

Thermal Studies and Oxidation Reactions

with

Room-Temperature Ionic Liquids

Dalice M. Pinero Cruz

DOE ERULF Program

University of Puerto Rico

National Renewable Energy Laboratory

Golden, Colorado

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Participant: _____

Research Advisor: Dr. Luc Moens

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Abstract

Thermal Studies and Oxidation Reactions with Room Temperature Ionic Liquids. Dalice M. Pinero Cruz (University of Puerto Rico, Rio Piedras Campus, San Juan, PR 00931)
Dr. Luc Moens (National Renewable Energy Laboratory, Golden, Colorado 80401).

Ionic liquids are being used for developing new chemical reactions. The synthesis of four ionic liquids and two solid salts with relative low melting points were performed. Thermal studies of these ionic compounds were made to evaluate their heat stability as potential heat transfer fluids for use in solar parabolic trough systems. In a second area of research, some of these ionic liquids were tested as solvents for organic oxidation reactions. The reactions were applied to the oxidation of syringyl and veratryl alcohol. The reagents used in the reactions were manganese dioxide and Co (salen) complex. The manganese dioxide was the only one that proved to be active in the ionic media. Further studies are needed to optimize these reactions.

Research Category

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School Author Attends: University of Puerto Rico

DOE National Laboratory Attended: National Renewable Energy Laboratory

Mentor's Name: Dr. Luc Moens

Phone: 303 384-6265

e-mail Address: luc_moens@nrel.gov

Presenter's Name: Dalice Pinero Cruz

Mailing Address: Calle Vidal y Rios 2M5

City/State/ZIP: Bairoa Park Caguas PR 00725

Phone: 787 746-0078

e-mail Address: sheccid_k@yahoo.com

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Introduction

The world of chemistry is being transformed by the discovery of room temperature ionic liquids (RTIL). Researchers around the world are discovering new paths in their investigations by the use of RTIL. These liquids are being studied for use in chemical synthesis, particularly in catalyst reactions, in separation technology, as electrolytes in batteries, and in solar cells. Our work focused on the development of different types of ionic liquids to evaluate their thermal stability, for they may be used in the future as heat transfer fluids in parabolic trough systems to capture solar heat. We have also used them as a solvent in organic synthesis.

Scientists at the Field Test Laboratory Building, where I did my research, are studying different types of biomass as a source of renewable energy and raw materials. In the process of breaking down the biomass a very complex component called lignin is isolated, which is notoriously difficult to process using standard chemical methodologies, and for which there are practically no significant applications other than for its energy content in boilers. My investigation focused on trying to establish oxidation reactions of lignin, using ionic liquids as a solvent. To facilitate this process, lignin model compounds were used instead of lignin itself.

RTILs are composed of a cation and an anion, whose forces of attraction are not sufficiently strong to hold them together as a solid at ambient temperature, and therefore these salts are liquids, unlike traditional molten salts such as for instance sodium chloride that melts above 800° C. RTIL's are organic fluids typically containing nitrogen-based organic cations and inorganic anions. This property allows them to dissolve organic compounds and serve as a potential solvents for industrially important organic reactions

(Welton 1999). Ionic liquids are environmentally benign because they have no detectable vapor pressure, which makes them non-volatile; and they are also non-flammable. They are emerging as a novel replacement for volatile organic compounds (VOC) traditionally used as industrial solvents (Freemantel M, 2000). More than 3.8 million tons of VOC's are used annually in the United States, most of them designated as toxic materials.

RTIL's might be a good possibility for helping create "greener" chemistry, since there are many ways of combining ions to make them. This has been referred to as 'designing' the solvent system for a particular reaction process, which could result in unique product selectivities or even new chemistry compared to the traditional solvents (1999).

In catalytic processes, ionic liquids may enhance the activity, selectivity and stability of transition metal catalysts as recently shown for a novel biphasic butane dimerization process, which is currently being evaluated for licensing and which could be one of the first large-scale applications of ionic liquids. Another application is the dissolution of spent nuclear fuels in ionic liquids, as it has been developed by the British Nuclear Fuels Laboratory (BNFL) in Sellafield, England. The Institute of Chemistry at the Tallinn Technical University is looking into RTIL's for their possible use in oil shale treatment. Oil shale is sedimentary rock that contains organic matter known as kerogen, which is burned in power stations to generate electricity. Because of their unique solvent properties and large thermal stability, they are good candidates for the development of efficient processes for the liquefaction, gasification or modification of oil shale kerogen. This process is routinely realized by pyrolysis, solvent extractions, direct hydrogenation, and the production of synthesis gas followed by the use of Fischer-Tropsch technology (Freemantle, 2000). The University of South Alabama is looking into the use of ionic

liquids as sequestering agents to remove hydrogen sulfide and carbon dioxide from contaminated natural gas supplies known as “sour gas”. This means that they could be used in the natural gas sweetening process (cleaning). RTILs are also known to be good solvents for Friedel-Crafts alkylations, hydrogenations, olefin isomerizations, Diels-Alder reactions, alkylations of heteroatoms and isomerization of fatty acids and ethers.

Another good characteristic about ionic liquids is that they are great electrolytes that can be applied in the battery industry. RTIL are inherently ionically conductive and they can mitigate self-discharge. Also, the electrochemical window of RTIL’s -that is, the electrochemical potential range over which the electrolyte is not reduced or oxidized at an electrode- is usually much greater than for aqueous electrolytes. Batteries that contain molten salt electrolytes require high operating temperatures, and they are called thermal batteries (Freemantle, 2000). Consequently, ionic liquids with low melting points promise to spur new concepts with much higher performance in the battery business. The Swiss Federal Institute of Technology, Lausanne (EPFL), has investigated the use of RTIL’s as electrolytes in dye-sensitized solar cells, electrochemical devices, and other photoelectrochemical devices (Freemantle, 2000).

In our research, we have investigated the thermal stability of the following ionic liquids, some of which were not previously known in the chemical literature:

trimethylphenylammonium bistriflamide

1,3-butylmethylpyrrolidinium bistriflamide

1,3-butylmethyylimidazolium bistrifamide

1,3-ethylmethyylimidazolium bistriflamide,

1,3- ethylmethylpyrrolidinium bistriflamide

1,3-trihexyltetradecanephosphonium bistriflate

The heat stability is important for evaluating the use of these salts as heat transfer fluids in solar parabolic trough systems that convert solar heat into electrical power. In these stations parabolic mirrors radiate solar heat onto a cylinder, located in the focal point, that contains heat transfer fluids. As the fluid heats up, the thermal energy is converted into electricity through the use of a heat exchanger that generates steam. The heat transfer fluids that are currently used are mineral oils or inorganic molten salts, both of which have high melting points that interfere with the operation of these energy systems during nighttime. Thermal cracking occurs when the organic oils are exposed to high temperatures. Both problems should be prevented. We have found that our ionic liquids are thermally stable up to the range of temperatures that occur within solar parabolic trough systems (400-450°C). An added advantage is their high hydrophobicity due to the bistriflamide anion, which means that they will not attract significant amounts of water upon exposure to air.

For the determination of the decomposition temperature of the ionic liquids synthesized here, we did thermogravimetric analysis (TGA) in which a small amount of the material is exposed to increasing temperatures and its degradation is monitored through its weight loss. If RTIL cannot be used alone in parabolic solar systems, it is proposed that they be used with other heat transfer fluids to give better efficiency and safety to those energy suppliers.

A second part of the research work involved the establishment of novel oxidation reactions with lignin in ionic liquids. However, since whole lignin is a very complex

material, we decided to focus on lignin model compounds that could facilitate the optimization of these new reactions. An important issue that needed to be addressed was the isolation of the final oxidation product(s) from the ionic reaction medium, and to this end we had to explore a number of extraction solvents. While the work is still incomplete, we have achieved the oxidation of syringyl alcohol into syringylaldehyde and 2,6-dimethoxy-p-benzoquinone, and veratryl alcohol into veratrylaldehyde. Both alcohols are common subunits of typical lignins. In future work, these reactions will have to be optimized, and exact product yields will have to be determined.

Materials and Methods

A-Syntheses of Ionic Liquids

After the exchange of anions, all the ionic liquids were washed three times with water, placed on the rotovap and then on the high vacuum oil pump.

- a- trimethylphenylammonium bistriflamide; 20.60 g of trimethylphenylammonium chloride and 34.44g of lithium bistriflamide. Both salts were dissolved in 100 and 200 ml of water, respectively. The reaction was stirred at room temperature.
- b- 1,3-Butylmethylimidazolium bistriflamide; 19.93 ml of 1-methylimidazole and 52.25 ml of 1-butylchloride. The removal of residual butyl chloride was carried out with ethyl acetate. 100 ml of water were added. 63.80g of lithium bistriflamide were dissolved in 200 ml of water and it was added to the flask.
- c- 1,3-Butylmethylpyrrolidinium bistriflamide; 50 ml of methylpyrrolidinium were transferred to a 250 ml round bottom flask with a syringe. 73.60 ml of butylchloride were added. The solid was filtrated. 10.55g of butylmethylpyrrolidinium chloride was

obtained and dissolved in 30 ml of water. 17.04g of lithium bistriflamide was dissolved in 30 ml of water and added to the chloride solution.

- d- Trihexyltetradecanephosphonium bistriflamide; 3.50 g Of trihexyltetradecanephosphonium chloride was dissolved in 20 ml of acetone. 2.49g of lithium bistriflamide was dissolved in 20 ml of water and added 250 ml flask with the chloride.
- e- 1,3-Ethylmethyylimidazolium bistriflamide and 1,3-ethylmethylypyrrolidinium bistriflamide (same method for both); 0.24 moles of methylimidazole placed in a Fisher-Porter bottle. Flow of argon was required. The gas ethyl chloride was added to the bottle with a system of valves. Dry ice and acetone were used to condense the gas. After there was 70 ml of liquid ethyl chloride, it was heated up to 70 C. 80 ml of water were added. 67.34g of lithium bistriflamide were dissolved in 60 ml of water. (20.50 ml of methylpyrrolidinium plus 51 ml of ethyl chloride, 80 ml of water; 55.30g of lithium bistriflamide in 80 ml of water).

B- Thermal Gravimetric Analysis

- a- Five milliliters of each ionic liquid or ionic salt were taken in 10 ml vials. The thermal gravimetric analysis were run in a CAHN TGA-131. The initial temperature was 0°C to 600°C on nitrogen atmosphere with a ramp of 20°C/min.

C-Oxidation reactions

All reactions were done in 25 ml round bottom flasks. Extractions were performed in a 25 ml separation funnel. Products from extractions were placed in 100 ml flasks, put in the rotovapor and then on the high vacuum oil pump. NMR's of all the products were taken. The reactions were monitored with Thin Layer Chromatography (TLC).

a.1- 0.555 g of syringyl alcohol dissolved in 6 ml of trimethylphenylammonium bistriflamide, heating was required. Manganese dioxide was used as a catalyst in equivalence of 5:1 (1.3049g). Argon atmosphere was used. The reaction was heated at 65 C during 24 hours. Three extractions were made with 12 ml chloroform. This reaction was repeated in a.2 and a.3 but with different parameters.

a.2- (a.1) , but heated at 70 C for two hours. Extractions were made with 12 ml of ether. The product was put to react again with a equivalence of 1:5 of the catalyst. It was heated at 57 C for 24 hours. Four extractions were made with 12 ml of ether.

a.3- (a.1), but the ionic liquid was changed to 1,3-butylmethylimidazolium bistriflamide. It was heated for two hours.

b.1- The substrate for this reaction was veratryl alcohol, 0.5322g were used in 6 ml of trimethylphenylammonium bistriflamide and 1.3745g of manganese dioxide. It was then heated for two hours under a flow of argon. Extractions were made in 24 ml of isopropanol (4:1). No separation was observed, so it was placed on the refrigerator at -8 C to achieve phase separation. Three more extractions of isopropanol were made, but with 12 ml only.

b.2- (b.1), but three separations were made with 12 ml of ether, instead of using isopropanol.

c.1- Syringaldehyde was used the starting material (0.1009g), in trimethylphenylammonium bistriflamide and 0.2410g of manganese dioxide. It was heated at 92 C for 24 hours and 53 C 24 more hours under argon atmosphere. Three extraction with 12 ml of ether were made.

c.2- (c.1), but the catalyst was changed to Cobalt (salen) complex. Oxygen pressure of 50 psi was required. The ionic liquid was also changed to the 1,3-butylmethylimidazolium bistriflamide (6 ml). It was heated for two hours at 50 C. Three extractions were made with chloroform.

c.3- (c.2), but the ionic liquid used was the 1,3-butylmethylpyrrolidinium bistriflamide.

Results

A- Synthesis of Ionic Liquids

After 46 days as ionic liquid, the methylphenylammonium bistriflamide turned into a solid, whose melting point was 65°C. The 1,3-ethylmethylpyrrolidinium bistriflamide was also a solid when it was synthesized, having a melting point of 88°C. The others were stable room temperature ionic liquids.

B- Thermal Gravimetric Analysis

- a- started decomposing at 410°C.
- b- started decomposing at 420°C.
- c- started decomposing at 415°C.
- d- starting decomposing at 405°C.
- e- starting decomposing at 425°C and at 415°C.

For diagrams, see attached pages.

C-Oxidation reactions

There was no yield data obtained for any of the reactions because their study is still in progress. All NMRs showed the presence of the ionic liquid used.

- a.1- NMR showed the product was 2,6-methoxy-p-benzoquinone. There was also present the ionic liquid used.

a.2- In the first part of the reaction was observed the formation of the syringaldehyde showed from a NMR. The NMR of the second part of the reaction showed the presence of both the syringaldehyde and the 2,6-methoxy-p-benzoquinone.

a.3-The NMR showed the formation of the syringaldehyde.

b.1- The product was 3,4-methoxybenzaldehyde.

b.2- The NMR showed the 3,4-methoxybenzoquinone.

c.1- Remaining aldehyde was observed in the NMR but also the presence of the 2,6-methoxy-p-benzoquinone.

c.2 and c.3- The starting material was the only thing observed in the TLCs, no reaction occurred with the substrates, and the NMR of the c.3 confirmed no formation of the 2,6-methoxy-p-benzoquinone with the system of the cobalt catalyst in the ionic liquids used.

Discussion and Conclusion

Of the six salts prepared, two of them turned out not to be a room temperature ionic liquid: the 1,3-ethylmethylpyrrolidinium bistriflamide and the trimethylphenylammonium bistriflamide. The latter remained in a supercooled state for up to 46 days before it crystallized spontaneously ! As a matter of fact, this supercooled liquid could be used as a solvent for some of the oxidation experiments.

The Thermal Gravimetric Analysis shows that imidazolium salts are somewhat more stable than pyrrolidinium moieties, since they seem to have a higher thermal decomposition temperature. Some of the graphs show a series of events (loss of weight) before the catastrophic point where it loses all the weight, but that could be due to the

presence of residual solvent, water or impurities left in the product, or even some kind of bond cleavage. Understanding these results will require further study.

It was demonstrated that some ionic liquids are excellent solvents for oxidation reactions. A most surprising result that could have significant consequences for future synthetic chemistry with ionic solvents was the discovery that the choice of ionic liquid can dramatically alter the synthetic pathway! Indeed, the oxidation of the syringyl alcohol afforded 2,6-methoxy-p-benzoquinone in the trimethylphenylammonium bistriflamide, while syringaldehyde was the sole product when 1,3-butylmethylimidazolium hexafluorophosphate was used as solvent. We have also made serious progress in determining the optimal solvent for extracting the products, but further research is needed to optimize these processes. New combinations of cations and anions should be explored to develop novel RTILs for their use in chemical biomass conversion and their possibility as heat transfer fluid in solar systems for parabolic troughs.

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References

Sun, J., Forsyth, M., MacFarlane, D.R. (1998). "Room-Temperature Molten Salts Based on the Quaternary Ammonium Ion." *J. Phys. Chem.*, Vol. 102, 8858-8864.

Heat Transfer Fluids, *HEAT-EXCHANGE TECHNOLOGY*, Vol. 12, pp 993-999.

Huddleston, J.G., Willauer, H.D., Swatloski, R.P., Visser, A.E., Rogers, R.D. (1998). "Room Temperature Ionic Liquids as a Novel Media for 'Clean' Liquid-Liquid Extraction." *Chemical Communications*, 1765-1766.

Freemantle, M., *Chem. Eng. News*, May 15, 2000, pp 37-50.

Welton, T. *Chem. Rev.* (1999), Vol. 99, pp. 2071-83