

Oxidation Reactions in Ionic Solvents for Lignin Conversion

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Abstract

Oxidation Reactions using Ionic Solvents for Lignin Conversion.
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Currently, petroleum is being used as a major source for new chemicals, materials, and fuels, but it raises concern due to its finite availability and increasing costs. An alternative raw material source is lignocellulosic biomass. Examples of such biomass are trees and plants, and can be broken down into two basic structures, i.e. carbohydrates and lignin, that are potential starting materials for new chemicals, materials, and fuels. However, unlike petroleum, biomass has a very complex structure, and new chemical technologies, in particular novel solvent systems, are needed for its processing. Ionic liquids, which are salt-like organic materials consisting of ions that form a liquid at room temperature, provide a unique medium for developing new chemistry and a potential solution for processing biomass. We are interested in the oxidative processing of lignin, and decided to focus on lignin model compounds that can provide sufficient insight in the fundamental chemistry. Since little information using ionic liquids as solvents is known, several oxidation reactions were run using benzylic alcohols as lignin models with MnO₂ as the oxidizing reagent. Although oxidation of the benzylic alcohol was observed, the reactions produced inconsistent yields. This work led to a hypothesis that the ionic solvent can react with the substrate by dealkylating the methoxy groups that are common to all lignins. This is considered to be a crucial finding that will be important to most future research work involving ionic solvents for lignin processing.

Research Category (Please Circle)

ERULF: Physics **Chemistry** Biology Engineering Computer Science Other _____
CCI: Biotechnology Environmental Science Computing

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Introduction

The use of fossil fuels such as petroleum, coal and , natural gas as sources of fuels and chemicals has created concern due to its finite availability and increasing costs. The recent record high price of gasoline in some US cities can be used to illustrate this point. The increasing demand for energy and fuel, the geopolitical and environmental implications, and the awareness of the problems that can arise from using these depletable resources, makes it imperative to search for alternative sources. A potential solution is the use of biomass as a naturally abundant renewable resource. However, due to its distinct chemical and physical characteristics, new processes must be developed for its chemical conversion.

Biomass is defined as materials produced by plants grown on land or in water or as the result of direct or indirect photosynthesis (Baizer, 1985). Therefore, biomass encompasses substances ranging from wood and crops to municipal solid wastes and sewage. The main sources of biomass are agriculture (i.e., grains and sugar cane), silviculture (i.e., hardwood and softwood trees), aquaculture, residues, and wastes (Baizer, 1985). The initial challenge in making use of biomass is breaking it down to a select group of smaller fractions. Although lignocellulosic biomass exists in many forms, its main structural components can be broken down into carbohydrates and lignin.

Once this separation of biomass into carbohydrates and lignin is accomplished, desired materials can be produced such as industrial chemicals, plastics, and pharmaceuticals. Carbohydrates can be further divided into hemi-cellulose and cellulose, which are important to the paper pulping industry or to the production of ethanol. Gasification of biomass to generate electricity through pyrolysis is now being applied in the Field Test Laboratory Building of the National Renewable Energy Laboratory.

Many biomass conversion processes currently practiced make use of the sugar fractions, leaving behind a lignin residue that is difficult to dissolve in traditional organic solvents. The complex structure of lignin has yet to be fully determined, although certain functional groups such as e.g. benzylic alcohols and ether linkages have been identified. The difficulty to break these bonds presents a challenge for which new methodologies are needed. In particular, the lignin leftover from the pulping process has a lower reactivity and a change in molecular structure from its native state.

Aside from their inability to dissolve lignin, traditional organic solvents create many other environmental and technological problems. Each year, the US industry uses more than 3.8 million tons of organic solvents, most of which are designated toxic (Pesticide, 2000). Chemical manufacturers are being pressured to minimize their use because of the emissions to air, soil, and water. Other disadvantages associated with using organic solvents include their high disposal and manufacturing costs.

With the increasing concern for the environment and the rapidly growing “green chemistry” movement, the need has arisen for new synthetic pathways using alternative feedstocks, the identification of alternative reaction conditions to improve selectivity, the minimization of energy consumption, and the design of less toxic chemicals (Clark, 1998). The discovery of solvents consisting of room-temperature ionic liquids has created much excitement among scientists from various parts of the world including USA, Europe, and South Africa (Freemantle, 2000). Ionic liquids are salt-like organic materials composed entirely of ions that exist as a liquid at room temperature and behave macroscopically like polar aprotic solvents. They have been referred to as “designer solvents” because they offer a choice of combinations of organic cations and inorganic or organic anions enabling scientists to design solvent properties to

influence the outcome of the reaction, thus making it possible to change more parameters and allow for a greater reaction selectivity. Along with this, their reusability may make synthetic processes more cost effective and may make the use of raw materials more efficient through lower production of waste materials. Since ionic liquids have an ionic character, as compared to the molecular character of traditional organic solvents, they can be designed to be excellent solvents for both inorganic and organic materials and offer new opportunities for novel catalytic processes. Furthermore, their lack of measurable vapor pressure represents another important environmental benefit that distinguishes them from traditional organic solvents.

Due to their high thermal stability, ionic liquids can be used for carrying out reactions at high temperatures in a liquid phase. This unique characteristic can also potentially be applied for use as heat transfer fluids in solar parabolic through systems where temperatures can reach 400-450°C.

Chemists from various parts of the world united to discuss their views on the potential uses of room-temperature ionic liquids at a workshop conducted by NATO in Crete, Greece, in April 2000. Some topics introduced included British Nuclear Fuels' (BNFL) development of a way to use ionic liquids to dissolve spent nuclear fuels, while the Czech chemical industry is researching their use in the syntheses of specialty and fine chemicals, polymer processing, and nuclear fuel processing. Also, Estonia is examining the possibility of using these liquids to treat oil shale, an important mineral resource for generating electricity. Along with these countries, the chemical industry in Europe and the United States is evaluating the use of ionic liquids as solvents for chemical processing, as well as electrolytes in electrical batteries, fuel cells and other energy systems (Freemantle, 2000).

The many benefits of using ionic liquids as solvents, in addition to the increasing need to convert renewable resources, in particular lignin from wood, into energy and new chemicals and materials has inspired our research. In nature, wood rot fungi have been found to carry out selective oxidation on the benzylic alcohols within the lignin structure as one of the initial steps in its decomposition. For this reason, we are currently using different types of benzylic alcohols as lignin models in oxidation reactions with ionic solvents in the presence of transition metal catalysts. Aside from learning how to carry out oxidation reactions in ionic media, our focus is to develop the basic protocols for simple work-up of the reactions, such as extracting and isolating desired reaction products. Once these fundamental principles are established, the information can then be applied to future lignin processing.

Materials and Methods

Solubility Tests of Ionic Liquids

To determine which solvents to use for extractions, solubility tests were done on each ionic liquid used, 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) and triisobutylmethylphosphonium tosylate. 0.5 milliliter portions of the ionic liquid were added to about 20 small 2-milliliter vials. Another 0.5 milliliters of the 20 different organic solvents listed on tables 1.1 and 1.2 were added. In addition, 1.0 milliliter of chloroform was added to each ionic liquid and 0.5 milliliter of both water and ether was added to triisobutylmethylphosphonium tosylate. Each vial was capped, shaken, and left to settle. Separations of phases were recorded.

Extraction of Pure Vanillin

Based on the solubility test results and their relatively low boiling points, ether and isopropanol were further tested to be used for extractions of products. Into each of 2 30 milliliter separatory funnels, 6 milliliters of [BMIM][PF₆] was added to about 460 mg of pure vanillin, an oxidation product of vanillyl alcohol. The product from one mixture was extracted with 6 10-milliliter portions of ether, while the same amount of isopropanol was used for the extraction from the other mixture. Each collection of product was purified through silica gel using ether and yields were calculated.

Oxidation Reactions of Primary Benzylic Alcohols in [BMIM][PF₆]

The substrates, Vanillyl Alcohol, Veratryl Alcohol, and Piperonyl Alcohol, were used in a series of oxidation reactions with MnO₂ as the reagent and [BMIM][PF₆] as the ionic solvent. The equivalents of MnO₂ used, temperature, length of reaction, and extraction solvents were varied for each to obtain the most efficient conditions for the maximum yield of pure product. Although many experiments were run, Table 2 shows the specific parameters used for the most significant trials. All reactions were done under an argon atmosphere while stirring. Extractions were performed using from 6 to 12 milliliter portions of the organic solvent. Product to starting material ratios were obtained through analysis of the proton NMR spectra by comparisons of the integration areas of the peaks produced from the protons of the aldehyde and alcohol.

Oxidation Reactions of a Secondary Benzylic Alcohol in

Triisobutylmethylphosphonium Tosylate

The secondary alcohol, acetovanillyl alcohol used in the oxidation reactions was prepared by adding 3.4 equivalents of sodium borohydride to a solution of 1330 milligrams of 4-hydroxy-

3-methoxyacetophenone, or acetovallinone, in 40 milliliters of 56% ethyl alcohol, aqueous. The reaction was run overnight and neutralized by bubbling carbon dioxide through the mixture. The alcohol product was extracted with 3 40-milliliter portions of ether, dried with Magnesium Sulfate, and purified through silica gel using 225 milliliters of ether.

The acetovanillyl alcohol was used in oxidation reactions with the ionic liquid solvent, triisobutylmethylphosphonium tosylate, a research sample from Cytec Canada, Inc. An experiment was run with and without the reagent MnO_2 and both were monitored by TLC. Refer to Table 3 for specific reaction conditions. The reaction with MnO_2 was purified by running a column chromatography using a column with a 1.5-cm diameter and a solution of 3 grams of silica gel with a 5% ether solution of ether/hexane. Fractions were monitored by ultra-violet light and proton NMR spectra were obtained and analyzed for each product collected.

Oxidation Reactions of Veratryl Alcohol in Triisobutylmethylphosphonium Tosylate

The substrate, Veratryl Alcohol, was mixed with the ionic liquid, triisobutylmethylphosphonium tosylate and no oxidation reagent was added. The mixture was heated at 40°C while stirring under argon for about 5 hours

Results

Solubility Tests of Ionic Liquids

Tables 1a lists the degree of phase separation for each organic solvent added to the ionic liquid, $[\text{BMIM}][\text{PF}_6]$, while Table 1b similarly lists their solubility in triisobutylmethylphosphonium tosylate.

Extraction of Pure Vanillin

The extractions of pure vanillin obtained from ether and isopropanol produced yields of 90.5% and 80.4% respectively.

Oxidation Reactions of Primary Benzylic Alcohols in [BMIM][PF₆]

The percent yields of pure product obtained from reactions gone to completion or the ratio of product to starting material of incomplete reactions are listed in Table 2 along with the respective reaction conditions used for each.

Oxidation Reactions of a Secondary Benzylic Alcohol in Triisobutylmethylphosphonium Tosylate

Analysis of the proton NMR spectra of the products collected from the column chromatography indicate the formation of methyl tosylate and tosylate acid. The expected aldehyde product was not obtained.

Oxidation Reactions of Veratryl Alcohol in Triisobutylmethylphosphonium Tosylate

The proton NMR spectra of the crude product obtained from mixing the veratryl alcohol substrate with the ionic liquid using no oxidizing reagent indicate the formation of aldehyde, as seen by the proton peak at about 9.8 ppm. Methyl tosylate was also present in the product.

Discussion and Conclusions

The solubility test results for each ionic liquid indicate that no particular pattern exists, although most mixtures produced homogeneous solutions. Nonetheless, an intriguing result was observed when testing the [BMIM][PF₆] in chloroform. When mixing equal parts of these substances, a homogeneous solution was produced. However, upon the addition of more chloroform, a separation of phases occurred. This phenomenon should be studied more closely

to determine the exact ratio of [BMIM][PF₆] to chloroform needed to optimize phase separation and use in further extractions.

Due to their relatively low boiling points and production of good yields of pure vanillin, ether and isopropanol were mainly used to extract the aldehyde products from the alcohol oxidation reactions. After performing many experiments on each alcohol substrate while changing various parameters, the best reaction conditions for each substrate were 5 equivalents of MnO₂ at 60°C. While the veratryl and piperonyl alcohol went to completion in 2 hours, the vanillyl alcohol required an overnight period for complete reaction to form aldehyde. Furthermore, the latter substrate presented much more difficulties in product extraction. Although extractions with ether and isopropanol produced 88% and 83% yields of pure aldehyde products from the veratryl and piperonyl alcohol systems, respectively, the 11% yield of vanillin raises curiosity and studies to optimize its yield should be continued.

The oxidation reactions of the secondary alcohol, acetovanillyl alcohol, produced surprising results also. The identical TLC plates observed from the reactions with and without MnO₂ reagent presented the first clue that products other than the expected acetovanillyl aldehyde were produced. The assumption that the ionic liquid, triisobutylmethylphosphonium tosylate, was reacting with the substrate was proven by the NMR spectra of the pure products from the column, i.e. methyl tosylate and its acid. A possible explanation is the dealkylation of the methoxy group in the substrate by the “naked” anion tosylate, which is a reactive nucleophile with minimum solvation due to the large phosphorous cation. Since the tosylate group is also a good leaving group causing the methyltosylate to be very prone to hydrolysis, it was not surprising that p-toluene sulfonic acid was also collected. NMR spectroscopy showed clearly that the methyl tosylate decomposed on the silica gel used for the column chromatography.

A completely unexpected observation was that veratryl aldehyde was formed from mixing only the veratryl alcohol in the ionic liquid, triisobutylmethylphosphonium tosylate, without the addition of MnO_2 or any other oxidizing reagent. This reaction should be studied more closely to determine the cause of the oxidation that took place. This information could be useful for lignin chemistry.

In conclusion, the most important and intriguing discovery from this research is the fact that ionic liquids are not necessarily inert solvents. Their “naked” anions have been shown to react with the alcohol substrate by removing a methyl group, which causes the desired aromatic product to dissolve in the ionic phase. This may be a reason for the difficulty in extracting good yields of pure aromatic products using various organic solvents.

Future research of this project should include an exploration of the reactivity of other anions in ionic liquids. Experiments should be continued to find an ionic liquid that will dissolve the substrate at room temperature along with an oxidizer to perform a fast oxidation of the desired alcohol substrate, without reaction between the anion of the ionic liquid and the substrate. In addition, optimization of methods for extracting the desired aromatic compounds is needed.

In spite of these results, it is clear that lignin model compounds can undergo reactions in an ionic solvent, and therefore it should be possible to develop useful reaction processes that make use of this abundant renewable resource.

Acknowledgements

I thank the United States Department of Energy for providing me with a tangible opportunity to further my knowledge and gain experience working in my field of study. I also

thank the National Renewable Energy Laboratory and its employees for taking action to try to utilize our renewable resources while helping the environment. Special thanks to my mentor, Dr. Luc Moens for his contagious enthusiasm in this project keeping me inspired to learn more about ionic liquids and synthetic chemistry. In addition, thanks to Dalice Pinero and Noshena Khan for their technical assistance in the laboratory. I also thank Cytec Canada, Inc. for providing the research sample of the new ionic liquid that has made these intriguing research conclusions possible.

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Tables

Table 1a. Solubility Tests of 1-butyl-3-methylimidazolium hexafluorophosphate

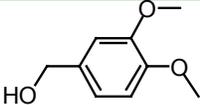
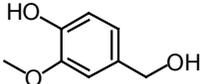
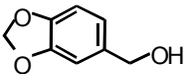
ORGANIC SOLVENT	SOLUBILITY
Methanol	Homogeneous solution
Ethanol	Biphase 1/1 v/v ionic/organic
Isopropanol	Biphase 1/1 v/v ionic/organic
Acetonitrile	Homogeneous solution
Dimethylsulfoxide	Homogeneous solution
Dimethylformaldehyde	Homogeneous solution
Acetone	Homogeneous solution
Dimethylchloride	Homogeneous solution
Pyridine	Homogeneous solution
Chloroform	Homogeneous solution
Ethyl acetate	Homogeneous solution
Tetrahydrofuran	Homogeneous solution
1,4-dioxane	Homogeneous solution
Benzene	Homogeneous solution
Toluene	Biphase 7/3 v/v ionic/organic
Diethyl ether	Biphase 1/1 v/v ionic/organic
Triethylamine	Biphase 1/1 v/v ionic/organic
n-hexane	Biphase 1/1 v/v ionic/organic
Cyclohexane	Biphase 1/1 v/v ionic/organic
4-methyl-2-pentone	Homogeneous solution
Chloroform to [BMIM][PF ₆] = 2:1	Biphase 3/7 v/v ionic/organic

Table 1b. Solubility Tests of Triisobutylmethylphosphonium Tosylate

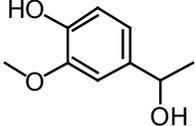
ORGANIC SOLVENT	SOLUBILITY
Methanol	Homogeneous solution
Ethanol	Homogeneous solution
Isopropanol	Homogeneous solution
Acetonitrile	Homogeneous solution
Dimethylsulfoxide	Homogeneous solution
Dimethylformaldehyde	Homogeneous solution
Acetone	Homogeneous solution
Dimethylchloride	Homogeneous solution
Pyridine	Homogeneous solution
Chloroform	Homogeneous solution
Ethyl acetate	Homogeneous solution
Tetrahydrofuran	Homogeneous solution
1,4-dioxane	Homogeneous solution
Benzene	Homogeneous solution
Toluene	Homogeneous solution
Diethyl ether	Biphase 6/4 v/v ionic/organic
Triethylamine	Biphase 1/1 v/v ionic/organic
n-hexane	Biphase 1/1 v/v ionic/organic
Cyclohexane	Biphase 1/1 v/v ionic/organic
4-methyl-2-pentone	Homogeneous solution
Chloroform to Ionic liquid = 2:1	Homogeneous solution
Diethyl ether to water to ionic liquid = 1:1:1	Biphase 7/3 v/v ionic/organic

Table 2. Oxidation Reactions of Primary Benzylic Alcohols

in [BMIM][PF₆]

ALCOHOL SUBSTRATE	MnO ₂ (equiv.)	TEMP. (°C)	TIME	EXTRACTION SOLVENT	PROD:SM RATIO	YIELD (%)
	2	Room temp.	Overnight	Ether	1:2	--
Veratryl Alcohol	2	60	2.5 hours	Ether	4:3	--
Veratryl Alcohol	5	Room temp.	2 hours	Isopropanol	2:1	--
Veratryl Alcohol	5	63	2 hours	Ether + Isopropanol	1:0	88
	5	57	2 hours	Isopropanol	1:3	--
Vanillyl Alcohol	5	60	Overnight	Isopropanol + Ether	1:0	11
	5	65	2 hours	Ether + Isopropanol	1:0	83
Piperonyl Alcohol						

**Table 3. Oxidation Reactions of a Secondary Alcohol
in Triisobutylmethylphosphonium Tosylate**

ALCOHOL SUBSTRATE	MnO ₂ (equiv.)	TEMP. (°C)	TIME	EXTRACTION SOLVENT	PROD:SM RATIO	YIELD (%)
						
Acetovanillyl Alcohol	5	40	2 hours	Water + Ether	--	--
Acetovanillyl Alcohol	0	35	Overnight	Water + Ether	--	--