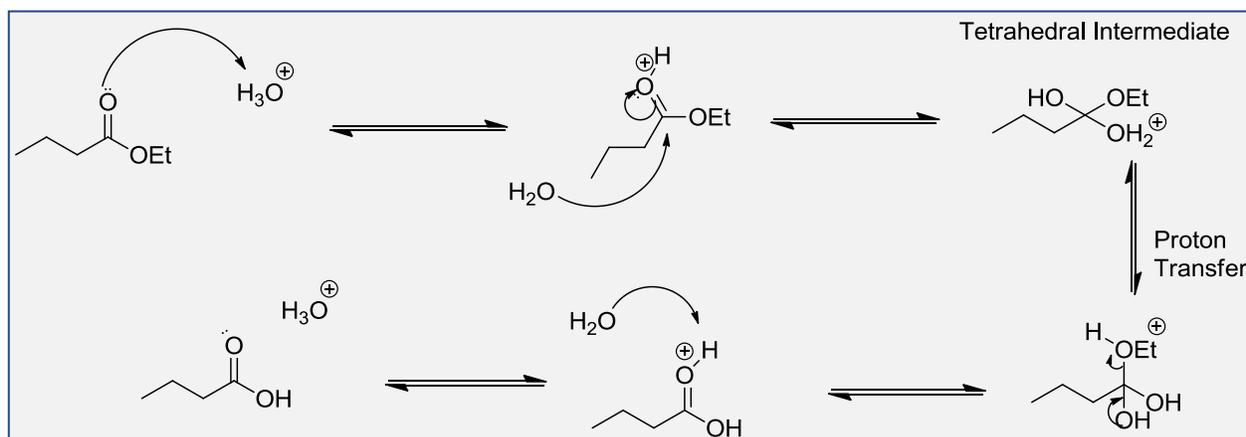


Figure 3: Mechanism of the hydrolysis of ethyl butanoate.

C. Menshutkin Substitution

Discovered by the Russian Chemist Nikolai Menshutkin in 1890, the Menshutkin reaction is used to convert tertiary amines to quaternary ammonium salts via substitution of alkyl halides⁶. While the reaction can also be used in the substitution of primary and secondary amines, achieving only the monosubstitution product is difficult due to the high nucleophilicity of the resulting secondary or tertiary amine. Much in the same fashion as the Arbuzov Rearrangement, the reaction proceeds through the substitution of an alkyl halide to form an ammonium halide salt. The Menshutkin Reaction bears significance to Ionic Liquids Chemistry in that it often serves as the precursor to several ionic liquid systems, such as the quaternization of N-methylpyrrolidine with bromobutane in figure 4⁷. While in this case the product is still a solid at room temperature, the bromide ion can readily be exchanged with a bulkier anion resulting in an IL, such as 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide.

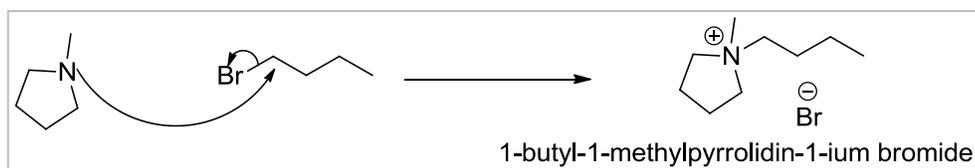


Figure 4: The formation of an pyrrolidinium bromide via the Menshutkin Reaction

Order of halide reactivity follows along the same pattern as given in the Arbusov Rearrangement. Furthermore, the rate of the reaction is typically increased by polar, aprotic solvents (e.g. acetone, acetonitrile). However, it is also common for the reaction to be run with little or no solvent in an excess of the bromoalkane in order to maximize interaction between the two reactants and increase yields.

III. Analysis/Purification Techniques

In order to ensure that the desired product in each step had been synthesized, the product of each reaction must first be purified and analyzed. A major challenge in the scheme was not only to synthesize the desired Ionic Liquid, but also to develop a scheme with which to practically synthesize it in large quantities. Furthermore, chromatographic visualization and spectroscopy of intermediates and substrates also presented a challenge due to the ionic character of select compounds. Here is reported the purification and analysis techniques used in the synthesis.

A. Purification by Vacuum Evaporation

In order to fulfill the requirement of making the synthesis practical for high quantities, vacuum evaporation proved to be the most effective method for large scale purification. Typically, once a reaction was complete, excess solvent and reagents would be removed via rotary evaporation, a type of distillation apparatus designed for the removal of large amounts of low-molecular weight solvents and reagents.

The apparatus, given in figure 5, consisted of a rotating glass cylinder connected to a condensing tube. The reaction mixture would be heated in a water bath under vacuum, thus removing lower molecular weight solvents. Once the largest amounts of solvent and excess reagent had been removed, the reaction mixture was placed under higher vacuum at high temperature in order to remove the final traces of excess material. This method of purification proved successful in removing large amounts of excess materials in the reaction mixture.



Figure 5: Image of the rotary evaporator used in the synthesis of IL systems

B. Analysis by Thin-Layer Chromatography

Based on the varied polarity of organic compounds, Thin-Layer Chromatography (TLC) was used to determine if a reaction had completely consumed its corresponding starting materials. The process was carried out as given in figure 6 by spotting a small amount of dissolved material onto a glass plate coated with silica gel. Plates were then set in a 100mL beaker filled with a small amount of a solvent system (usually ethyl acetate and hexane) designed to properly elute the compounds by capillary action. Once the plates had completed eluted, they were dipped into a developing solution, which revealed the position and purity of the materials. Primary developing stains for the experiment consisted of Silver Nitrate, Bismuth Subnitrate, Cerium (IV) Sulfate, and Potassium Permanganate solutions.

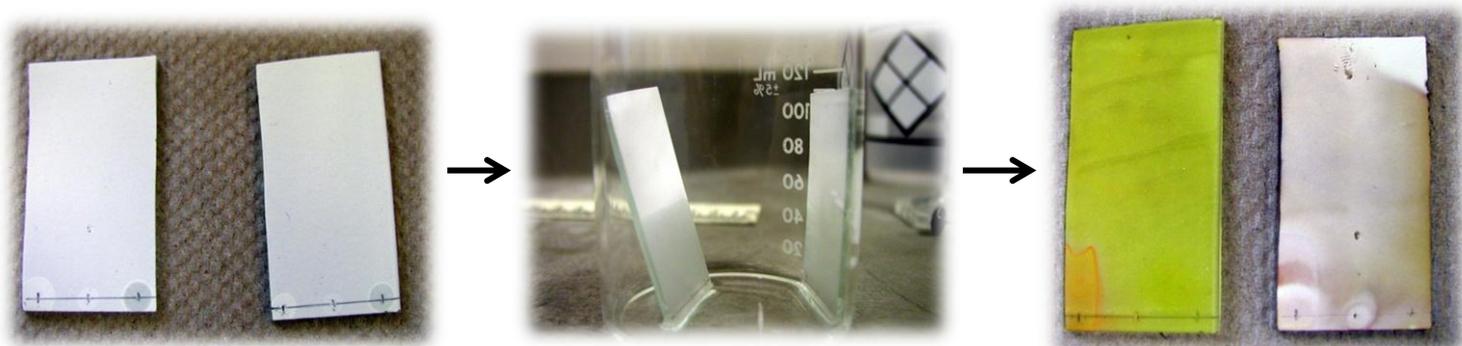


Figure 6: Illustration of analysis of substrates via Thin-Layer Chromatography

However, the above procedure for TLC could be only applied to the elution of strictly covalent compounds. For substrates in the synthesis that contained anionic and cationic centers, the silica gel plates were pretreated according to the procedure given by Li⁸. The silica gel plates were immersed in a 6% weight/volume Sodium Bromide solution for 5 minutes. The plates were then dried in an oven at 40° C until needed for use. The solvent system for elution consisted of a varied percentage mixture of methanol/dichloromethane. This method proved to be both a practical and effective method to elute and visualize ionic compounds.

C. Analysis by ¹H Nuclear Magnetic Spectroscopy

In order to effectively confirm the presence of the desired product after each reaction, information via ¹H Nuclear Magnetic Resonance Spectroscopy was gathered. In each case, the sample to be acquired was dissolved in deuterated dimethyl sulfoxide. The resulting solution was pipeted into a cylindrical tube designed for NMR measurements and was then ready for data collection.

Using the University of Alabama in Huntsville Varian© 500Mhz NMR Spectrometer, spectra of each intermediate were taken (sample of a raw spectra is given in figure 7). Once the raw spectra had been collected, the data was processed in order to determine the character and purity of the sample. Upon this processing, a definitive conclusion could be drawn regarding the identity of the sample.

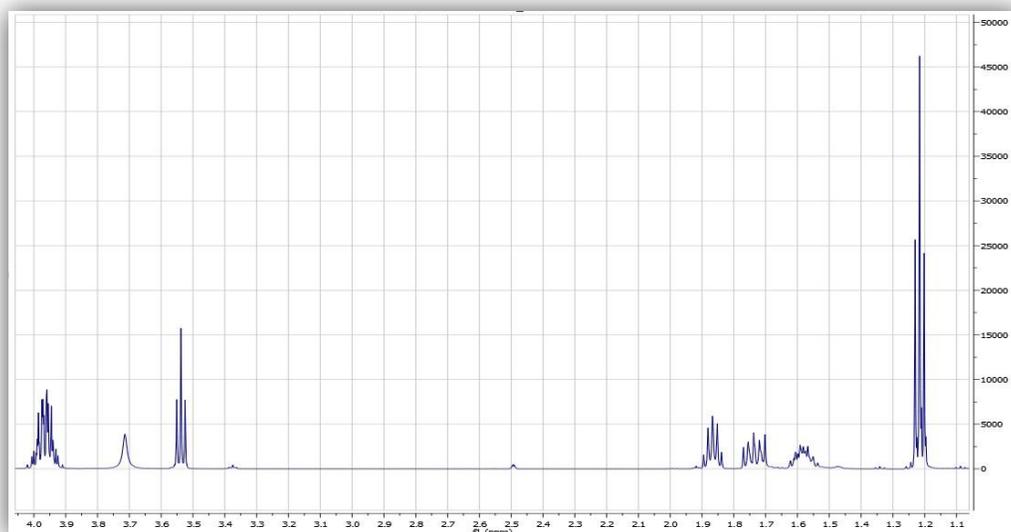


Figure 7: Sample Spectrum collected during work on the synthesis of the desired IL product.

IV. Results and Discussion

¹HNMR results showed that while the desired intermediates in the synthesis had been synthesized, a “clean” spectrum of the final product was not obtained.

While many of the reactions in the synthesis followed through in high yield, purification of the substrates proved to be the largest obstacle. The Arbuzov Rearrangement, while reported in chemical literature to be purified via simple evaporation, required rigorous distillation to completely isolate the pure material. Furthermore, the Menshutkin reaction consistently produced unwanted, insoluble side products that were difficult to identify via ¹HNMR. It was postulated that these side products could either have resulted from unwanted elimination reactions or also from the presence of starting materials not removed from the previous reaction. These side products were removed from the mixture via centrifuge and discarded.

Regarding TLC analysis, the process of visualizing ionic materials took several days to refine. It was found that if the eluting solvent system was greater than ~20% methanol/dichloromethane, the plate would show severe streaking upon development, making it virtually impossible to make any conclusions. Furthermore, only the bismuth subnitrate stain was found to be a suitable developing solution for the ionic intermediates.

It was also observed during the synthesis of the desired ionic liquid that at least one of the intermediates of the synthesis was itself an ionic liquid, and this result was further confirmed via ¹HNMR. However, there was not enough available time to further study the properties of these intermediate ILs.

Further observations made during this work currently remain proprietary and will be released in the future.

V. Conclusions

The scheme developed for the total synthesis of the desired IL product was shown to be effective. It is suggested that in order to further refine the synthesis, other routes with which to purify the intermediates should be explored that would be both practical in large scale and more efficient than the methods previously discussed. Furthermore, it was concluded that some of the excess, unreacted reagents in each step (e.g. haloalkanes, tertiary amines) might be able to be recovered via distillation and reused, thus improving the cost-effectiveness of the synthesis. Finally, it is suggested that some of the intermediate ILs also be studied for their use and effectiveness in the lunar regolith experiment.

Acknowledgments

R. J. Sharpe thanks Dr. William Kaukler (UAH/NASA) for arranging for the use of the NMR facility at the University of Alabama in Huntsville.

R. J. Sharpe thanks Dr. Bernhard Vogler (UAH) for measuring NMR spectra.

References

- ¹Walden, P. "Molecular weights and electrical conductivity of several fused salts". *Bull. Russian Acad. Sci.*: 1914. pp. 405–422
- ²Rogers, R. and Seddon, K., *Ionic Liquids: Industrial Applications to Green Chemistry*. ACS Symposium Series 818. Washington D.C. 2002.
- ³Michaelis, A.; Kaehne, R. "Ueber das Verhalten der Jodalkyle gegen die sogen. Phosphorigsäureester oder O-Phosphine". *Berichte*. Vol. 31, 1898 p. 1048
- ⁴Arbuzov, B. A. "Michaelis–Arbusow- und Perkow-Reaktionen". *Pure Appl. Chem.*, Vol. 9: 1964 pp. 307–353.
- ⁵Stock, N., Feyand, M., Sonnauer, A., "Synthesis of 4-Phosphonobutanesulfonic Acid and Systematic Investigation of Copper Phosphonobutanesulfonates by High-Throughput Methods" *Crystal Growth and Design*. Vol. 9, No. 1, 2009 pp. 586-592.
- ⁶Menshutkin, N., "Beiträgen zur Kenntnis der Affinitätskoeffizienten der Alkylhaloide und der organischen Amine" *Z. Physik. Chem.* Vol. 5, 1890 p.589.
- ⁷Burrell, A., Del Sesto, R., Baker, S., McClesky, T., Baker, G. "The large scale synthesis of pure imidazolium and pyrrolidinium ionic liquids." *The Royal Society of Chemistry* Vol. 9 2007 pp. 449-454.
- ⁸Li, T., Bluhm, L. "Chromatographic purification of quaternary ammonium and pyridinium compounds on normal phase silica gel" *Tetrahedron Letters*. Vol. 39 No. 22 1998. pp. 3623-3626.